POTENTIAL OF PALM OIL LEAVES EXTRACT AS CORROSION INHIBITOR IN CARBON DIOXIDE (CO_2) ENVIRONMENT

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Thesis submitted in partial fulfilment of the requirements
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Dedicated to my supervisor, family and friends for their support and encouragement.

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ABSTRACT

This study describes on effect of palm oil leaves extract as corrosion inhibitor in carbon dioxide corrosion. Corrosion is defined as the process of corroding of a material or metal due to the reaction with its environment. For this study, we focus more on corrosion in carbon dioxide environment. CO_2 corrosion is one of the main threats in oil and gas industry and have been recognized as one of the problems in oil and gas production and also transportation facilities for many years. In industry, a huge amount of money is wasted for each year due to metal corrosion usually in piping system. It is informed that, this problem can be prevented with proper corrosion prevention techniques or technologies. In this study, green inhibitor will be used to prevent corrosion. It has been found that green inhibitor could be used as one of the corrosion inhibitor in industry. This is due to the green inhibitor containing heteroatoms with high electron density such as phosphorus, nitrogen, sulfur, oxygen together with double or triple bonds are effective as corrosion inhibitor. Green inhibitor will not cost much and easy to find. Corrosion inhibitor in carbon steel in carbon dioxide environment using Palm Oil leaves is being studied. Electrochemical method with several electrode (anode and cathode) is use as an apparatus to examine the rate of corrosion of metal and the effectiveness of inhibitor, Palm Oil Leaves. Usage of Palm Oil Leaves extract in CO_2 corrosion is believed can be good inhibitor for corrosion on carbon steel. The objective of this study is to study the corrosion rate of carbon steel in CO_2 environment in the presence of extraction of palm oil leaves use as corrosion inhibitor by using two different method, which are weight loss method and electrochemical method. The inhibitor's concentrations are varied from 0 ppm to 25 ppm. From the experiment, it is found that increased in inhibitor's concentration will decreased the corrosion rate.

ABSTRAK

Kajian ini menerangkan mengenai potensi ekstrak daun kelapa sawit sebagai penghalang pengaratan dalam larutan karbon dioksida. Karat ditakrifkan sebagai proses menghakis yang penting kerana tindak balas dengan persekitarannya boleh membawa kepada kesan negatif yang teruk terutamanya di dalam industri. Untuk kajian ini, kami memberi tumpuan lebih kepada karatan dalam persekitaran karbon dioksida. Karatan CO_2 adalah salah satu ancaman utama dalam industri minyak dan gas dan telah diiktiraf sebagai salah satu masalah dalam pengeluaran minyak dan gas dan juga kemudahan pengangkutan untuk bertahun-tahun. Dalam industri, sebesar jumlah wang telah dikeluarkan bagi setiap tahun disebabkan oleh hakisan logam biasanya dalam sistem paip. Adalah dimaklumkan bahawa, masalah ini boleh dielakkan dengan teknik pencegahan karatan yang betul atau teknologi yang lebih maju. Dalam kajian ini, penghalang ‘hijau’ akan digunakan untuk mencegah kakisan. Ia telah mendapati bahawa penghalang ‘hijau’ boleh digunakan sebagai salah satu daripada penghalang hakisan dalam industri. Ini adalah kerana penghalang hijau mengandungi heteroatoms dengan ketumpatan elektron tinggi seperti fosforus, nitrogen, sulfur, oksigen. Penghalang ‘hijau’ tidak akan menggunakan kos yang banyak dan mudah untuk didapati di Malaysia. Penghalang karatan dalam keluli karbon dalam persekitaran karbon dioksida menggunakan daun kelapa sawit sedang dikaji dengan menggunakan kaedah elektrokimia dengan beberapa elektrod (anod dan katod) adalah digunakan sebagai alat untuk memeriksa kadar kakisan logam dan keberkesanan penghalang yang digunakan.

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LIST OF ABBREVIATIONS

CO_2	Carbon Dioxide
CO_3^{2-}	Carbonate
CR_i	Corrosion Rate Inhibitor
CR_o	Corrosion Rate Control
CrO_4^{-2}	Chromate
e^-	Electron
Fe	Iron
H_2	Hydrogen
H_2CO_3	Carbonic acid
H_2O	Water
IE	Inhibitor Efficiency
LPR	Linear Polarization Resistances
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
NO_2─	Nitrite
NO_3─	Nitrate
O_2	Oxygen
PO_{43}-	Phosphate
Sb_2O_3	Antimony (III) oxide
SnO	Tin (II) chloride
W_f	Weight after corrosion take places
W_i	Initial weight before corrosion take places

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Corrosion have been the main concern for a long time ago. Actually, it is almost impossible to prevent corrosion from take place in the industry but we can make an effort or find the way to control the corrosion rate (Brondel et al., 1994). For this study, carbon dioxide corrosion also have been recognised as one of the problems in oil and gas production and also transportation facilities for many years. Carbon dioxide corrosion is one of the most studied corrosion in oil and gas industry. This is generally due to the facts that the crude oil contains some level of carbon dioxide. The major concern with carbon dioxide corrosion in oil and gas industry is that carbon dioxide corrosion can cause failure on the equipment especially the main down hole tubing and it can disrupt the oil or gas production. Theoretically, when water and carbon dioxide is mixed and eventually form carbonic acid thus making the environment of the fluid is acidic. Factors that have influenced in CO_2 corrosion are the temperature, pH value, flow conditions and metal characteristics (Popoopla et al., 2013).

Nowadays, people start to investigate the power of green inhibitor in order to prevent corrosion. The facts about the plant extract have become more important as an environmental friendly, easy to get and renewable source for wide range of inhibitors (Raja et al., 2007). Thus, this project or study will concentrate on findings the relationship between different concentration of inhibition towards CO_2 corrosion by using green inhibitor which is palm oil leaves extract.

1.2 Motivation

Corrosion in the modern world is one of the difficult problems in the industry. Most industrial design can never neglect the effect of corrosion on the life span of the equipment. Corrosion in industrial sector worsening every minute and keep causing a huge loss which the machine or equipment need to be replaced as it would take a lot of time to replace. Theoretically, carbon dioxide system are one of the common environment in process equipment used in piping system, production and transfer of oil. Corrosion associated with aqueous environment containing CO_2 is a well known phenomenon in oil and gas industries (Olvera-Martinez et al., 2015).

However, in most cases the corrosion are influenced by many parameters such as pH, temperature, carbon dioxide partial pressure and corrosion product film. The significance of this study is to discover the effect of time for extraction process and effect of temperature in the presence of inhibitor. Green inhibitor like palm oil leaves extracts can adsorbs on the metal surfaces and can be uses as corrosion inhibitor in this study. Generally, green inhibitors are excellent inhibitors for a variety corrosive environments for most of metals despite the fact that environmental friendly and low in cost. From this findings, it will give benefits to the industry to avoid corrosion by using low budget in cost.

1.3 Problem Statement

Carbon dioxide system are one of the common environment in process equipment used in production of oil in industries. The corrosion are influenced by many parameters such as pH, temperature, carbon dioxide partial pressure and corrosion product film. There are three areas of concern when corrosion are considered, which are economics, safety and environmental damage (Sastri, 2012).

The fact that corrosion usually occur in industries, it will effect the electrical power plants or chemical processing plant (Davis, 2000). Plant shutdown can and do occur as a result of corrosion. Corrosion can lead to failures in plant infrastructure and machines which are usually need a big cost to repair, costly in terms of lost or contaminated product, environmental damage and human safety.

In this study, by using palm oil leaves extract as corrosion inhibitor can help to reduce the activity of corrosion in pipeline or plant infrastructure system. Green inhibitor is used due to the current technologies which is high in cost and do not environmental friendly. Many study involving the usage of green inhibitor, but some of the study using expensive natural resources like onion. However, in this study the sources of the green inhibitor which is palm oil leaves is low in cost and abundant sources in Malaysia. Next, carbon steel is a common material used for making industrial units because of its low in cost and excellent mechanical properties. However, its suffers severe attack of corrosion particularly in oil and gas production system (Zamri, 2008).

1.4 Objectives

Based on research background and problem statement described in the previous section, the objectives of this research :

1. To extract the palm oil leaves to use as corrosion inhibitor.
2. To investigate experimentally the corrosion rate of carbon steel in CO_2 environment in the presence of extraction of palm oil leaves use as corrosion inhibitor.
3. To measure efficiency of inhibitor in carbon dioxide, CO_2 environment.

1.5 Scopes of Study

For this research, several scopes have been identified and the scopes of this study are :

- Using Palm Oil Leaves extract as corrosion inhibitor in carbon dioxide environment.
- Experimental analysis of corrosion rate of carbon steel using electrochemical method and weight loss method.
- Parameter use is different inhibitor’s concentration for both electrochemical method and weight loss method and different in pH value for weight loss method to study the efficiency of inhibitor in carbon dioxide medium.

1.6 Organisation of the Study

The structure of the reminder of the thesis is outlined as follow :

Chapter 1, in this section, includes the introduction which explains more detailed about the background of the study, motivation of this study, problem statement, objectives and scope of the study. In this chapter, shows more detail on why we run this experiment or study.

Chapter 2 which will be discussed in the next chapter, provides a description of the concept of how the corrosion and carbon dioxide corrosion occurs. It also discussed the condition needed for the corrosion to occur. Other than that, it also contains the type of corrosion that probably occur in the industries and the prevention method for corrosion that can be applied in industries. In this chapter, green inhibitor and palm oil leaves extract also will be discussed in detail for the knowledge before run the experiment. In chapter 2, there are also stated some previous study related to the corrosion inhibitor using deferent plant extract.

Chapter 3 includes of descriptions of the materials used in the electrochemical reaction and weight loss method. Electrochemical experimental procedures and each step methods are also presented. For the methodology, its start with preparation of the coupon and followed by the step to get the extract of palm oil leaves by using methanol.

Chapter 4 presents the results and discussion of the experiment. All of the results and discussion is shown and discussed in this chapter. More detail of explanation is discussed for both method which are electrochemical method and weight loss method.

Chapter 5 includes the conclusion and recommendation of this study. In this chapter, we can conclude that either our objective of this study is achieved or not. A few recommendation will be presented in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

As we can see nowadays, oil and gas is utterly crucial to our society. Chemical industry is one of the main industry that used oil and gas in their process. It converts raw material such as oil, natural gas, air water, metals and minerals into more than 70,000 different products in world. Chemical industry always used acid or carbon dioxide in the process which can cause corrosion to the metal surface of the equipment. The fact that carbon steel are generally used for the petroleum industry for transportation of crude oils and gases from offshore to different refining platform and to different destination (Desimone et al., 2011). This is because carbon steel is malleable, ductile and have strength with good wear resistance. Despite the fact that carbon steel is available in most countries and easy to weld. Since carbon steel is the basic metal used in the most equipment in chemical industries, then it will easily exposed with corrosion. Tbale below shows the chemical composition of carbon steel.

Table 2.1: Chemical compositions of carbon steel coupons for API 5L X-70 by using GDS technique.

Element	**Si**	**Ni**	**Cr**	**S**	**C**	**P**	**Mn**	**Cu**	**Nb**	**Ti**	**Mo**	**Fe**
Content (%wt)	0.27	0.02	0.02	0.002	0.06	0.006	1.05	0.24	0.05	0.02	0.08	Bal

Corrosion is defined in different ways, but the main interpretation or meaning is an attack on a metallic material by reaction with its environment (Bardal, 2004). Corrosion can lead to disastrous event where it will make the system shutdown and life span of equipment will become shorter. Therefore a corrosion prevention or control method is needed to reduce or to prevent the corrosion rate. The figure 2.1 below illustrate the corrosion life cycle of a product that happened in the industries.

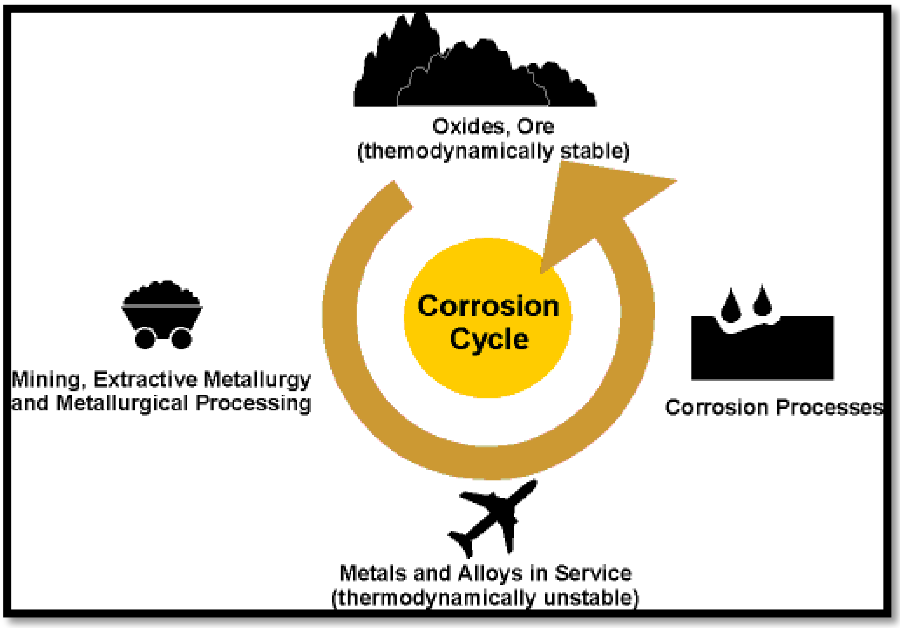


Figure 2.1: Corrosion cycle which is happened in the industries

2.2 Basis of Corrosion

Corrosion have been the main concern since a long time ago. Most people familiar with corrosion, particularly in cases like rusting of an iron fence and the degradation of steel pilings or boats and boat fixtures (Roberge et al., 1999). Corrosion is one of the natural process or phenomenon which converts a metal to a more stable form such as oxide or hydroxide, commonly defined as deterioration of metal surfaces caused by the reaction with the surrounding environmental conditions. Corrosion is defined in different ways, but the main interpretation or meaning is an attack on a metallic material by reaction with its environment (Bardal, 2004). Besides that, corrosion is also defined as potential hazard associated with oil and gas production.

2.2.1 The Corrosion Cell

Other than above definition, corrosion also defined as an electrochemical process in which a metal reacts with its environment to form an oxide or other compound (Obot et al., 2009). For this method, we need an anode, a cathode and electrolyte where the anode is the site for corroding metal, the cathode forms the electrical conductor and the electrolyte is the corrosive medium that will ensure the transfer of electrons from anode to cathode. The anode is the site of the corroding metal which passes into the electrolytes positively charged ions and releasing electrons which participate in the cathodic reaction. The cathode forms the electrical conductor in the cell that is not consumed in the corrosion process and the electrolyte is the corrosive medium that will ensure the transfer of electrons form anode to the cathode is happen. (Chatterjee, 2001). Hence as we can see, the corrosion happen between anode and cathode consists of electrons flowing within the metal and ions flowing within the electrolyte. Figure 2.2 shows the movement of the ions in electrolyte.

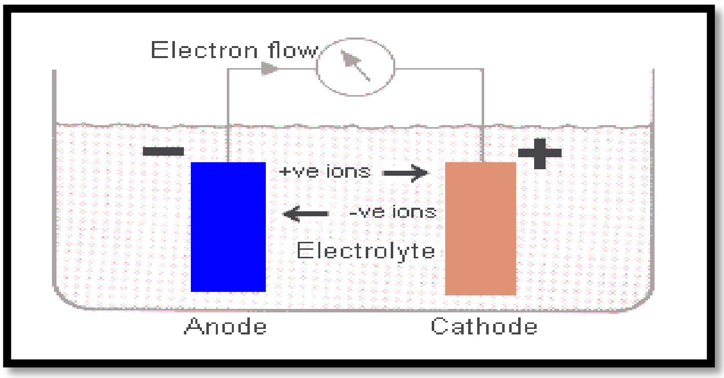


Figure 2.2: Anodic and cathodic reaction in electrolyte

. The special characteristic of most of the corrosion is the oxidation and reduction process that occur at different locations on the metal. This is due to the metals are conductive, so the electrons can flow freely through the metal from anodic to the cathodic regions (Raja et al., 2007) . With the presence of water is quite necessary and important in order to complete the transportations of ions to and from the metal .

For a specific example, the corrosion of iron in acid solution (Raja et al., 2007) :

Anodic reaction : $Fe \longrightarrow Fe^{2+} + 2e^-$

Cathodic reaction : $2H^+ + 2e^- \longrightarrow H_2$

Overall reaction : $Fe + 2H^+ \longrightarrow Fe^{2+} + H_2$

The reaction due to the presence of oxygen :

Anodic reaction : $Fe \longrightarrow Fe^{2+} + 2e^-$

Cathodic reaction : $\frac{1}{2} O_2 + 2H^+ + 2e^- \longrightarrow H_2O$

Overall reaction : $Fe + \frac{1}{2} O_2 + 2H^+ \longrightarrow Fe^{2+} + H_2O$

Note that which part of the metal serve as anodes and cathodes can depend on many factors. Atoms in regions that have undergone stress, as might be produced by forming, often tend to have higher free energies, and thus tend to become anodic (Palmer A.C, 2008). We can see the overall reaction occur in pipeline system as shown in the figure 2.3 below.

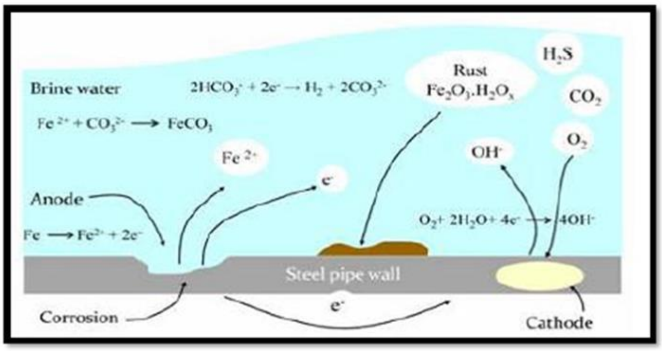


Figure 2.3: Model CO_2 corrosion of crude oil in pipeline system.

2.2.2 Effect of Corrosion

Corrosion is the process which is most dangerous that occurs in major of industrial plants. Plant shutdown do occur as a result of corrosion. The effect of corrosion is very dangerous as not only cost replacement of corroded equipment but additional cost as well for loss of efficiency of product, loss of valuable product, maintenance cost and contamination of product. In case for social, it will effect safety and health. For example, when corroded lead to sudden failure, it can cause fire, explosion or release of toxic product and it will lead to pollution that will give bad effect on health. Therefore, most industrial design can never neglect the effect of corrosion on the life span of equipment.

2.3 Type of Corrosion

Corrosion of metal materials can be divided into three main group which is wet corrosion, corrosion in other fluids and dry corrosions (Bradal, 2004). Wet corrosion, where the corrosive environment is water with dissolved species. Usually, the liquid is electrolyte and the process is typically the electrochemical. Next, corrosion in other fluids such as fused salts. Dry corrosion, where the corrosive environment is dry gas. For this study, we focused on wet corrosion. There are eight forms of wet corrosion that can be identified based on appearance of the corroded metal such as:

i. Uniform or general corrosion
ii. Pitting Corrosion
iii. Crevice corrosion
iv. Galvanic corrosion
v. Erosion corrosion
vi. Intergranular corrosion
vii. Dealloying
viii. Cracking.

In theory, the eight forms of corrosion are clearly distinct, however there are corrosion cases that fit in more than one catogery (Horvath, 1998). The type of environment causing corrosion fatigue are many and are not specific. In addition, if a metal are being apply a constant tensile stress and exposed simultaneously to a specific environment, the metal will cracks immediately or after a given time, the failure is called stress-corrosion cracking. This happen as a result of absorption of hydrogen generated by a corrosion reaction by following this definition. Figure 2.4 shows the schematic diagram of the common type of corrosion.

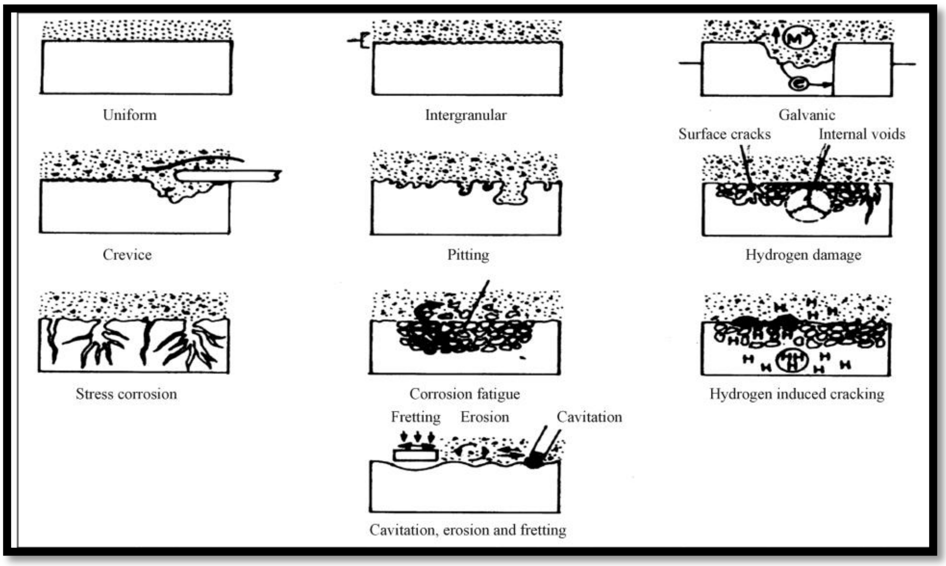


Figure 2.4: Schematics of the common type of corrosion

2.3.1 Uniform or General Corrosion

Uniform corrosion or general corrosion, is defined as a type of corrosion that attack more or less uniformly distributed over the exposed surface of a metal. Corrosion of this type are attacked over the surface, and leads to a relatively uniform thickness reduction. Uniform corrosion usually results from the atmospheric exposure, especially polluted industrial environments. Uniform or general corrosion corresponds to the most common form of corrosion and responsible for the attack with the greatest metal weight loss, where the steel structures are abandoned to rust. In fact, general or uniform corrosion not one of the dangerous form of corrosion, because prediction of thickness reduction rate can be done by means simple tests. Other than that, available protection methods are usually so efficient that the corrosion rate is reduced to an acceptable level. Usually, common rusting of iron or resulting silver to become dull and grey are one of the common example of uniform or general corrosion. Besides that, fogging of nickel as an example, and high temperature oxidation of metals are also one of example that can be included as general or uniform corrosion. From the figure 2.5 below, we can see example of general or uniform corrosion.

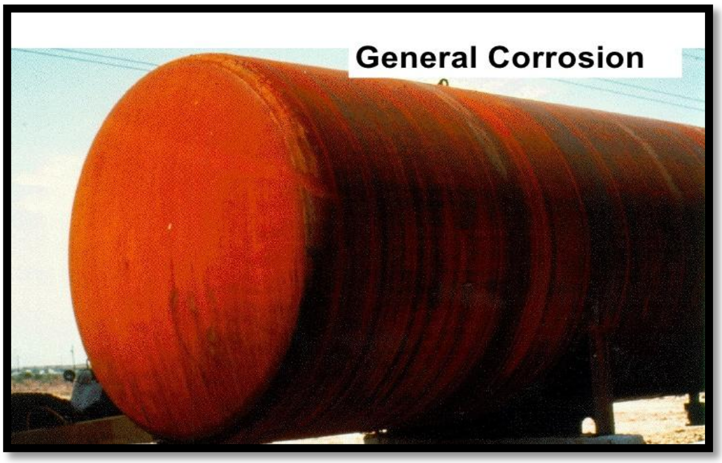


Figure 2.5: Uniform or General Corrosion at the surface of the tank.

2.3.2 Pitting Corrosion

Pitting corrosion is a localized form of corrosion by holes that are produced in the material. These holes can be small or large, but usually, they are relatively small. This is type of corrosion occurs when one area become anodic and cause accelerated localized attack. Pitting corrosion can be considered as one of the most dangerous corrosion more than uniform corrosion because it is more difficult to detect. A small pit can cause failure of an entire system. Pitting corrosion usually occurs on more or less passivated metals and alloys in environments containing chloride, bromide or iodide. Pitting is a localized type of corrosion attack, additionally with the rate of corrosion are greater at some areas compared to others. This form of corrosion is characterized by narrow pits with a radius of the same order or magnitude. Normally, pitting corrosion is difficult to measure because the number and size of the pits vary from region to region and within each region.

For describing about Pitting further, if the attack is confined to a small, fixed area of metal and act as anode, the resultant pits are described as deep. Meanwhile, if the area of metal is relatively larger and not so deep, the pits are named shallow. For detailed, pitting corrosion process involved four stages, which is, pit nucleation, early pit growth, late growth and repassivation.

There are some factors contributing to initiation and propagation of pitting corrosion. Some of the factors are localized chemical or mechanical damage to a protective oxide film and localized damage to or poor application of protective clothing. Besides that, pitting occurs in most commonly used metals and alloys. Despite their good resistance to general corrosion, stainless steels are more susceptible to pitting compare to other metal (Davis, 2000).

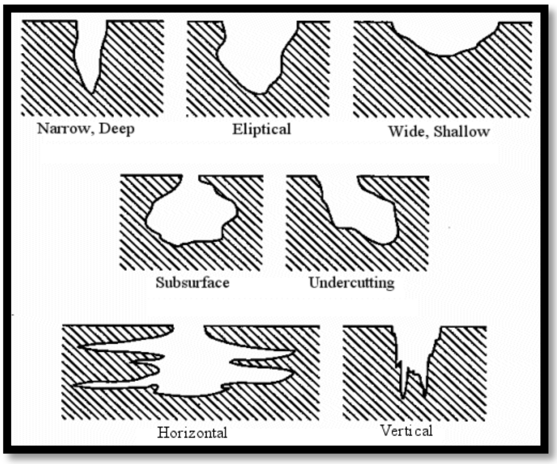


Figure 2.6: Variations of the cross- sectional shape of pits occur in pitting

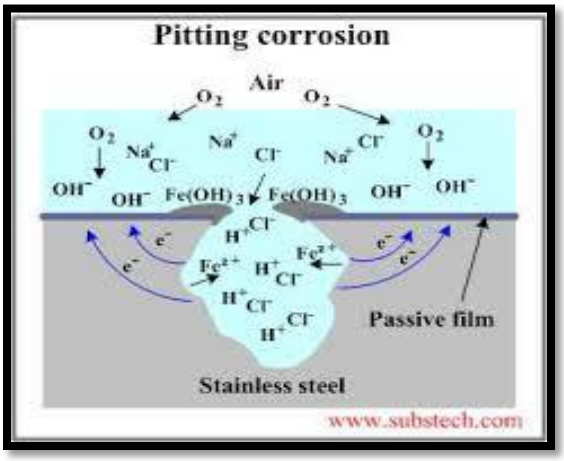


Figure 2.7: Schematic diagram of the pitting corrosion propagation mechanism

2.3.3 Crevice Corrosion

Different than pitting corrosion, crevice corrosion is a localized attack occur at narrow spaces or opening between two joining surfaces. This is localized corrosion concentrated in crevices in which the gap is sufficiently wide for liquid to penetrate into the crevice and sufficiently narrow for the liquid in the crevice to be stagnant. Crevice corrosion results from a concentration cell formed between the electrolyte outside the crevice. The damage caused by crevice corrosion is normally confined to one metal at localized area within or close to the joining surfaces. Factors that can affect the crevice corrosion are indicated in table 2.2 below.

Table 2.2 : Factors that can affect the crevice corrosion resistance of various alloy (Davis , 2000).

Factor	Type
Geometrical	Type of crevice - Metal to Metal - Nonmetal to metal Crevice gap (thightness) Crevice depth Exterior-to-interior surface area ratio
Environmental	Bulk Solution - Oxygen content - pH - Chloride level - Temperature Mass transport, migration Diffusion and convection Crevice solution : hydrolysis equilibria
Electrochemical reactions	Metal dissolution - Oxygen reduction - Hydrogen reduction
Metallurgical	Alloy composition - Major elements - Minor elements - Impurities

The crevice corrosion propagation can be illustrated schematically in Figure 2.8 for stainless steel corrosion in sodium chloride solution. From the figure, the anodic metal dissolution reaction within the crevice, $M \longrightarrow M^{n+} + ne^-$, is balanced by the cathodic reaction , $O_2 + 2\,H_2O + 4e^- \longrightarrow 4OH^-$ (Kermani et al., 2003).

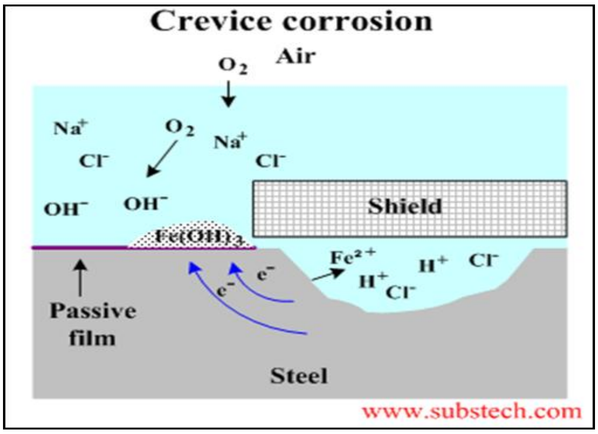


Figure 2.8: Schematic diagram of the crevice corrosion propagation mechanism

2.3.4 Galvanic Corrosion

Another type of corrosion is galvanic corrosion. Galvanic corrosion usually occur in an electrochemical reaction or process. Galvanic corrosion occurs when a metal or alloy is electrically react to another metal or conducting nonmetal in the same electrolyte. In order to galvanic corrosion to occur, three conditions must be present:

i. Material possessing different surface potential
ii. The metals must be exposed to an electrolyte
iii. These metal must be in electrical contact

Galvanic series is a list of freely corroding potentials of the materials. All metals can be classified into a galvanic series which is representing the electrical potential they develop in a given electrolyte against a standard reference electrode. The material with the most negative (anodic), corrosion potential has a tendency to suffer accelerated corrosion when the metal is electrically connected to a material with a more positive (cathodic).

A common example of galvanic corrosion is the rusting of iron sheet. To reduce galvanic corrosion to occur, there are several ways or methods of reducing and preventing this form of corrosion. One of the method is apply cathodic protection measures. Magnesium, zinc, and aluminium galvanic anodes are used in a wide range of cathodic protection applications. This will make the metal are not in electrical contact, therefore no galvanic couple will occur. For an example, piping system can be isolated with a spool of pipe made of plastic materials. One of the other methods is apply coatings with caution. For example, when painting, do ot paint less noble material without also coating the more noble material. Otherwise, it will attack on the less noble metal.

2.3.5 Erosion Corrosion

Erosion corrosion is an acceleration in the rate of corrosion attack metal due to the relative motion of a corrosion fluid and a metal surface. This is due to the mechanical wear abrasive contributions in combination with corrosion. Erosion corrosion occur when there is a relative movement between fluid and metallic material that will increased corrosion. Most metals and alloys used in industry owe their corrosion resistance to the formation and retention of a protective film. Most metals are susceptible or acceptable to erosion corrosion which is under specific conditions.

Metals that depend on a relatively thick protective coatings of corrosion product for corrosion resistance are frequently exposed to erosion corrosion. This is due to the poor adhesion of these coatings relative to the thin films. Note that the thin films is formed by the classical passive metals, such as stainless steel and titanium (Mardhiah Ismail, 2014). Figure 2.9 shows a schematic of a erosion corrosion of a condenser tube wall. From the figure, the direction of flow and the resulting attack where the protective film on the tube has broken down are indicated.

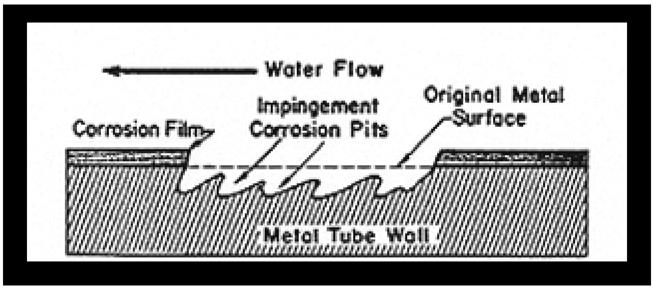


Figure 2.9 : Schematic diagram of erosion corrosion on a condenser tube

2.3.6 Intergranular Corrosion

Next is intergranular corrosion also one of the main type of corrosion (Lindeburg, 2012). Intergranular corrosion is defined as the selective dissolution of grain boundaries or closely adjacent regions. This localized type of attack at the grain boundaries of a metal thus resulting in a loss of strength and ductility. As the name suggest, this is a form of corrosive attack within the grain boundaries. Positive identification of this type of corrosion usually requires microstructure examination under a microscopy (El Etree, 1999). The figure below show the microstructure of a stainless steel which is susceptible to intergranular corrosion. Certain precipitate phases such as Mg_5Al_8, Mg_2Si, $MgZn_2$, $MnAl_6$, are also known to cause of the intergranular attack for a high strength aluminium alloys. Figure 2.10 below, shows the microstructure of stainless steel.

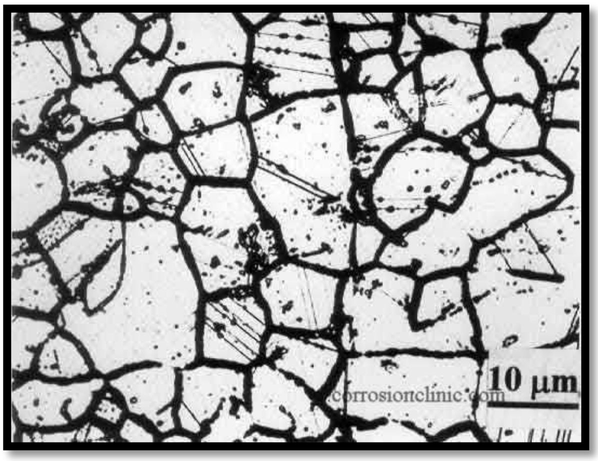


Figure 2.10 : Microstructure of stainless steel

2.3.7 Dealloying Corrosion

Another type of corrosion is dealloying, which is the selective removal of an element from an alloy by corrosion (ASTM, 2005). In this type of corrosion, normally two mechanism occurs. Dezincification is one form of dealloying, is a type of attack occuring with zinc alloys in which zinc corrodes and leaves a porous residue of copper and corrosion products. Dezincification is frequently encountered with slowly moving solutions or slightly acidic water. In dezinfication, there are two major forms which are layer type and plug-type dealloying.

Figure 2.11 : Example of dezincified brass occurs on steel

Other than dezincification, graphitic corrosion also one form of dealloying, refers to a form of selective leaching specific to gray cast iron which leaves only the graphite phase of the material. Generally, graphitic corrosion is a form of dealloying to cast irons. Graphitic corrosion generally occurs only when corrosion rates are low. Graphitic corrosion is quite common on water pipes made of gray a cast iron, a typical material of choice of water utilities. Graphitic corrosion usually occurs in three ways which are sometimes just the surface of the pipe graphitizes, forming a graphitic coating on the exterior. Theoretically, this process protects the pipe very well and quite long time. But, if a pressure surge occurs, the plug may blow out. The impact of graphitic corrosion is that the cast iron easy loses its strength and metallic properties. We can see form the figure 2.11 above, an example of dezincified brass occurs on steel.

2.3.8 Cracking Corrosion

Last but not least, cracking corrosion can be defined as crack formation. Cracking occur if a metal cracks when subjected to repeated or alternate tensile stresses in a corrosive environment and it is said to fail by corrosion fatigue. The tensile stresses may be come from external load or temperature changes. The cracks are mainly formed in planes to the tensile stresses. Fatigue limit or endurance limit is when in absence of a corrosive environment, the metal been stressed similarly, but at values below a critical stress resulting non-failure because of fatigue eventhough after a very large, or infinite number of cycles (William, 2011). A true endurance limit does not commonly exist in a corrosive environment because the metal will fails after a number of stress cycles no matter how low the stress. The types of environment causing corrosion fatigue are many and are not specific. In addition, if a metal are being apply a constant tensile stress and exposed simultaneously to a specific environment, the metal will cracks immediately or after a given time, the failure is called stress-corrosion cracking. This happen as a result of absorption of hydrogen generated by a corrosion reaction by following this definition. Actually, almost all structural metals (e.g., carbon- and low-alloy steels, brass, stainless steels, duralumin, magnesium alloys, titanium alloys, nickel alloys, and many others) are subject to stress-corrosion cracking in some environment. Lucky for us, either the damaging environment are often restricted to a few chemical species, or the necessary stresses are sufficiently high to limit failures of this kind in engineering practice. By the knowledge about the media that can cause cracking and about the limiting stresses necessary to avoid failure within a given time period, we can design metal structures without the incidence of stress-corrosion cracking.

Figure 2.12 : Cross section of typical cracking corrosion

2.4 Carbon Dioxide (CO_2) Corrosion

Sweet corrosion (CO_2 corrosion) also been recognized as one of the problems in oil and gas production and also transportation facilities for many years (Palmer, 2008). As we know, the most serious corrosion problem in oil and gas production is caused by CO_2. Generally, water and CO_2 will mix together and eventually form carbonic acid thus making the environment of the fluid is acidic. Sweet corrosion or CO_2 corrosion is defined as the deterioration of metal due to a contact with carbon dioxide (CO_2) or similar corrosive agents. But excluding hydrogen sulfide (H_2S). The economic impact of sweet corrosion or CO_2 corrosion has been well known to the oil and gas industries for a long time.

2.4.1 CO_2 Corrosion Mechanism

As mentioned before, carbon dioxide gas often uses in oil and gas industries and will lead to corrosion. The CO_2 will reacts with ground water which is H_2O to produce carbonic acid (H_2CO_3).

$$CO_{2\,(gas)} \longrightarrow CO_{2\,(aq)}$$

$$CO_{2(aq)} + H_2O_{(l)} \longrightarrow H_2CO_3$$

For the production of carbonic acid (H_2CO_3), the reactants used only small amount of CO_2 to converted into H_2CO_3. Then the carbonic acid will dissociate into carbonate (CO_3^{2-}).

$$H_2CO_3 + e^- \longrightarrow H^+ + HCO^{3-}$$

$$HCO^{3-} + e^- \longrightarrow H^+ + CO_3^{2-}$$

For the third cathodic reaction also includes the hydrogen ions that are present in the ground water. Noted that, the selectivity of the cathode reaction is determined by certain environmental factors. The anode reaction is the dissolution of iron metal at the pipe surface into iron ions.

$$2H^+ + 2e^- \longrightarrow H_2$$

$$Fe \longrightarrow Fe^{2+} + 2e^{-}$$

Therefore, the overall electrochemical reaction of CO_2 corrosion is given by :

$$Fe + CO_2 + H_2O \longrightarrow FeCO_3 + H_2$$

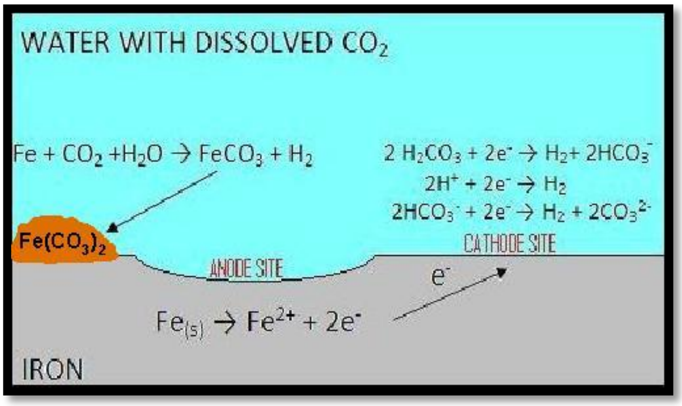


Figure 2.13 : Schematic diagram of carbon dioxide mechanism

2.5 Factor Affect CO_2 Corrosion

The rate of CO_2 corrosion is affected by several factors such as temperature, pressure, pH and flow velocity (Kermani et al., 1997). The most common factors that affect the CO_2 corrosion will be discussed in this section.

2.5.1 pH

For the pH value, it is also an important parameter in corrosion of carbon and low alloy steels (Lindeburg, 2012). The pH has the most effect which is indirectly on corrosion rate through its relationship with the formation of iron carbonate precipitation (William et al., 2011). Form the past research, the worst case scenario happens to the bare metal surfaces, where from the results in experiments shows that, at low pH ($pH<4$), a flow sensitive H^+ reduction dominates the cathodic reaction. Instead the amount of dissolved CO_2 controls the cathodic reaction rate at higher pH ($pH > 5$), (Kermani & Smith, 1997). Therefore, it has been proved that changing the pH of corrosion environment will change the rate of corrosion. Figure 2.14 summarised how CO_2 pH influence the corrosion rate.

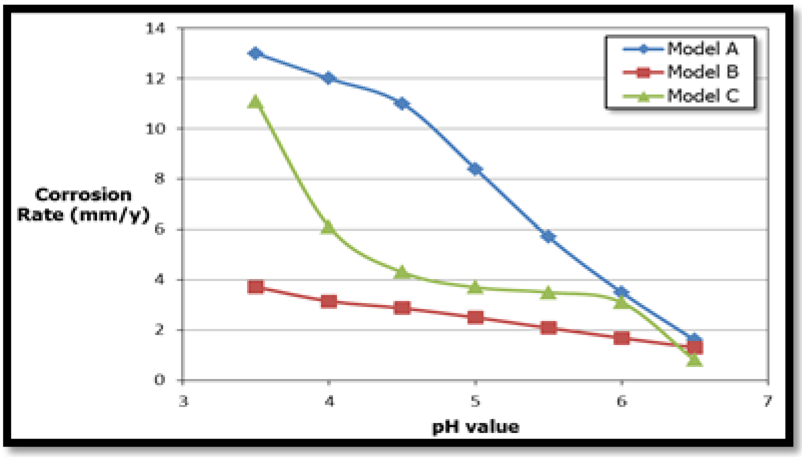


Figure 2.14 : Corrosion rate comparison as a function of pH value with T = 40ºC, 1mol% CO_2 and P = 200 bar

2.5.2 Temperature

For temperature, in industries, any component that is exposed to high temperature is potentially at risk. Basically, temperature accelerates all the processes involved in CO_2 corrosion. Theoretically, temperature can either increase or decrease the corrosion rate. The rate steadily increase with temperature when the precipitation of iron carbonate does not occur in reaction (Nesic.S, 2007). However, at higher temperature for an instance 80°C, the iron carbonate solubility is decreased to such an extent that scale formation is more likely (Khairi et al., 2013). Another laboratory study studies show that the initial rate of uniform corrosion increases up to 70° - 90°, probably due to the increase of mass transfer and charge transfer rates (Malik et al., 2011). Above these temperatures , the corrosion rate starts to decrease. This happened because the formation of a more protective scale due to a decrease in the iron carbonate solubility and also to the competition between the mass transfer and corrosion rates (Chen et al., 2000). From the figure below, we can see the corrosion rate increase and decrease generally.

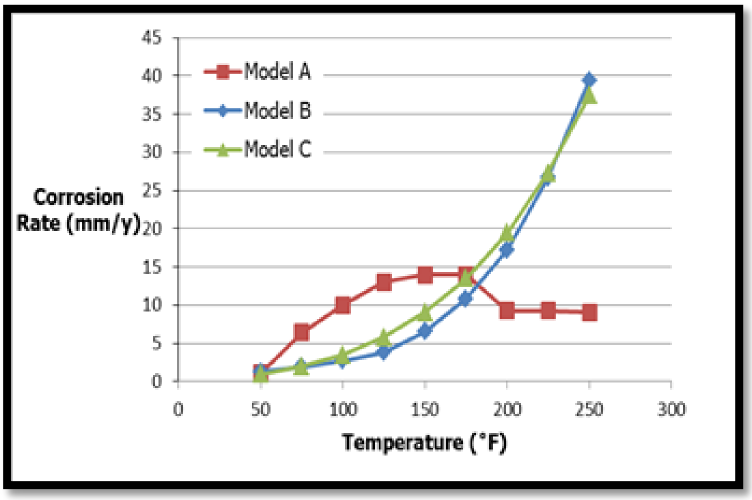


Figure 2.15 : Corrosion rate comparison as a function of temperature under the following defined conditions

2.5.3 CO_2 Partial Pressure

For the next effect is the CO_2 partial pressure. The maximum concentration of dissolved CO_2 in water is 800 ppm (Desimone et.al, 2011). After previous study, it proved that CO_2 partial pressure affect the corrosion rate. The corrosion rate increase significantly with the increase of CO_2 partial pressure. From the experimental data from previous study, when the partial pressure of CO_2 is 30 psi, normally it will indicates corrosion. When the partial pressure between 7 – 30 psi, it may indicate the corrosion and lastly when the partial pressure drop to 7 psi, its normally considered as non-corrosive (Daniyan et.al, 2011).

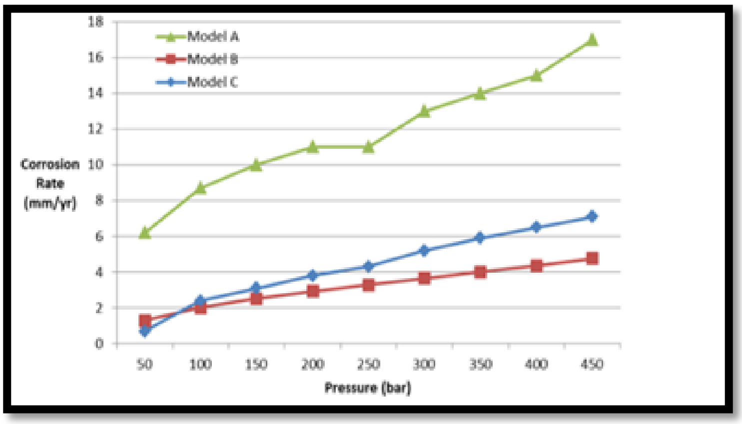


Figure 2.16 : Corrosion rate comparison as a function of pressure

2.6 Corrosion Inhibitors

One of the way to prevent or controlling the damaged done by corrosion is corrosion inhibitor. Corrosion inhibitors continue to play a major part in controlling the damaged done by corrosion associated with oil and gas production and transportation system. A corrosion inhibitor is a chemical compound that when added to a liquid or gas, it will decreases the corrosion rate of a material, typically metal or alloy (Obot,2009). For corrosion inhibitor, it depends on the material that needs to protected and corrosive agents. The typical corrosive agents are generally oxygen, hydrogen sulfide or carbon dioxide. Inhibitors slow corrosion processes by increasing the anodic or cathodic polarization behavior, reducing the movement or diffusion of ions to the metallic surfaces and lastly increasing the electrical resistance of the metallic surface.

2.7 Type of Corrosion Inhibitor

There are two types of corrosion inhibitor which are organic inhibitor and inorganic inhibitor (Jones, 1996). The function of inhibitor is to decrease the rate of corrosion and it will bring more advantages for oil and gas industries :

i. Prevent shutdowns of plant

ii. Prevent loss of heat transfer

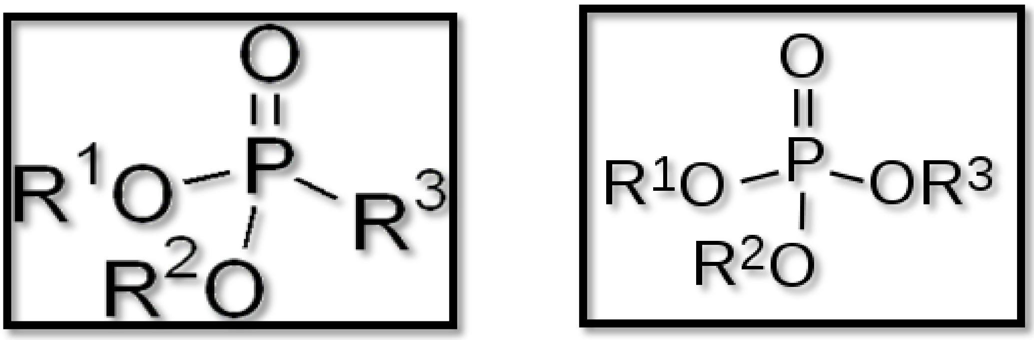
iii. Extend the life of equipment

iv. Prevents accidents resulting from failures

v. Avoid product contamination

2.7.1 Organic Inhibitor

Organic inhibitors are characterized by high molecular weight structures or phosphorous groups which is normally, they are highly polar molecules such as phosphate esters and phosphonates (Sylyester et al., 2012). Molecular structure for both phosphate ester and phosphonate are shown in figure 2.17 below. From the previous study, according to Speller's research, a number of explanations have been proposed as the mechanism of protecting iron from the corroding action by organic inhibitors. Theoretically, this type of inhibitor function to prevent the discharge of hydrogen on the cathodic area of iron. Thus will elimination and avoiding the corrosion from occur.



(a) (b)

Figure 2.17 : Molceular structure (a) phosphate (b) phosphate ester

Theoretically, organic inhibitors usually designated as film forming, and function to protect the metal by forming hydrophobic film on the metal surface. Generally, the effectiveness depends on the chemical composition, their molecular structures and lastly their affinities for the metal surface (Okafor et al., 2009). Organic inhibitors will adsorbed to the ionic charge of inhibitors and the charge of the surfaces.

For CO_2 corrosion, the way organic corrosion inhibitors inhibiting the corrosion is more likely related to their surfaces active properties (El-Lateef et al., 2012) :

i. Adsorption onto the steel surface

ii. Changing the wettability of the steel surfaces

iii. Accumulation at the oil-water interfaces

2.7.2 Inorganic Inhibitor

Inorganic inhibitors can be divided into two which is anodic inhibitors and cathodic inhibitor. Anodic inhibitor or also known as passivating inhibitors cause a large anodic shift of the corrosion potential, forcing the metallic surface into the passivation range (Camila, 2014). For anodic inhibitor, there are two types of passivating inhibitor which are oxidizing anions such as chromate (CrO_4^{-2}), nitrite (NO_2–) and nitrate (NO_3–) that can passivate steel in the absence of oxygen (Ayeni et al., 2007). The other one is nonoxidizing ions such as phosphate (PO_{43}-), tungstate and molybdate that require the presence of oxygen to passivate the steel (Abd ElNabey et al., 2012). Molybdate structure compound can be seen in figure 2.18 as shown in below.

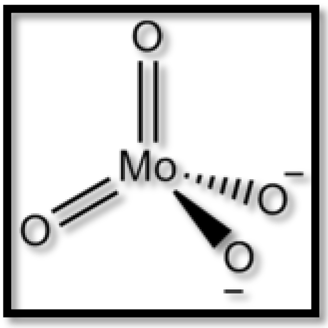


Figure 2.18 : Structural compound for Molybdate Compound

Cathodic inhibitor is one of the inorganic inhibitors and its reacts selectively precipitate on cathodic areas to increase the surfaces impedance and limit the diffusion on the area (Abbasov et al., 2000). Example of cathodic inhibitors are arsenic, antimony, calcium, zinc and magnesium. The cathodic inhibitors will forms a barrier of insoluble precipitates over the metal and will cover it, thus it will restrict the metal from in contact with corrosion process (Roberge et al., 1999).

2.8 Green Inhibitor

Green inhibitor are one of the corrosion inhibitor that can be used in oil and gas industry. Green inhibitors contains without any heavy metals and other toxic compounds. Green inhibitors can be used due to the low in cost and have a good corrosion inhibiting abilities. Other than that, green inhibitor are renewable and easy to get in many countries. Generally, plant extracts contains many organic compound, having polar atoms such as O, P, S, and N. These compound are adsorbed on the metal surfaces by these polar atoms and protective film. For this study, we are using Palm Oil Leaves extract as our green inhibitor to act as corrosion inhibitor.

2.9 Palm Oil Leaves

Palm oil (*Elaeis guineensis)* are one of the common production by Malaysia. In Malaysia, the first plantations of palm oil were mostly established by British plantations owner, such as Sime Darby. In 1917, the first commercial planting took place in Tennamaran Estate in Selangor, which laying the foundations for the vast oil palm plantations and the palm oil industry in Malaysia. Fact, in 1995, Malaysia was the one of the world's largest producer of palm oil, with a 51% of world share. This means that, Malaysia also produce as many as palm oil leaves as a by-product.

For this study, we are using palm oil leaves for extraction as our corrosion inhibitor. We are using palm oil leaves due to the low in cost despite the fact that palm oil leaves acts as a environmental friendly. Thus, it will give positive impact to the environment, safety and health. Other than that, palm oil leaves is very easy to get in Malaysia. This is due to the fact that our country, Malaysia use 1 hectares of land to plants 143 palm oil tree. And to be estimated, in Malaysia, the government spend 4.43 million hectares of land for plantation of palm oil tree. The figure below shows the palm oil leaves that used in this experiment.

Figure 2.19 : Palm Oil Leaves taken from Lepar Estate

2.10 Previous Study of Green Inhibitor

There are different kind of green inhibitor that can be used as corrosion inhibitor. But, reminds that different plant extracts have different value of corrosion rate.

2.10.1 Extract of Tobacco in NaCl Solution

Experimentally, to protect the mild steel in solutions from corrosion, extract of tobacco leaves can be used. Extract tobacco from twigs, stem, and leaves can protect the steel and aluminium in saline solutions (J Buchweishaja, 2000). The result are shown in Figure 2.20.

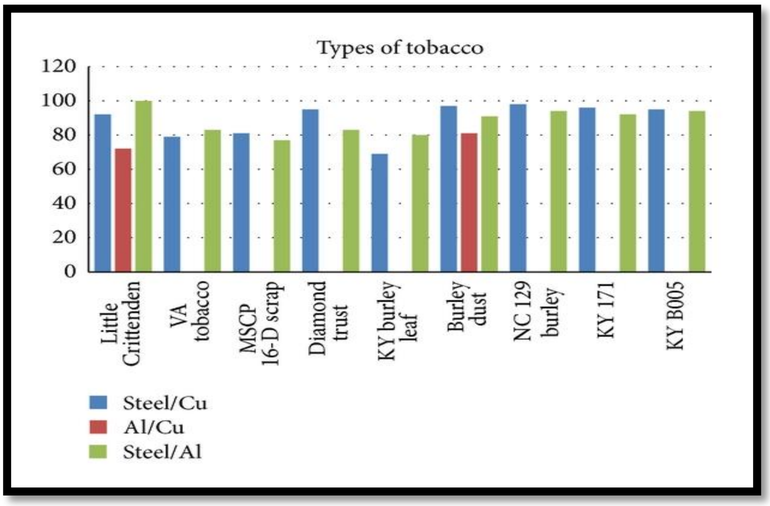


Figure 2.20 : Inhibition efficiency of Tobacco extract for steel/Cu, Al/Cu and Steel/Al (Neha Patni et al., 2013)

From the result shows in Figure 2.20, it was found that maximum inhibition efficiency is 96% with only 0.01% tobacco concentration. That means, tobacco extracts contain high concentration of chemical compound such as alcohol, polyphenols, nitrogen-containing compounds that may exhibit electrochemical activity such as corrosion inhibitor (Neha Patni et al., 2013).

2.10.2 Inhibition of Hot rolled Steel by the *Flavin Mononucleotide (FMN)* in HCl medium

Based on this research, Flavin mononuclotide, (7, 8-dimethyl-10-ribityl-isoalloxazine-5′ phosphate monosodium salt dihydrate) is a phosphate monosodium dehydrated salt of Vitamin B2 (Riboflavin). It consists of a heterocyclic isoalloxazine ring attached to the sugar alcohol and ribitol (Bhola S.M, 2013). From this study, it was found that FMN is a potential inhibitor for corrosion of hot rolled steel in acidic medium. Based on the results, the inhibition efficiency of FMN increases with both concentration and temperature. The highest inhibition efficiency is 94% at high temperature.

2.10.3 Inhibition of the corrosion of mild steel in HCl by the extraction leaves of *Nypa fructicans* Wurmb.

From this research, the weight loss method techniques was used. From the result, it shows that the inhibition was found to increase with the increasing of concentrations of the leaves extract. Based on the result from the previous study, the highest inhibition efficiency is 75.11% at temperature 30°C. The inhibition is higher at low temperature for the extracts, shows that the solution of the leaves *Nypa fructicans* Wurmb could serve as effective inhibitor of the corrosion steel in HCl medium.

2.10.4 Green Inhibitor Summary

Table 2.3 : Summarization of green inhibitor past research

No	**Metal**	**Medium**	**Inhibitor**	**Method**	**References**
1	Zinc	2M of HCl	Aloe vera	• Langmuir adsorption isotherm. • Infrared spectrophotometer • Thermodynamic adsorption	Abiola *et. al*, 2010
2	Concrete steel	NaOH	Banana plant juices	• Weight loss method	El-Sayed *et.al*, 2001
			Mangrabe banana stem	• Galvanostaic polarization techniques	Tantawi *et.al*, 1996
3	Mild Steel	0.1 M Sulphuric acid	Caffeic acid	• Weight loss method • Electrochemical impedance • Raman Spectroscopy	F.S de Souza *et.al*, 2009
4	Carbon Steel	1M HCl	Aqueous extract of mango, orange, passion fruit and cashew peels.	• Electrochemical impedance spectroscopy • Potentiodynamic polarization curves • Weight loss method	J.C da Rocha *et.al*, 2009
5	Al	0.5 M NaOH	Hibiscus Teterifa	• Weight loss measurements	Ayeni *et.al*, 2007
6	Al	0.5 M HCl	*Azadirachta indica (*AZI) plant	• Potentiodynamic polarization • Impedance techniques	Arab *et.al*, 2008
7	Al	1 M HCl	Root of Ginseng	• Weight loss techniques (temp 30° - 60°C)	Obot *et. al*, 2009

2.11 Corrosion Techniques

In order to analysis the corrosion rate in the experiment, there are previous method or way to analysis the inhibitor and corrosion. The two of them are weight loss method and electrochemical method. For this study, we using both of the method to determine the corrosion rate of palm oil leaves inhibitor

2.11.1 Weight Loss Method

Weight loss method is one of the simplest method of estimating corrosion losses in plant. For this method, a weighed sample coupon of the metal or alloy is using in the process and will be removed later after a certain time interval. The coupon is then will be cleaned of all corrosion product and reweighed. Then follow up by weight loss measurement.

Weight loss (%) = $(W_i - W_f) \times 100$

Where , W_i = initial weight before corrosion take places
W_f = weight after corrosion take places

From this value, we can calculate the corrosion rate :

$$\text{Corrosion rate} = \frac{Weight\ Loss\ (g) \times K}{Density\ of\ Metal\ \left(\frac{g}{cm3}\right) \times exposed\ area\ (A) \times Exposure\ time\ (hr)}$$

Where the value of $k = 8.76 \times 10^4$

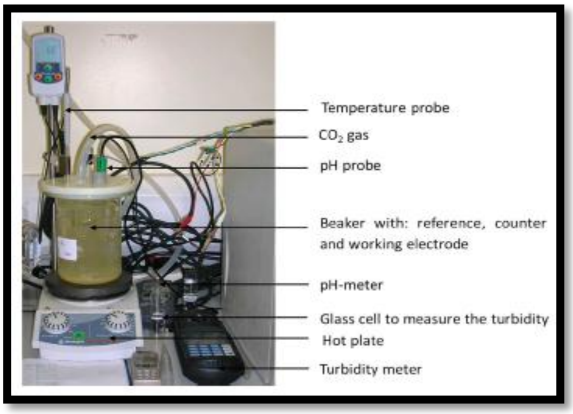


Figure 2.21 : Test apparatus (Sanders et al., 2014)

2.11.2 Electrochemical Method

When corrosion occurs, electrons are released by the metal which is oxidation process take places and gained by elements which reduction process occurs. Electrochemical corrosion experiments measure the current or potential of the reaction occurs by using the polarization resistances method. The polarization resistances method are function to measure the instantaneous corrosion rates compared to other methods. The word instantaneous means that each reading can be translated directly into corrosion rate (Olvera Martinez et al., 2015). This experiment can be done in a short period of time, if there are no disturbances in the system which is polarization from corrosion potential (El-Sayed et al., 2001). The measurements can be monitored through the screen and the graph will spread continuously if the disturbances exist.

Polarization resistances techniques can be used in order to accurately measuring very low corrosion rates which is less than 0.1 mpy (J.C.Rocha et al., 2010). One of the advantage electrochemical corrosion rate measurements are it can measuring the corrosion rate of metal or material that cannot be done by weight loss method. A potentiostat experiment imposes a constant potential on the working electrode for a specific time period. After record the reading, the inhibition efficiency (IE%) will be calculated by charge transfer resistance, as below equation :

$$\boxed{Inhibition\ efficiency\ (\%IE) = \frac{R_{ct(i)} - R_{ct}}{R_{ct}} \times 100}$$

Then, the efficiency of all the paramaters will be compared to know which one is the best condition for palm oil leaves to act as corrosion inhibitor.

From this study, we are using electrochemical and weight loss method as our method to measure the corrosion rate. Therefore, both of the method will be explained further in Chapter 3.

2.11.3 Comparison between methods

As mentioned before, for this study, we are using the electrochemical method and weight loss method, but will focus more on the electrochemical method. Both of the method which is weight loss and electrochemical method both have their own speciality and benefits. But for this study electrochemical method is choosen to explained more because the data of the corrosion rate will be accurate. This is because, we will get the data directly from the software compared to weight loss method, we must weighed the coupon and compare the weighed before and after the corrosion. Other than that, electrochemical method will using a shorter time compared to weight loss method, where weight loss method needed a plenty of time for the coupon to corrodes. Despite the fact that electrochemical method is more effective compared to weight loss method.

CHAPTER 3

METHODOLOGY

3.1 Overview

This chapter is about material and methodology. In this Chapter 3, will be discussing the methodology used for this study with more details and clear. As mentioned before in Chapter 2, we using weight loss method and electrochemical method to calculate the corrosion rate. Below are the Overall flow chart of electrochemical method and weight loss method for this study.

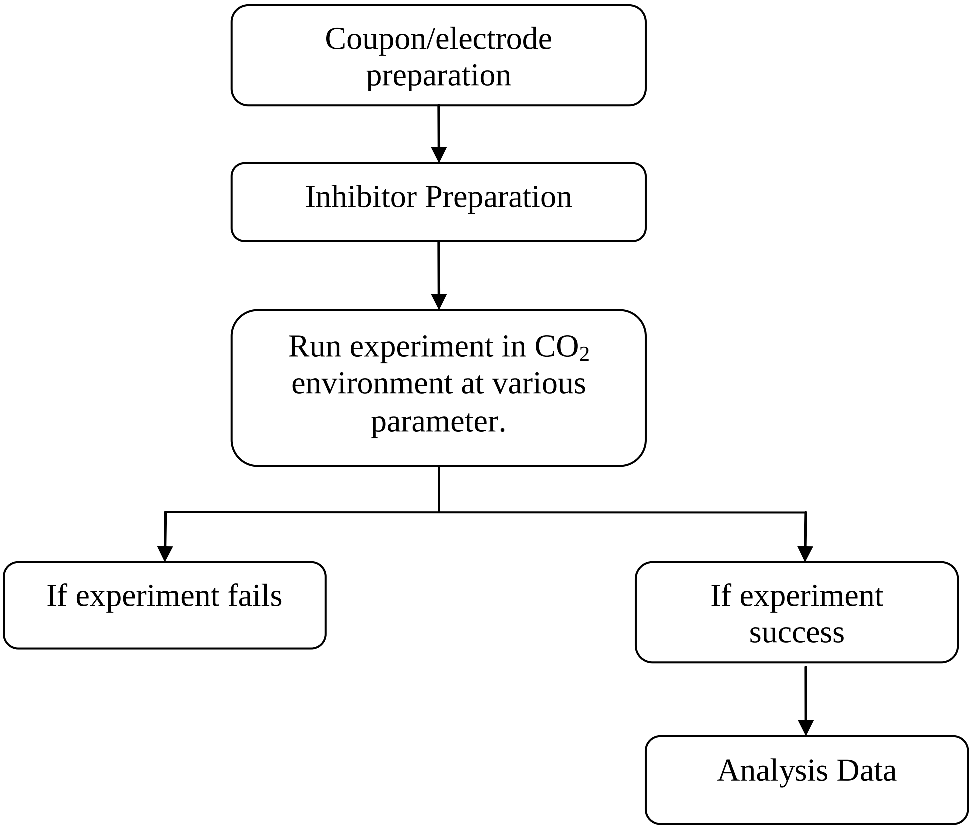
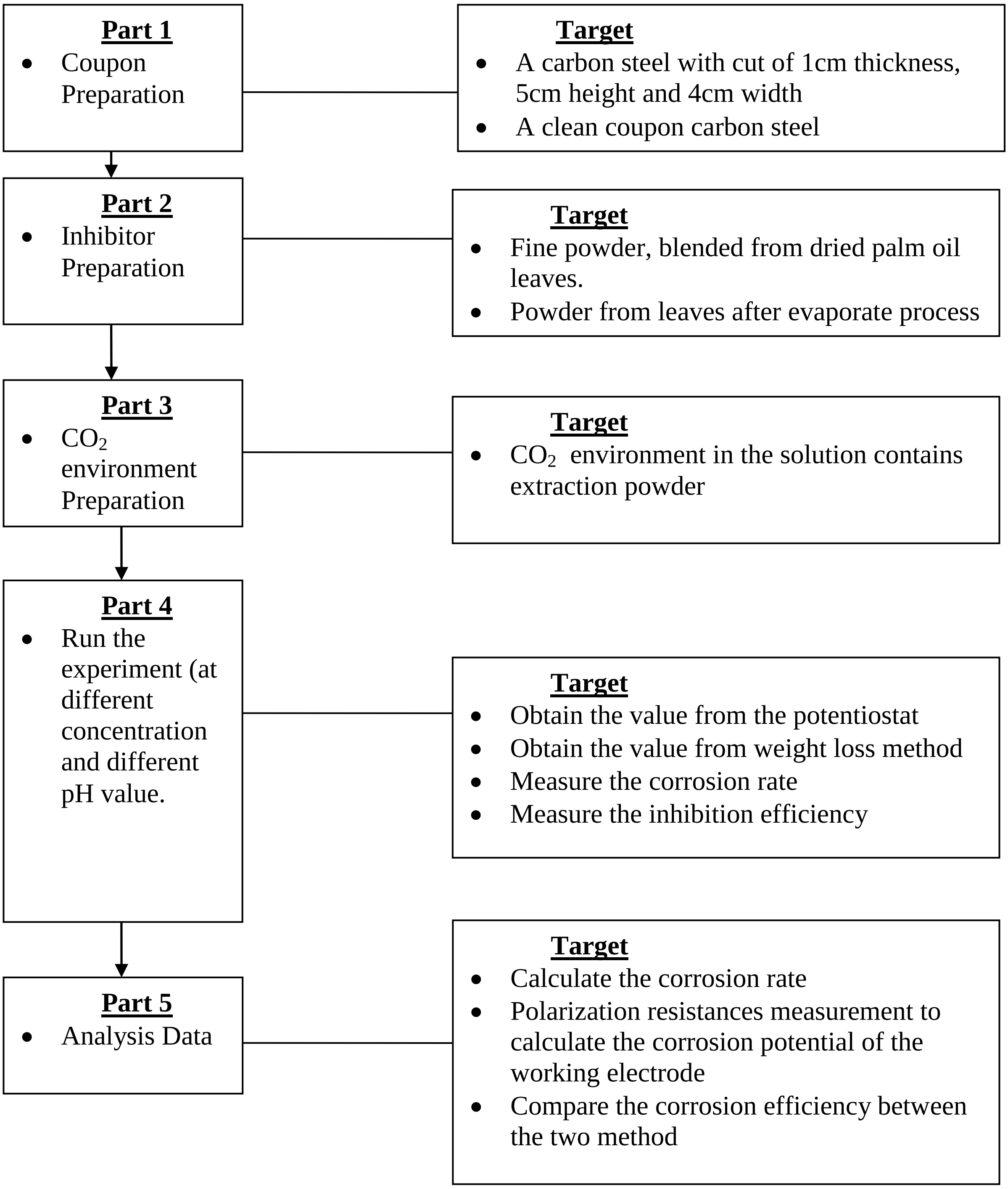


Figure 3.1 : Overall Flow Chart Process

3.2 Introduction

From the overall flow chart process, we can divide this experiment or study into a small part. This is for the purpose to understand the methodology much better in order to run the experiment successfully.



Part 1
- Coupon Preparation

Target
- A carbon steel with cut of 1cm thickness, 5cm height and 4cm width
- A clean coupon carbon steel

Part 2
- Inhibitor Preparation

Target
- Fine powder, blended from dried palm oil leaves.
- Powder from leaves after evaporate process

Part 3
- CO_2 environment Preparation

Target
- CO_2 environment in the solution contains extraction powder

Part 4
- Run the experiment (at different concentration and different pH value.

Target
- Obtain the value from the potentiostat
- Obtain the value from weight loss method
- Measure the corrosion rate
- Measure the inhibition efficiency

Part 5
- Analysis Data

Target
- Calculate the corrosion rate
- Polarization resistances measurement to calculate the corrosion potential of the working electrode
- Compare the corrosion efficiency between the two method

3.3 Test Matrix

Table 3.1 below indicates that six test are carried out by using the inhibitor concentration as parameter for both method weight loss method and electrochemical method. In addition, for weight loss method, different pH are used as tabulate in table 3.2.

Table 3.1 : Test matrix for the laboratory works for weight loss and electrochemical method

Concentration Inhibitor (ppm)	Weight Loss & Electrochemical Method
0	Test 1
5	Test 2
10	Test 3
15	Test 4
20	Test 5
25	Test 6

Table 3.2 : Test matrix for the laboratory works for weight loss method

pH (Control)	**pH (with inhibitor)**	**Weight Loss & Electrochemical Method**
3.20	3.20	Test 1
5.47	5.47	Test 2
6.11	6.11	Test 3
7.01	7.01	Test 4
8.62	8.62	Test 5
9.71	9.71	Test 6

3.4 Materials

Carbon steel sheets was used for the medium of corrosion to take places and the main focus of this study. Carbon dioxide (CO_2) in gaseous state was used to create a CO_2 environment for the solution. Other than that, the chemicals used in this study is methanol for the palm oil leave extract process. Antimony (III) oxide (Sb_2O_3) and tin (II) chloride (SnO) was used for the purpose of cleaning the coupon after experiment was conducted. Lastly, palm oil leaves was used to be as corrosion inhibition.

3.5 Equipment

There are a few of equipment used for this study. There are CO_2 gas facilities, corrosion cell, SCE electrode for electrochemical method and potentiostat supplied by ACM Instrument to measure the corrosion rate.

3.5.1 CO_2 Gas Facilities

In order to make the carbon dioxide environment, CO_2 cylinder was used as the container of CO_2 in gaseous phase. Then, the pressure regulator was used to reduce the supply pressure. Note that the pressure used for this study is 1 atm (Olvera Martinez et al., 2015).

Figure 3.3 : CO_2 Gas Tank as a supplier of carbon dioxide.

3.5.2 Corrosion Cell

Ointment jar was used as corrosion cell in this experiment. Six ointment jar was needed to make a constant concentrations at six different concentrations and six different pH. At the cover of the ointment jar, a hole was make in order to flow the carbon dioxide gas.

Figure 3.4 : A clear ointment jar

3.5.3 SCE Electrode

Saturated calomel electrode (SCE) is reference electrode based on the reaction between elemental mercury and mercury (I) chloride. It normally linked via a porous to the solution in which the other electrode is immersed. This porous frit is a salt bridge. SCE is one of the most common electrodes used in corrosion studies. The SCE is connected to the potentiostat in order to get the readings.

Figure 3.5 : One of the saturated colonel electrode (SCE)

3.5.4 Potentiostat

Potentiostat is the electronic hardware required to control a three electrode cell. It is an electronic device that maintain a metal at a constant potential either respect to a references electrode. A potentiostat capable in controlling two working electrodes and more than two electrodes (Raja P.B et al., 2007). From the figure 3.6 below, it shows that the potentiostat has the three terminals which one was connected to the tank, another one to the cathode and the last to the references electrode which is SCE.

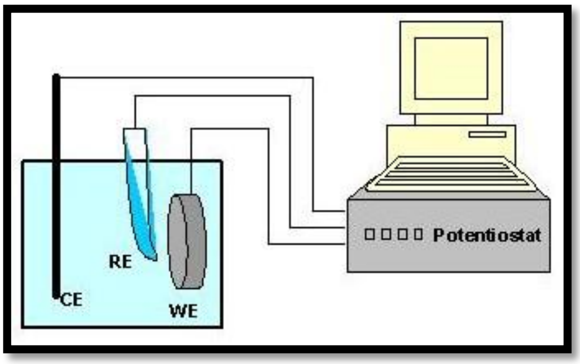


Figure 3.6 : Drawing of potentiostat that using in electrochemistry experiment

Figure 3.7 : Gamry Potentiostat used in electrochemical method

3.6 Procedure

3.6.1 Plant Collection (Palm Oil Leaves)

Fresh leaves of palm oil (*E.guineensis)* were collected from Lepar Estate, Gambang and used as the corrosion inhibitor for this study. The leaves were cut into smaller pieces and washed carefully under the tap water. The leaves were dried in an oven at temperature 50ºC for 48 hours. The dried leaves were blended to fine powder by using a mechanical blender as shown in the figure below (N.Yin et al., 2013). A detail picture is shown in the appendix A1.

Figure 3.8 : Palm Oil Leaves Powder after blended

3.6.2 Coupon Preparation

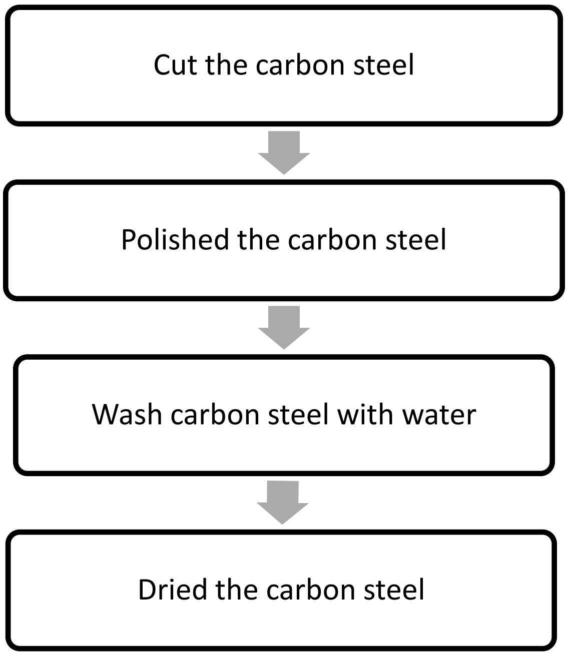


Figure 3.8 : Flowchart of carbon steel preparation

From the flowchart shows above, a sheets of carbon steel was obtained and was cut into a specific measurements. The carbon steel coupons was polished in order to get the shining surfaces. This is play an important part, because the result might be different if the carbon steel is not clean. The steel was washed with distilled water and dried before using for the experiment. Below are the example of clean carbon steel that we used for the experiment.

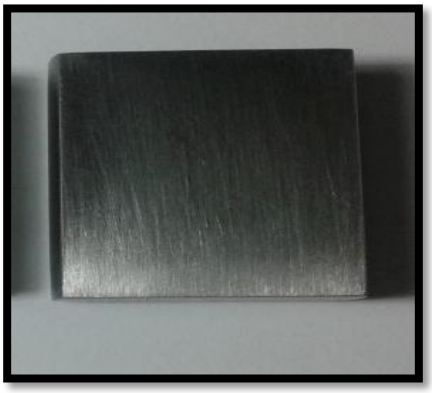


Figure 3.9 : Clean carbon steel after being polished

3.6.3 Electrode Preparation

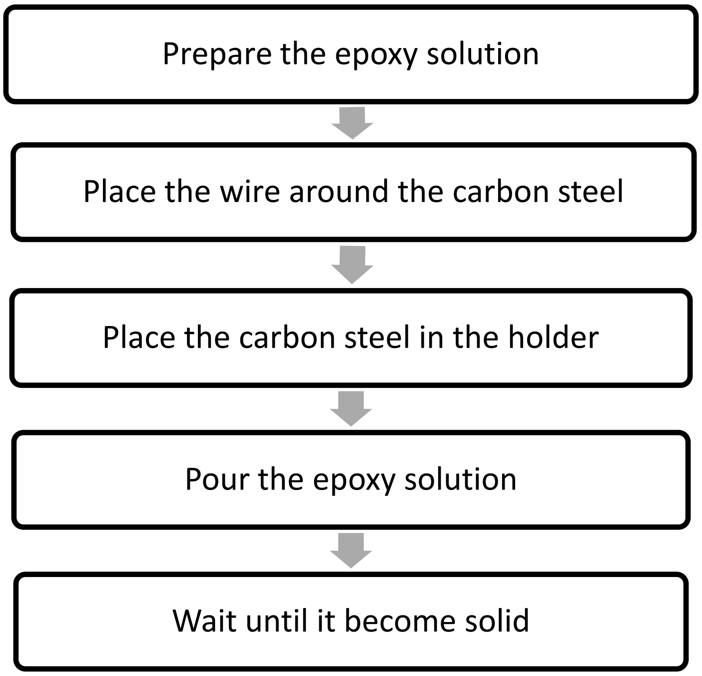


Figure 3.10 : Flowchart of electrode preparation

Based on the flowchart above, the epoxy solution was prepared by using epoxy resin and epoxy hardness as shown in the appendix A1. The sample (carbon steel) wes cleaned before encapsulating. Ratio 5 to 1 (5:1) was used to make the epoxy solution. For one electrode, 25mL epoxy resin and 5mL epoxy hardness was used to make the solution. The solution was stirred continuously for two minutes by using stirring stick. 20cm wire was cut and winded around the carbon steel. The carbon steel was placed in the mold and epoxy solution was poured into the holder. The solution was hardener after a few hours.

3.6.4 Inhibitor Preparation

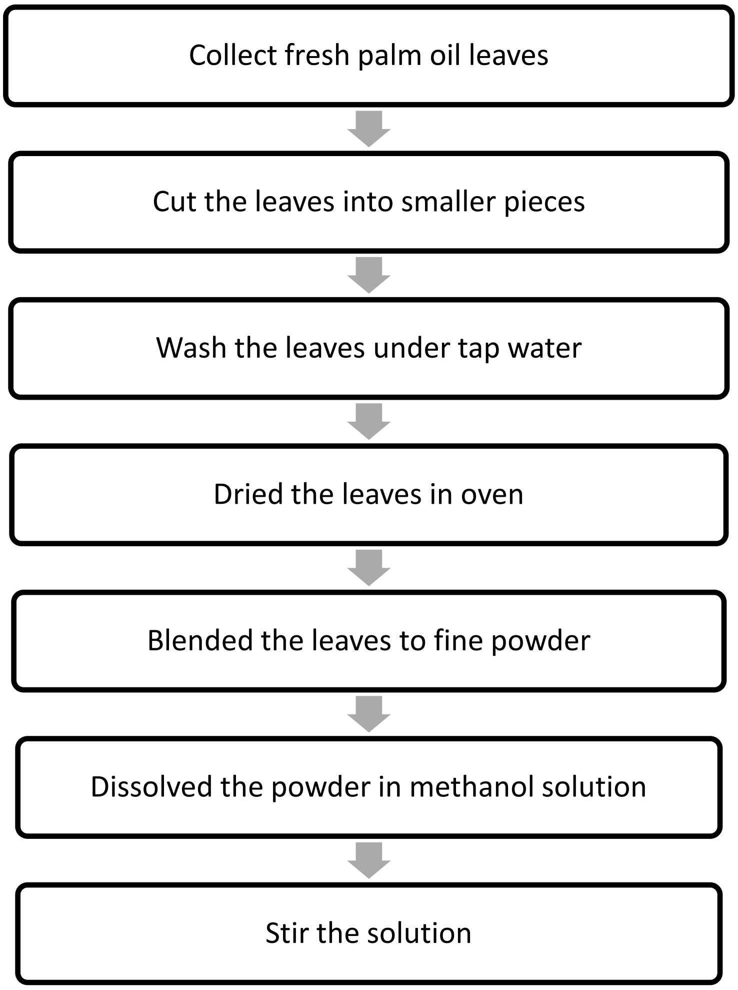


Figure 3.11 : Flowchart for inhibitor preparation

Inhibitor preparation must undergo extraction process to get the inhibitor solution. For extraction process, organic solvent such as methanol was used. 50g leaves powder were dissolved in 500mL of methanol into conical flask. The conical flask will be covered with aluminium foil and the solution will be mixed for 12 hour by using magnetic stirrer in fumehood. Another set of experiment were carried out at different speed and different temperature. Lastly, the extraction were filtered by using filter paper and the juice were evaporated in fumehood until dry.

3.6.5 CO_2 Corrosion Preparation

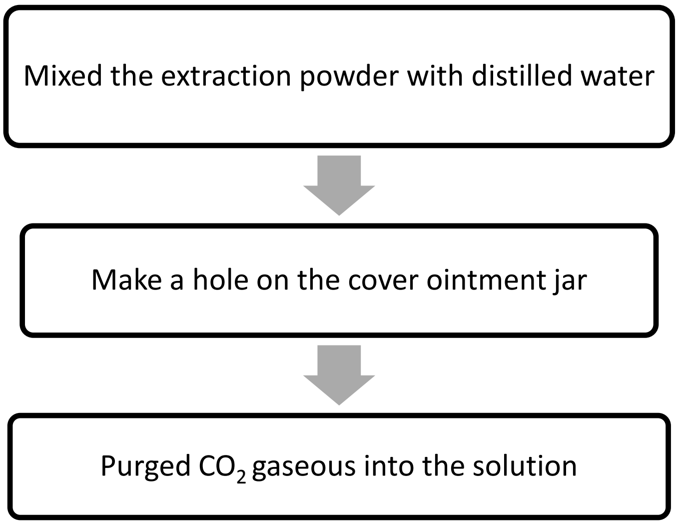


Figure 3.12 : Flowchart for CO_2 corrosion or environment preparation

These are the steps before initialize the experiments. Two holes on the cover of the ointment jar were prepared as shown in the figure below. One hole was connected to CO_2 gas tank to create the CO_2 environment. The CO_2 was purged into the solution through the hole to create the CO_2 environment. The CO_2 gasseous were pumped by using pressure regulator from the CO_2 cylinder or tank in the solution to create the CO_2 environment.

Figure 3.13 : Ointment jar with two holes

3.6.6 Electrochemical Measurements

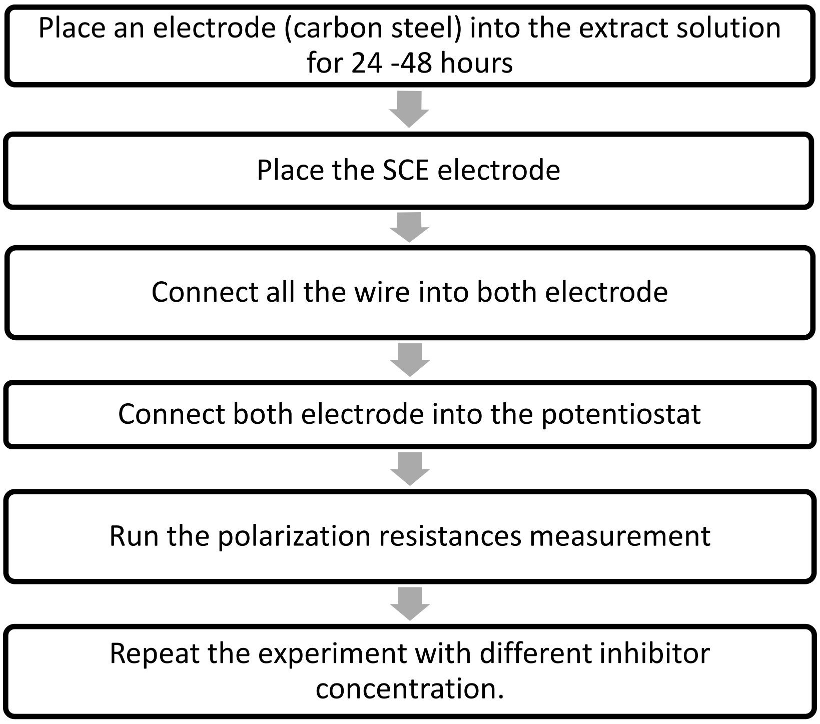


Figure 3.14 : Flowchart of experimental procedure for polarization measurement

An experiment was conducted at the room temperature with different inhibitor concentration to study the corrosion rate in CO_2 corrosion. The corrosion rate was determined using the electrochemical method which is polarization resistance by using potentiostat as the equipment. For this experiment, the polarization resistances test were conducted at a scan rate of 0.125 mV/s. The LPR measurements were taken at ±0.02 V by using the potentiodynamic scan rate at 0.125 mV/s. The step were repeated by using different inhibitor concentration which are control, 5ppm, 10ppm, 15ppm, 20ppm and 25ppm.

Table 3.3 : Experimental parameters for inhibitor concentration.

Parameter	Value
Initial E (V)	-0.02
Final E (V)	0.02
Scan rate (mV/s)	0.125
Sample Period (s)	2
Density (g/cm^3)	7.85
Time (s)	180
Stab. (mV/s)	0.1
IR Comp	Off
Equivalent Time (s)	0
Open Circuit (V)	-0.5220616

3.6.7 Weight Loss Measurements

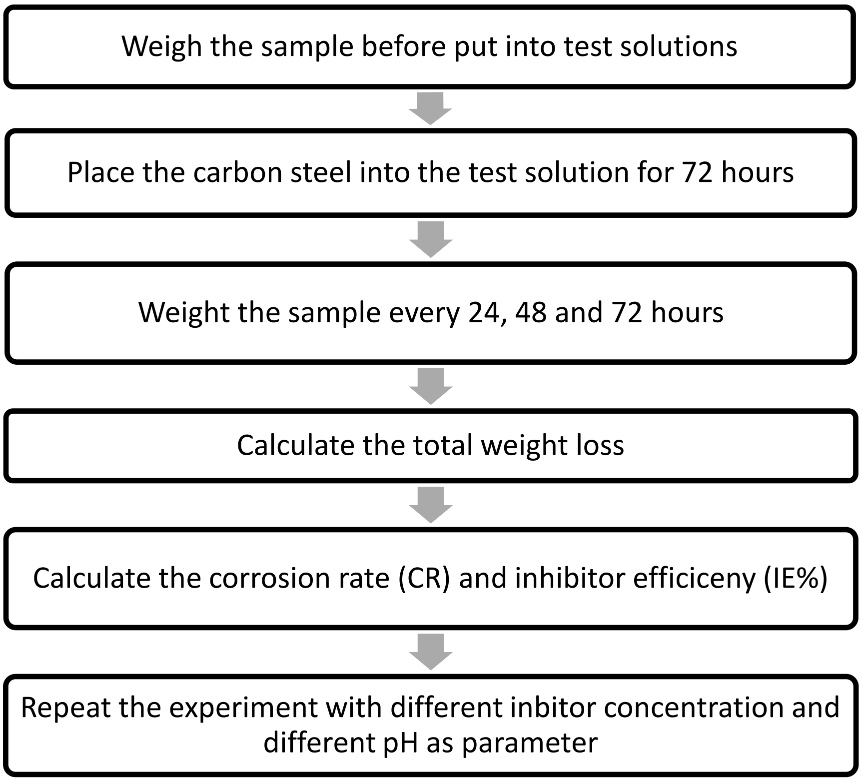


Figure 3.15 : Flowchart of experimental procedure for weight loss method

An experiment was conducted at standard room temperature with different inhibitor's concentration to study the corrosion rate in CO_2 environment. The corrosion rate was determined by using weight loss method for 72 hours of immersion. The inhibitor efficiency was calculated by using equation (1) and the corrosion rate (CR) were calculated by using :

$$\text{CR (mm/yr)} = 87.6 \times \frac{W}{D \times A \times T}$$

Where W is weight loss (mg), D is metal density (g/cm^3), A is area (cm^2) and T is time of immersion (hr).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter shows results and discussion of the palm oil leaves as corrosion inhibitor for a carbon steel in CO_2 corrosion using electrochemical and weight loss method. Analysis of polarization resistances is needed to identify the corrosion rate of the sample. Discussion and comparison based on two method and parameters which are inhibitor concentration and pH in CO_2 corrosion also presented.

4.2 Electrochemical (Polarization Resistances) Method

4.2.1 Effect of Inhibitor Concentrations

An experiment was conducted at the room temperature with different inhibitor concentration to study the corrosion rate in CO_2 corrosion. The corrosion rate was determined using the electrochemical method which is polarization resistance by using potentiostat as the equipment. In the case of inhibitor, the corrosion rate (CR) decrease as the inhibitor concentration increase, where getting the maximum inhibition efficiency at 99.53% at 25ppm as shown in the table 4.1. The inhibition efficiency (IE) was calculated according to the following equations:

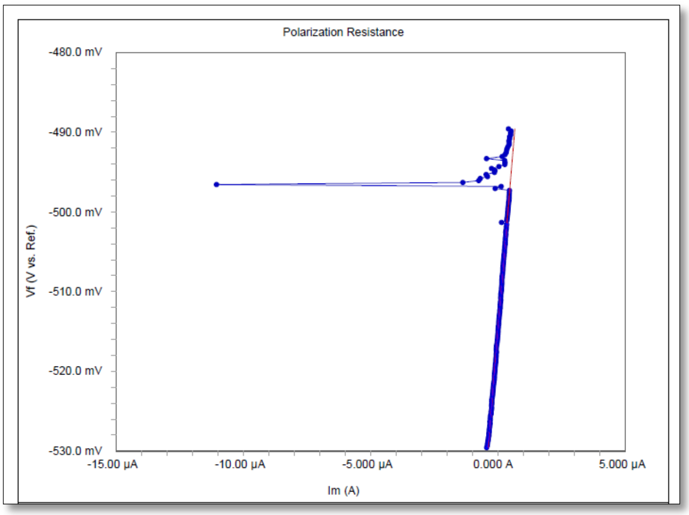
$$IE = [\ (CR_o - CR_i)/\ CR_o\ ] \times 100$$

where CR_o is the corrosion rate without inhibitor and CR_i is the corrosion rate with addition of inhibitor concentration.

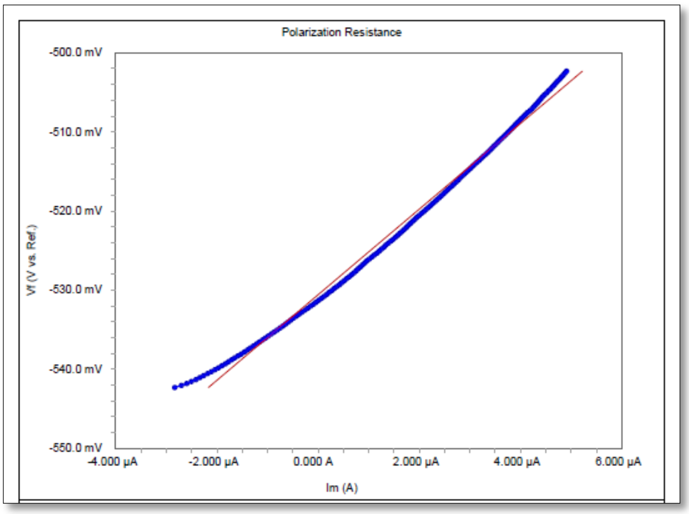
Figure 4.1 represent the results which are obtained for the test performed in CO_2 test medium with different inhibitor's concentration. Table 4.1 shows the summarization of various parameter of polarization of polarization resistance which is obtained from the experiment.

Table 4.1: Corrosion rate value (CR) and corrosion inhibitor concentration at different inhibitor concentrations.

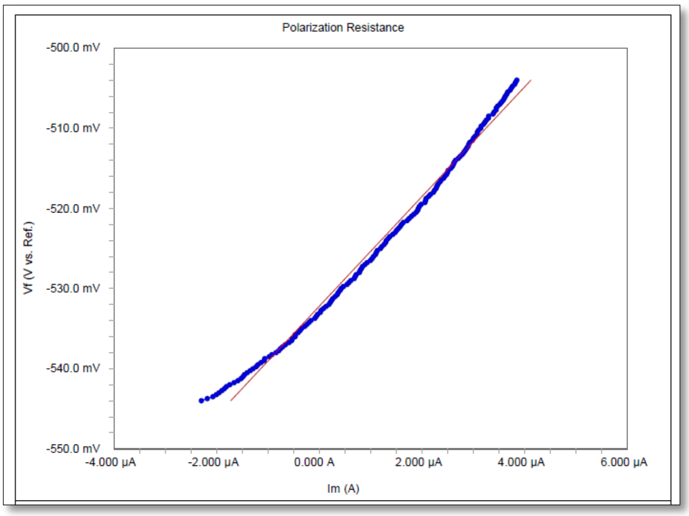
Concentration (ppm)	**E_{corr} (V)**	**I_{corr} (V)**	**Corrosion Rate (mm/y)**	**IE (%)**
0	-0.5151	6.8508E-06	7.2827	-
5	-0.5313	4.8157E-06	2.0440	71.93
10	-0.5330	3.8079E-06	1.9591	73.10
15	-0.5837	4.5566E-06	0.7220	90.09
20	-0.5534	8.3380E-06	0.0646	99.11
25	-0.4254	7.6695E-06	0.0340	99.53



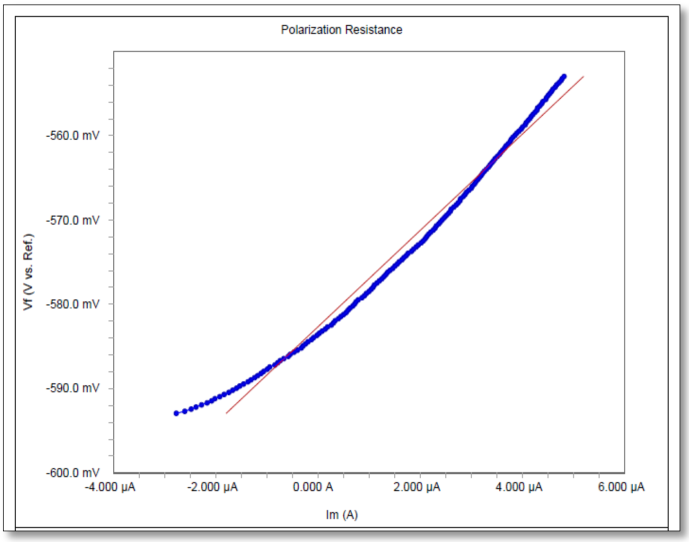
(a)


Polarization Resistance
-500.0 mV
-510.0 mV
-520.0 mV
-530.0 mV
-540.0 mV
-550.0 mV
Vf (V vs. Ref.)
-4.000 µA
-2.000 µA
0.000 A
2.000 µA
4.000 µA
6.000 µA
Im (A)

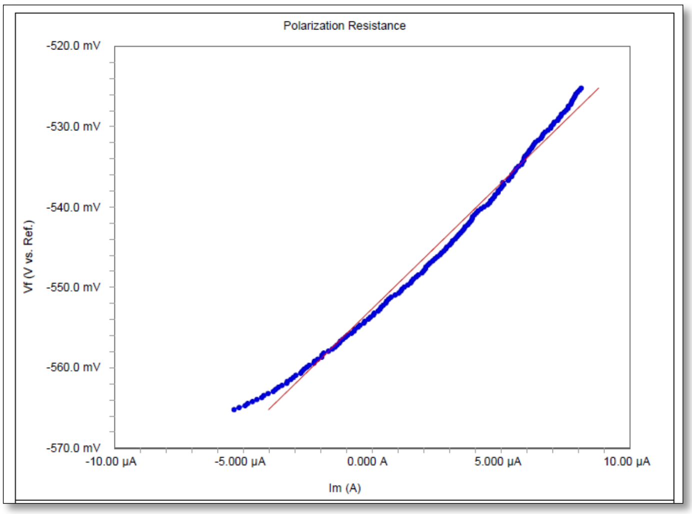
(b)


Polarization Resistance
-500.0 mV
-510.0 mV
-520.0 mV
-530.0 mV
-540.0 mV
-550.0 mV
Vf (V vs. Ref.)
-4.000 µA
-2.000 µA
0.000 A
2.000 µA
4.000 µA
6.000 µA
Im (A)

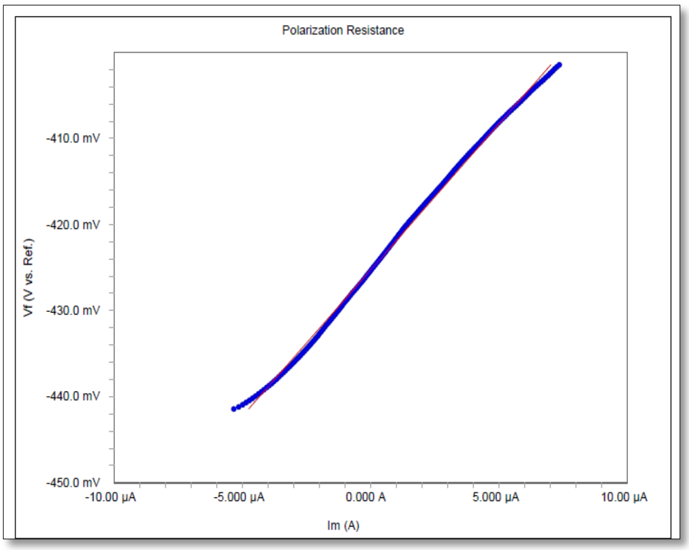
(c)


Polarization Resistance
-560.0 mV
-570.0 mV
-580.0 mV
-590.0 mV
-600.0 mV
Vf (V vs. Ref.)
-4.000 µA
-2.000 µA
0.000 A
2.000 µA
4.000 µA
6.000 µA
Im (A)

(d)



(e)



(f)

Figure 4.1 : Polarization Resistance Graph at ±0.02 V by using the potentiodynamic scan rate at 0.125 mV/s with different inhibitor's concentrations (a) Blank (b) 5ppm (c) 10ppm (d) 15ppm (e) 20ppm and (f) 25ppm.

The table shows that by increasing the inhibitor concentration it will decreasing the corrosion rate thus increasing the inhibitor efficiency (%). By using polarization techniques, we can get the applied current linear polarization curve as shownabove. It can be observed that, the change in voltage (V) with current (A) after adding the corrosion inhibitor for different inhibitor concentration. All electrochemical measurement were using a potentiostat equipment. The detail result for polarization resistances measurement can be seen at Appendix A3.

For this experiment, the polarization resistances test were conducted at a scan rate of 0.125 mV/s. The LPR measurements were taken at ±0.02 V by using the potentiodynamic scan rate at 0.125 mV/s. From the table 4.1, the control or blank set of experiment, showed the highest corrosion rate which is 7.2827 mm/yr with the value of I_{corr} is 6.8508E-06 A and E_{corr} is -0.5151 V respectively. For inhibitor concentration 5ppm, the value of corrosion rate started to decreased compare to control which is 2.0440 mm/yr and have the value of I_{corr} and E_{corr} which are 4.8157E-06 A and -0.5313 V. At 5ppm inhibitor concentration, inhibitor efficiency can be obtained and the value of IE% at 5ppm is 71.93%. The test with 25% inhibitor concentration recorded the lowest corrosion rate value which is 0.0340 mm/yr and the highest inhibitor efficiency which is 99.53% were calculated as below. More detail for the calculation at Appendix A2.

Inhibitor concentration : 25ppm

$$\text{IE}(\%) = \frac{(\,7.2827-0.0340\,)}{7.2827} \times 100 = 99.53\%$$

The value of corrosion rate decrease with the increasing of inhibitor's concentrations is due to the active sites blocking effect that occurs when the inhibitor is added (Nordsveen.M et al., 2003). CO_2 acts in two ways in the solution, which are it will increasing the amount of hydrogen formed on the cathode and will forms carbonate oxide films on the surface of the metal (Hany et al., 2012).

4.3 Weight Loss Method

4.3.1 Effect of Inhibitor Concentrations

An experiment was conducted at standard room temperature with different inhibitor's concentration to study the corrosion rate in CO_2 environment. The corrosion rate was determined by using weight loss method for 72 hours of immersion. The inhibitor efficiency was calculated by using equation above and the corrosion rate (CR) were calculated by using :

$$\text{CR (mm/yr)} = 87.6 \times \frac{W}{D \times A \times T}$$

where W is weight loss (mg), D is metal density (g/cm^3), A is area (cm^2) and T is time of immersion (hr).

Presented in the Table 4.2 is the results obtained for the weight loss experiments which is performed at different concentrations of extract used as inhibitor. Figure 4.2 shows the different in weight loss for different concentration for 72 hours of immersion.

Table 4.2 : Weight loss study in different concentration

Concentration (ppm)	**Weight (g)**				**Weight Loss (g)**	**Corrosion Rate (mm/yr)**	**Inhibitor Efficiency (IE%)**
	After 0 hours	**After 12 hours**	**After 24 hour**	**After 72 hours**			
0	33.5247	33.5004	33.3489	33.3106	0.2141	0.2950	-
5	31.2450	31.2294	31.2083	31.1711	0.0739	0.2291	22.34
10	33.5192	33.5073	33.4817	33.4764	0.0428	0.0590	80.00
15	37.4388	37.4364	37.4235	37.4223	0.0165	0.0338	88.54
20	31.4087	31.4042	31.4006	31.3978	0.0109	0.0227	92.31
25	31.1309	31.1294	31.1278	31.1259	0.0050	0.0069	97.66

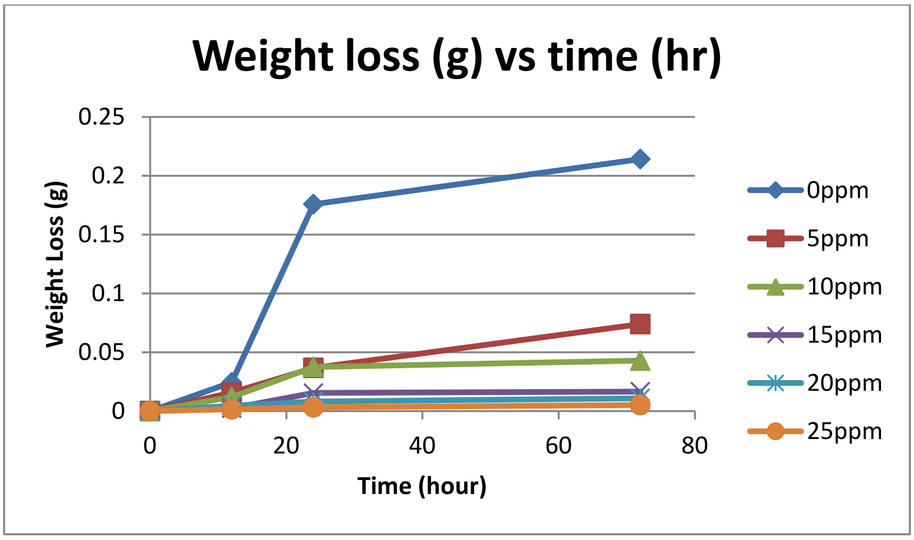


Figure 4.2 : Plot of weight loss with exposure time for carbon steel with different inhibitor concentration with immersion of 72 hours.

It is cleared that the carbon steel immersed in the extract solution with no inhibitor (control) lost the most weight within 72 hours of the experiment, with the total of weight loss of 0.2141 g. As the inhibitor is added to the samples, the weight loss of carbon steel starts to decreased. As shown in figure 4.2, it is cleared that the number of weight loss decreased drastically compared sample with no inhibitor. For the 5ppm, the total weight loss is 0.0731g and for the concentration 25ppm the total weight loss is 0.0050g.

As shown in the table 4.2, the carbon steel sample immersed in the solution containing inhibitor showed an improvement effect in corrosion inhibitor efficiency where it started to increase starting from 5ppm to 25ppm. The figure 4.3 shows the pattern of inhibitor efficiency (IE%) at different inhibitor concentration. The highest value of inhibitor efficiency (IE%) is 97.66% at 25ppm. This proves that the extraction of palm oils can act as a good natural inhibitor, since 25ppm of inhibitor can reduce about 97.66% of the rate corrosion.

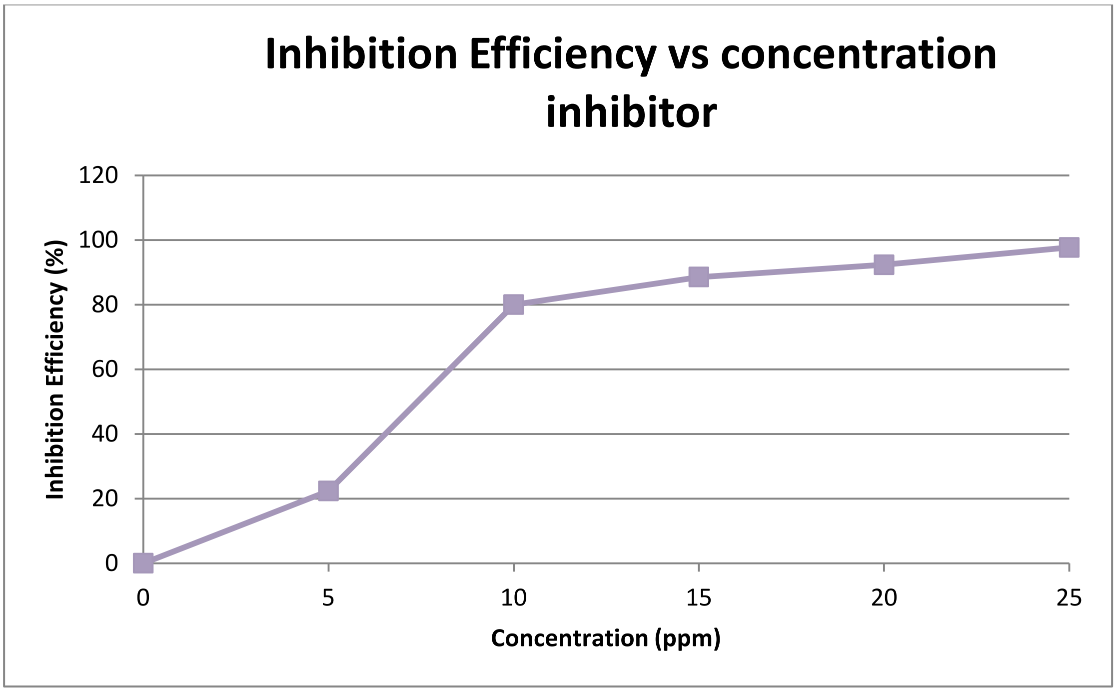


Figure 4.3 : Pattern of inhibitor efficiency (IE%) at different inhibitor concentration (control, 5ppm, 10ppm, 15ppm, 20ppm and 25ppm).

Calculation of the corrosion rate (CR) and inhibitor efficiency (IE%) are shown as below and more detail for the calculation at different concentration at Appendix A2.

Inhibitor concentration : 25ppm

$$\text{CR (mm/yr)} = 87.6 \times \frac{0.50}{7.85 \times 11.25 \times 72} = 0.0069 \text{ mm/yr}$$

$$\text{IE(\%)} = \frac{(0.2950 - 0.0069)}{0.2950} \times 100 = 97.66\%$$

4.3.2 Effect of pH

Series of experiment were carried out at standard room temperature with different pH value of test solutions. The pH values are ranging from 3.20 to 9.71 and the carbon steel were placed in test solutions. The corrosion rate was determined by using weight loss method for 72 hours of immersion, and the value for corrosion rate (CR) and inhibition efficiency (IE%) were calculated by using the same equation as before.

Presented in the Table 4.3 and 4.4 are the results obtained for the weight loss experiments which is performed at different pH of test solutions. Table 4.3 shows the result for test solutions with inhibitor at concentration 25ppm, while table 4.4 shows the result for test solution with no inhibitor. Table 4.5 shows the inhibitor efficiency (IE%) from both of the sample. Figure 4.3 shows the comparison in weight loss for both with inhibitor and no inhibitor for 72 hours of immersion. Figure 4.4 shows the relationship inhibition efficiency (IE%) and pH in this experiment. Comparison also can be seen through all the figure.

Table 4.3: Weight loss study in different pH with inhibitor concentration 25ppm.

pH	Weight (g)				Weight Loss (g)
	After 0 hours	After 12 hours	After 24 hour	After 72 hours	
3.2	31.2369	31.2178	31.2001	31.1902	0.0467
5.47	34.1082	34.1004	34.0791	34.0350	0.0732
6.11	41.5214	41.5047	41.4780	41.4675	0.0539
7.01	41.5363	41.5208	41.5173	41.5101	0.0262
8.62	31.4608	31.4259	31.3811	31.3703	0.0905
9.71	33.4851	33.4753	33.4683	33.4455	0.0396

Table 4.4: Weight loss study in different pH with no inhibitor concentration (control)

pH	Weight (g)				Weight Loss (g)
	After 0 hours	After 12 hours	After 24 hour	After 72 hours	
3.2	41.4237	41.3269	41.1487	40.9961	0.4276
5.47	34.0327	33.9828	33.6081	33.6222	0.4105
6.11	32.7895	32.5157	32.5070	32.4803	0.3092
7.01	37.7139	37.7106	37.7083	37.4286	0.2853
8.62	31.0433	30.9939	30.6842	30.6674	0.3759
9.71	31.2586	31.2178	31.1936	30.8574	0.4012

Table 4.5: Inhibitor Efficiency in different pH value

pH	**Weight Loss (g)**		**IE(%)**
	Inhibitor	**Control**	
3.2	0.0467	0.4276	89.08
5.47	0.0732	0.4105	82.17
6.11	0.0539	0.3092	82.57
7.01	0.0262	0.2853	90.82
8.62	0.0905	0.3759	75.92
9.71	0.0396	0.4012	90.13

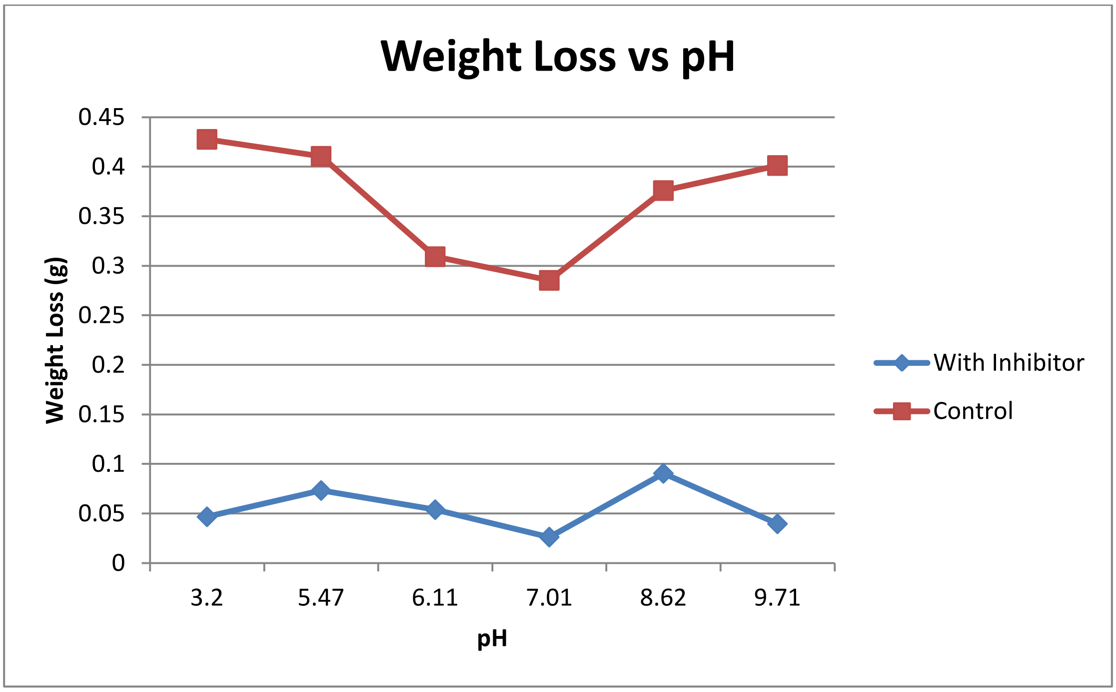


Figure 4.3: Plot of weight loss with exposure time for carbon steel with different pH with immersion of 72 hours.

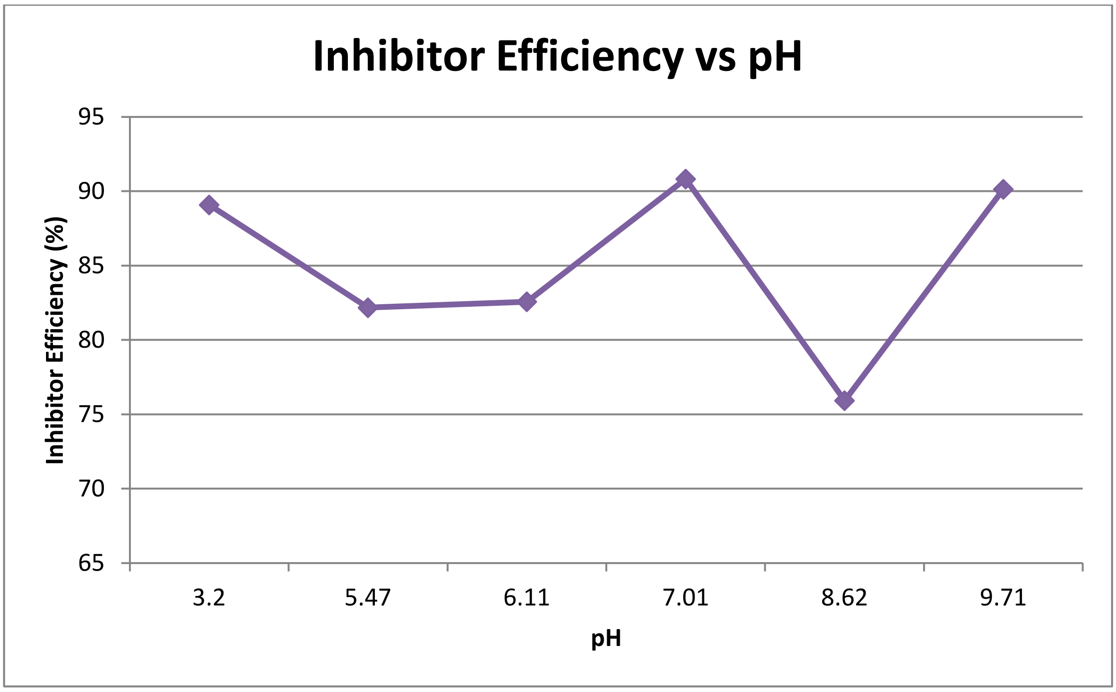


Figure 4.4: Plot of inhibitor efficiency for carbon steel with different pH with immersion of 72 hours.

Based on results shown in the table above, we can see the comparison between these pH value (acid, neutral and alkali). Table 4.3 shows the weight loss between different pH value at concentration of inhibitor 25ppm. The highest weight loss occur at alkali state which is at pH 8.62 with the weight loss 0.0905g. The lowest weight loss is 0.0262g, at neutral state where the pH value is 7.01. During acid state at pH 5.47, the weight loss is also high compared to neutral state where the value is 0.0732g.

Different with no inhibitor added to the test solutions, the amount of weight loss is particularly high compared to with inhibitor in the test solutions. The highest weight loss value is during acid state with pH is 3.20 where the value is 0.4206g. Followed by alkali at pH 9.71 and the lowest weight loss is at pH 7.01, 0.2853g.

Table 4.5 and figure 4.4 shows the pattern of inhibitor efficiency for the carbon steel at different pH value. The highest inhibitor efficiency is 90.82% at pH value 7.01, followed by 90.13% at alkali state with pH 9.71. The lowest inhibitor efficiency is 75.92% at pH 8.62%.

As the pH value increase from 3.2 to 5.47, the inhibition efficiency start to decrease before gradually gain the momentum of growth start from pH 6.11 to 7.01. But the inhibitor efficiency start to decrease again at pH 8.62 and increase when the pH value is 9.71. It can be concluded that it can highly influence corrosion when the solution is highly acidic or highly alkaline (Mardhiah et al., 2014).

The pH represent the hydrogen ion concentration in a given solution. Changing pH has a very strong effect on localized corrosion and general corrosion theoretically. At a pH lower than 4, the proton reduction is the dominated cathodic reaction, while at a pH higher than 4, the dominated reaction is the reduction of carbonic acid.

In the pH 4 to pH 10, the corrosion rate of iron is relatively independent of the pH of the solution. In this pH range, the corrosion rate is governed largely by the rate at which oxygen reacts with absorbed atomic hydrogen, thereby depolarizing the surface thus allowing the reduction reaction to continue (Horvath et al., 1998).

4.4 Discussion on the Inhibitor Concentration

With the presence of inhibitor can slow down the corrosion rate. It has been proved by the past and current study. Basically, the corrosion inhibitor must contain a polar group such as amino group and these compounds able to adsorbed on the metallic surface and isolate it from the corrosive environments. Most organic inhibitors contains at least one nitrogen functional group. Theoretically, these nitrogen-based inhibitors are reacted with organic acid or oxygen functional groups (Bott R, 2014). This is the main reason why extraction of palm oil can be used as corrosion inhibitor. The presences of nitrogenous compounds in the extract formed a layer which keeps the water away from the metal surface.

In this experiment, palm oil leaves extract was used as corrosion inhibitor. From the result before, it can be seen that the corrosion rate values decreased and the inhibitor efficiency increased with increasing of inhibitor's concentration. This is due to the fact that the adsorption coverage of the inhibitor on carbon steel surface increases with the concentration of the inhibitor (Khairi et al., 2013). Palm oil leaves extract contains organic compound such as like oxygen, sulphur and nitrogen, which is excellent to acts as corrosion inhibitor. Based on the previous study, when the inhibitor concentration increased, thus it will decrease the weight loss of carbon steel in any state of solutions (Nwigbo et al., 2012).

The table below shows the inhibitor efficiency of other green inhibitor from previous study in any type of medium for corrosion. The inhibitor concentration used for each of the experiment is 20ppm-25ppm. The comparison between all of these green inhibitor can be seen at the inhibitor efficiency (IE%), thus we can know whether the palm oil leaves extract are the good green inhibitor or not.

The highest inhibitor concentration for electrochemical method is 99.53% whereas the weight loss method is 97.66%. From the table below, the highest IE% for green inhibitor is *Tagetes eracta* (Marigold Flower) in acidic medium at 98.19%. Thus, it can conclude that palm oil leaves extract is one of the good inhibitor .

Table 4.6: Previous study about green inhibitor at inhibitor concentration 20-25ppm

No	**Green Inhibitor**	**IE%**	**References**
1	Fig Leaves Extract in HCl medium	81.00	
2	Ginko Leaves	79.00	
3	Watermelon Rind Extract in acidic medium	91.00	(Odewunmi N.A et al., 2015)
4	*Tinospora crispa* extract in HCl medium	87.73	(Hazwan Hussin et al., 2011)
5	Thyme leaves extract in H_2SO_4	75.60	(Taleb Ibrahim et al., 2012)
6	Olive pomace extract in HCl medium	92.10	(Driss Bouknna et al., 2014)
7	Date palm seed extract in acidic medium	89.30	(Saviour Alumoren et al., 2013)
8	Bamboo leaf extract in HCl medium	90.3	(Xianghong Li et al., 2012)
9	Nypa *fructicans wurmb* leaves extract in acidic medium	92.8	(Oruble K.O et al., 2004)
10	Gingko leaves extract in H_2SO_4 medium	91.40	(Shuduan Deng et al., 2012)
11	*Elais guineensis* agricultural waste in CO_2 medium	93.42	(Hazwan Hussin et al., 2015)
12	Gingko *biloba* fruit extract in CO_2 medium	54.11	(Ambish Singhea et al., 2015)
13	Nicotania tobacum leaves extract in acidic medium	80.03	(Jeetandra et al., 2015)
14	*Tagetes eracta* (Marigold Flower) in acidic medium	98.19	(Punita Mourya et al., 2014)
15	Pimenta dioica leaf extracts in acidic medium	97.38	(Anupama K.K et al., 2015)
16	Lannea colomandelica leaf extract	45.10	(Muthukrishan et al., 2013)

4.5 Discussion on Method

As mentioned before, electrochemical polarization resistances and weight loss method were used in this study. Both of the method perform a very excellent result in different inhibitor concentration, which the inhibitor efficiency for electrochemical method is 99.53% whereas weight loss method performed 97.66%.

Electrochemical polarization resistances method, is the most accurate method compared to the weight loss method, as we can see the electrochemical polarization resistances, the data is more precise compared to the weight loss method. However, weight loss method can be concluded as one of the significant method that can be used to measure the corrosion rate.

From the table 4.2, at 5ppm the value inhibitor efficiency (IE%) is at 22.34% but it starts to increase up to 80.00% when the inhibitor concentrations at 10ppm. This pattern continuously to increase until the IE% is 97.66% at 25ppm. This proved that the weight loss method have the significant result, thus weight loss method can be used to measure the corrosion rate of the sample.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This research is to identify whether the inhibitor extracted from palm oil leaves can inhibit corrosion in carbon steel. By conducting this study, inhibitor from natural substances will become more popular for inhibitor selection due to the fact that it is cheaper and less harmful to the environment. From this study, it can conclude that the efficiency of the corrosion inhibitor depends on its concentrations. The selected inhibitors exhibited excellent inhibition for carbon steel immersed in a CO_2 saturated environment. The introduction of a small amount of inhibitor concentration, such as 5ppm, brought about a significant decrease in the corrosion rate. It was found that subsequent additions of each inhibitor resulted in further decreasing the corrosion of carbon steel in the cases studied. The electrochemical test offered conclusive proof that increasing the concentrations of the inhibitor resulted in decreasing the corrosion rate. In the polarization resistances measurements, it was determined that increasing the concentration of the inhibitor brought an increase in the polarization resistances values obtained. This trend was also observed in the weight loss method, where by the addition of inhibitor resulted in decreasing the value of corrosion rate.

From the results, electrochemical method and weight loss method, both can measured the corrosion rate, but to be precise electrochemical method where polarization resistances measurements have the more accurate value compared to weight loss method. The highest inhibitor efficiency for electrochemical method is 99.53% while for weight loss method is 97.66%. As a conclusion, the efficiency of the corrosion inhibitor depends on its concentration.

5.2 Recommendation

The recommendation is to further investigate the other parameters such as partial pressure and temperature. Therefore, the efficiency of the inhibitor can be explained clearly whether it is suitable for CO_2 corrosion. Used various of green inhibitor to compared the value of the corrosion rate and inhibitor efficiency. Thus to proved the excellent of green inhibitor.

In order to get more accurate result, more useful tools and equipment can be used such as Liquid Chromatography Mass Spectroscopy (LCMS) and Fourier Transfer Infrared Spectroscopy (FTIR) for further analysing the corrosion inhibitor

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APPENDIX

A1) Methodology

Plant Collection

A1-1: Plant Collection at Lepar Estate, Pahang.

A1-2: Mechanical Blender used to make palm oil leaves powder

A1-3: Palm Oil Leaves Powder after being grinded using mechanical blender

Coupon Preparation

A1-4: Carbon steel before polished

A1-5: Carbon Steel after polished

Electrode Preparation

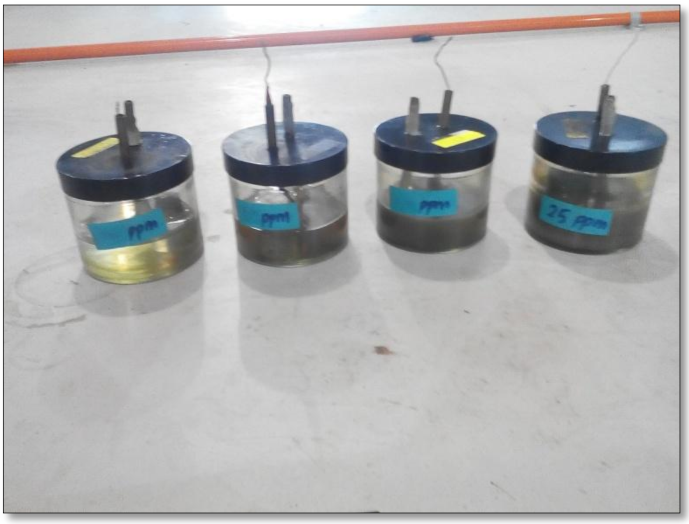
A1-6: The holder of epoxy solution.

A1-7: The electrode obtained after mounded with epoxy solution

Inhibitor Preparation

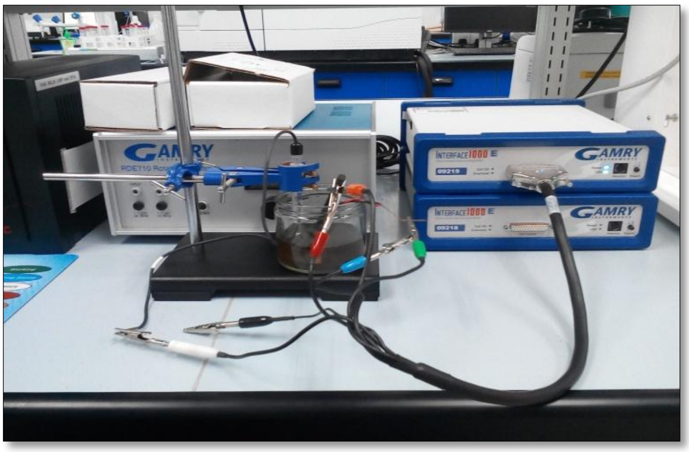
A1-8: Extraction of palm oil leaves powder by using methanol and stir by using magnetic stirrer and hotplate.

CO_2 Preparation



A1-9: The ointment jar with hole to purged the CO_2 gas into the test solution

Electrochemical Measurements



A1-10: Electrochemical measurement by using potentiostat as equipment, polarization resistances test were carried out.

A2) Result

Electrochemical Measurements

Table : Inhibitor efficiency of electrochemical measurements

Concentration (ppm)	**E_{corr} (V)**	**I_{corr} (V)**	**Corrosion Rate (mm/y)**	**IE (%)**
0	-0.5151	6.8508E-06	7.2827	-
5	-0.5313	4.8157E-06	2.0440	71.93
10	-0.5330	3.8079E-06	1.9591	73.10
15	-0.5837	4.5566E-06	0.7220	90.09
20	-0.5534	8.3380E-06	0.0646	99.11
25	-0.4254	7.6695E-06	0.0340	99.53

The table below shows the result for electrochemical measurements by using polarization resistances technique. The inhibitor efficiency (IE%) were calculated by using equation:

$$IE\% = [\ (CR_o - CR_i)/\ CR_o\ ] \times 100$$

Sample 1: No inhibitor added

Sample 2: 5ppm

$$IE\ \% = \frac{7.2827-2.0440}{7.2827} \times 100 = 71.93\%$$

Sample 3: 10ppm

$$IE\ \% = \frac{7.2827-1.9591}{7.2827} \times 100 = 73.10\%$$

Sample 4: 15ppm

$$IE\ \% = \frac{7.2827-0.7220}{7.2827} \times 100 = 90.09\%$$

Sample 5: 20ppm

$$\text{IE \%} = \frac{7.2827-0.0646}{7.2827} \times 100 = 99.11\%$$

Sample 6: 25ppm

$$\text{IE \%} = \frac{7.2827-0.0340}{7.2827} \times 100 = 99.53\%$$

Weight Loss Method

Table : Weight loss measurements in different inhibitor concentrations

Concentration (ppm)	**Weight (g)**				**Weight Loss (g)**	**Corrosion Rate (mm/yr)**	**Inhibitor Efficiency (IE%)**
	After 0 hours	**After 12 hours**	**After 24 hour**	**After 72 hours**			
0	33.5247	33.5004	33.3489	33.3106	0.2141	0.2950	-
5	31.2450	31.2294	31.2083	31.1711	0.0739	0.2291	22.34
10	33.5192	33.5073	33.4817	33.4764	0.0428	0.0590	80.00
15	37.4388	37.4364	37.4235	37.4223	0.0165	0.0338	88.54
20	31.4087	31.4042	31.4006	31.3978	0.0109	0.0227	92.31
25	31.1309	31.1294	31.1278	31.1259	0.0050	0.0069	97.66

The table below shows the result for weight loss method in different concentration. The corrosion rate (CR) were calculated by using equation:

$$\text{CR (mm/yr)} = 87.6 \times \frac{W}{D \times A \times T}$$

where W is weight loss (mg), D is metal density (g/cm^3), A is area (cm^2) and T is time of immersion (hr).

Sample 1: No inhibitor

$$CR_0 = 87.6 \times \left(\frac{21.41}{7.85 \times 11.25 \times 72} \right) = 0.2950 \text{ mm/yr}$$

Sample 2: 5ppm

$$CR_5 = 87.6 \times \left(\frac{7.39}{7.85 \times 5.0 \times 72} \right) = 0.2291 \text{ mm/yr}$$

Sample 3: 10ppm

$$CR_{10} = 87.6 \times \left(\frac{4.28}{7.85 \times 11.25 \times 72} \right) = 0.0590 \text{ mm/yr}$$

Sample 4: 15ppm

$$CR_{15} = 87.6 \times \left(\frac{1.65}{7.85 \times 7.57 \times 72} \right) = 0.0338 \text{ mm/yr}$$

Sample 5: 20ppm

$$CR_{20} = 87.6 \times \left(\frac{1.09}{7.85 \times 7.44 \times 72} \right) = 0.0227 \text{ mm/yr}$$

Sample 6: 25ppm

$$CR_{25} = 87.6 \times \left(\frac{0.50}{7.85 \times 11.25 \times 72} \right) = 0.0069 \text{ mm/yr}$$

After value corrosion rate (CR) were calculated, the value of inhibitor efficiency (IE%) were calculated by using :

$$IE\% = [\ (CR_o - CR_i) / CR_o\ ] \times 100$$

Sample 1: No inhibitor

Sample 2: 5ppm

$$\text{IE \%} = \frac{0.2950-0.2291}{0.2950} \times 100 = 22.34\%$$

Sample 3: 10ppm

$$\text{IE \%} = \frac{0.2950-0.0590}{0.2950} \times 100 = 80.00\%$$

Sample 4: 15ppm

$$\text{IE \%} = \frac{0.2950-0.0338}{0.2950} \times 100 = 88.54\%$$

Sample 5: 20ppm

$$\text{IE \%} = \frac{0.2950-0.0227}{0.2950} \times 100 = 92.31\%$$

Sample 6: 25ppm

$$\text{IE \%} = \frac{0.2950-0.0069}{0.2950} \times 100 = 97.66\%$$

Table: Weight loss method at different pH value

pH	**Weight Loss (g)**		**IE(%)**
	Inhibitor	**Control**	
3.2	0.0467	0.4276	89.08
5.47	0.0732	0.4105	82.17
6.11	0.0539	0.3092	82.57
7.01	0.0262	0.2853	90.82
8.62	0.0905	0.3759	75.92
9.71	0.0396	0.4012	90.13

The inhibitor efficiency (IE%) were calculated by using equation:

$$IE\% = [\ (WL_o - WL_i)/\ WL_o\ ] \times 100$$

Sample 1: pH value 3.20

$$IE\ \% = \frac{0.4276-0.0467}{0.4276} \times 100 = 89.08\%$$

Sample 2: pH value 5.47

$$IE\ \% = \frac{0.4105-0.0732}{0.4105} \times 100 = 82.17\%$$

Sample 3: pH value 6.11

$$IE\ \% = \frac{0.3092-0.0539}{0.3092} \times 100 = 82.57\%$$

Sample 4: pH value 7.01

$$IE\ \% = \frac{0.2853-0.00262}{0.2853} \times 100 = 90.82\%$$

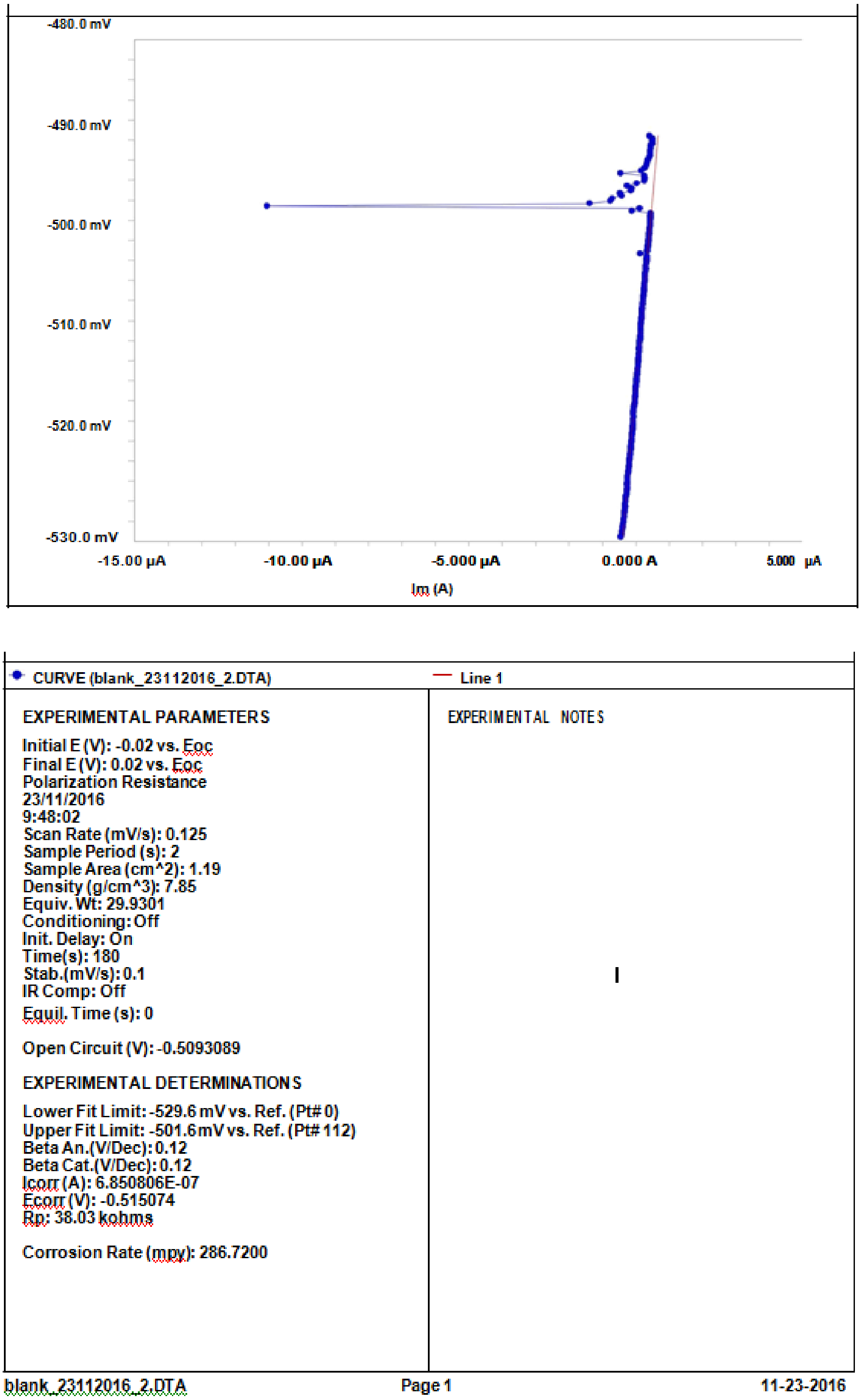
Sample 5: pH value 8.62

$$IE\ \% = \frac{0.3759-0.0905}{0.3759} \times 100 = 75.92\%$$

Sample 6: pH value 9.71

$$IE\ \% = \frac{0.4012-0.0396}{0.4012} \times 100 = 90.13\%$$

A3) Graph from Polarization Resistances



● CURVE (blank_23112016_2.DTA) — Line 1

EXPERIMENTAL PARAMETERS

Initial E (V): -0.02 vs. Eoc
Final E (V): 0.02 vs. Eoc
Polarization Resistance
23/11/2016
9:48:02
Scan Rate (mV/s): 0.125
Sample Period (s): 2
Sample Area (cm^2): 1.19
Density (g/cm^3): 7.85
Equiv. Wt: 29.9301
Conditioning: Off
Init. Delay: On
Time(s): 180
Stab.(mV/s): 0.1
IR Comp: Off
Equil. Time (s): 0

Open Circuit (V): -0.5093089

EXPERIMENTAL DETERMINATIONS

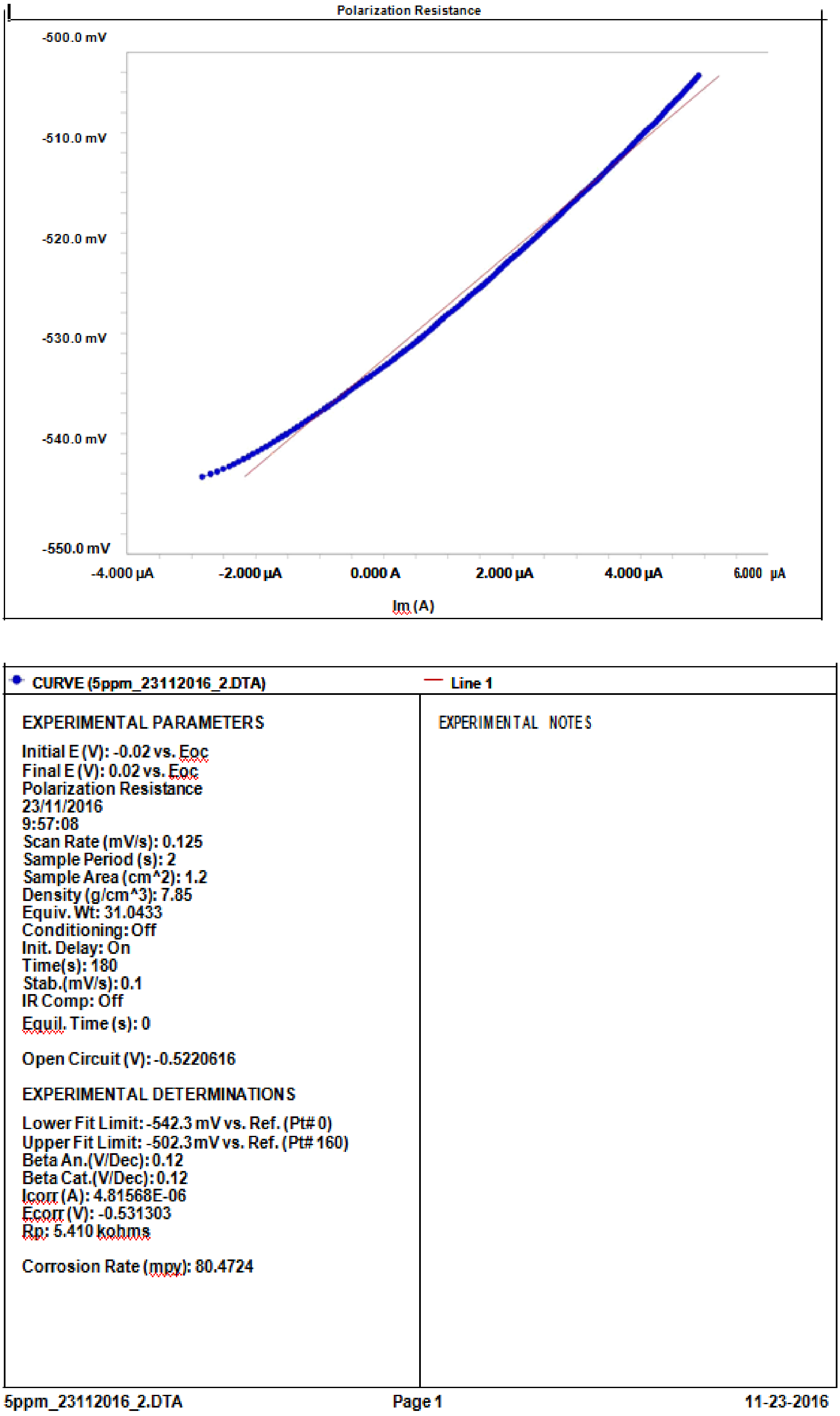
Lower Fit Limit: -529.6 mV vs. Ref. (Pt# 0)
Upper Fit Limit: -501.6 mV vs. Ref. (Pt# 112)
Beta An.(V/Dec): 0.12
Beta Cat.(V/Dec): 0.12
Icorr (A): 6.850806E-07
Ecorr (V): -0.515074
Rp: 38.03 kohms

Corrosion Rate (mpy): 286.7200

EXPERIMENTAL NOTES

blank_23112016_2.DTA Page 1 11-23-2016

A3-1: Result for Blank Data



EXPERIMENTAL PARAMETERS

Initial E (V): -0.02 vs. Eoc
Final E (V): 0.02 vs. Eoc
Polarization Resistance
23/11/2016
9:57:08
Scan Rate (mV/s): 0.125
Sample Period (s): 2
Sample Area (cm^2): 1.2
Density (g/cm^3): 7.85
Equiv. Wt: 31.0433
Conditioning: Off
Init. Delay: On
Time(s): 180
Stab.(mV/s): 0.1
IR Comp: Off
Equil. Time (s): 0

Open Circuit (V): -0.5220616

EXPERIMENTAL DETERMINATIONS

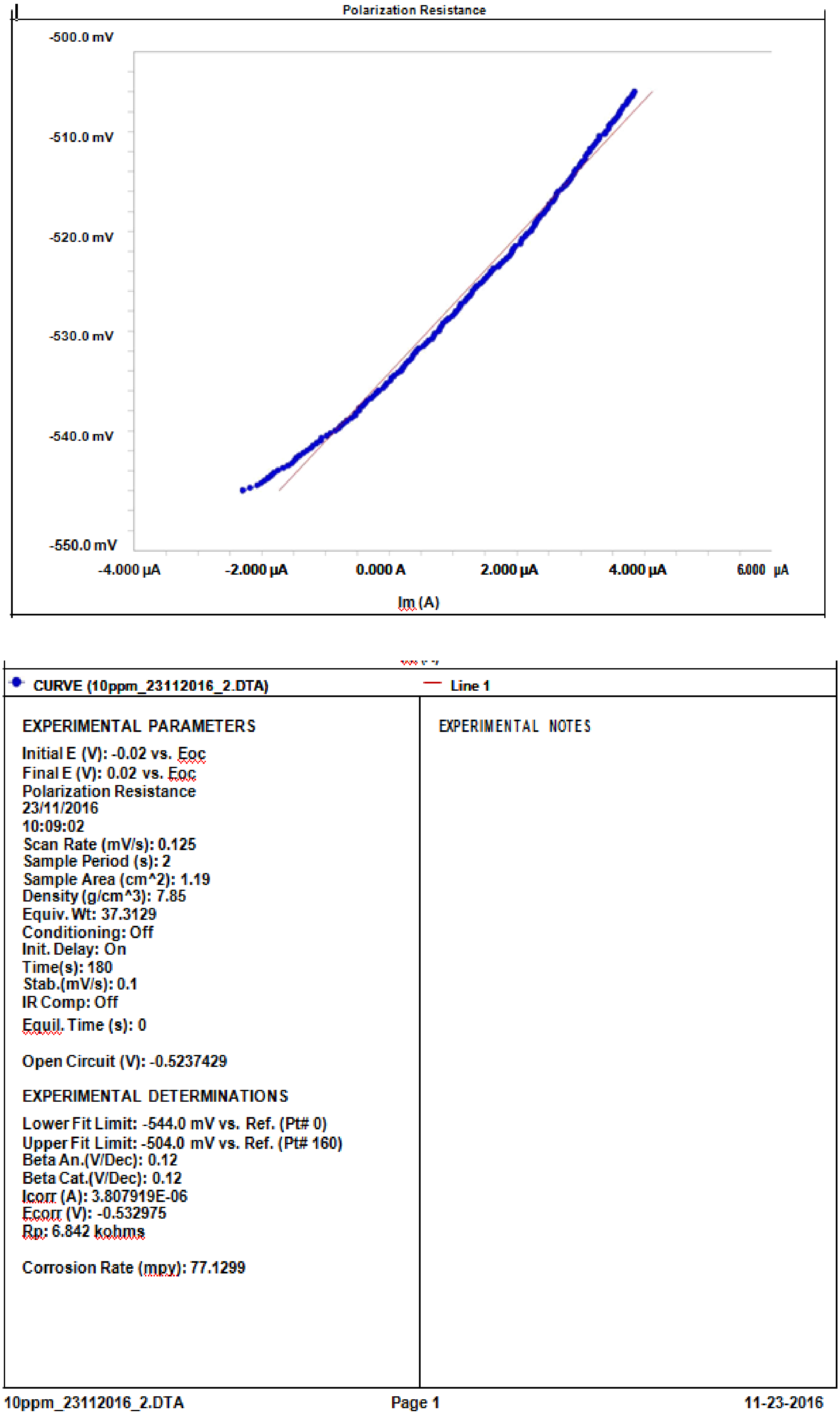
Lower Fit Limit: -542.3 mV vs. Ref. (Pt# 0)
Upper Fit Limit: -502.3 mV vs. Ref. (Pt# 160)
Beta An.(V/Dec): 0.12
Beta Cat.(V/Dec): 0.12
Icorr (A): 4.81568E-06
Ecorr (V): -0.531303
Rp: 5.410 kohms

Corrosion Rate (mpy): 80.4724

EXPERIMENTAL NOTES

5ppm_23112016_2.DTA Page 1 11-23-2016

A3-2: Result for 5ppm



EXPERIMENTAL PARAMETERS

Initial E (V): -0.02 vs. Eoc
Final E (V): 0.02 vs. Eoc
Polarization Resistance
23/11/2016
10:09:02
Scan Rate (mV/s): 0.125
Sample Period (s): 2
Sample Area (cm^2): 1.19
Density (g/cm^3): 7.85
Equiv. Wt: 37.3129
Conditioning: Off
Init. Delay: On
Time(s): 180
Stab.(mV/s): 0.1
IR Comp: Off
Equil. Time (s): 0

Open Circuit (V): -0.5237429

EXPERIMENTAL DETERMINATIONS

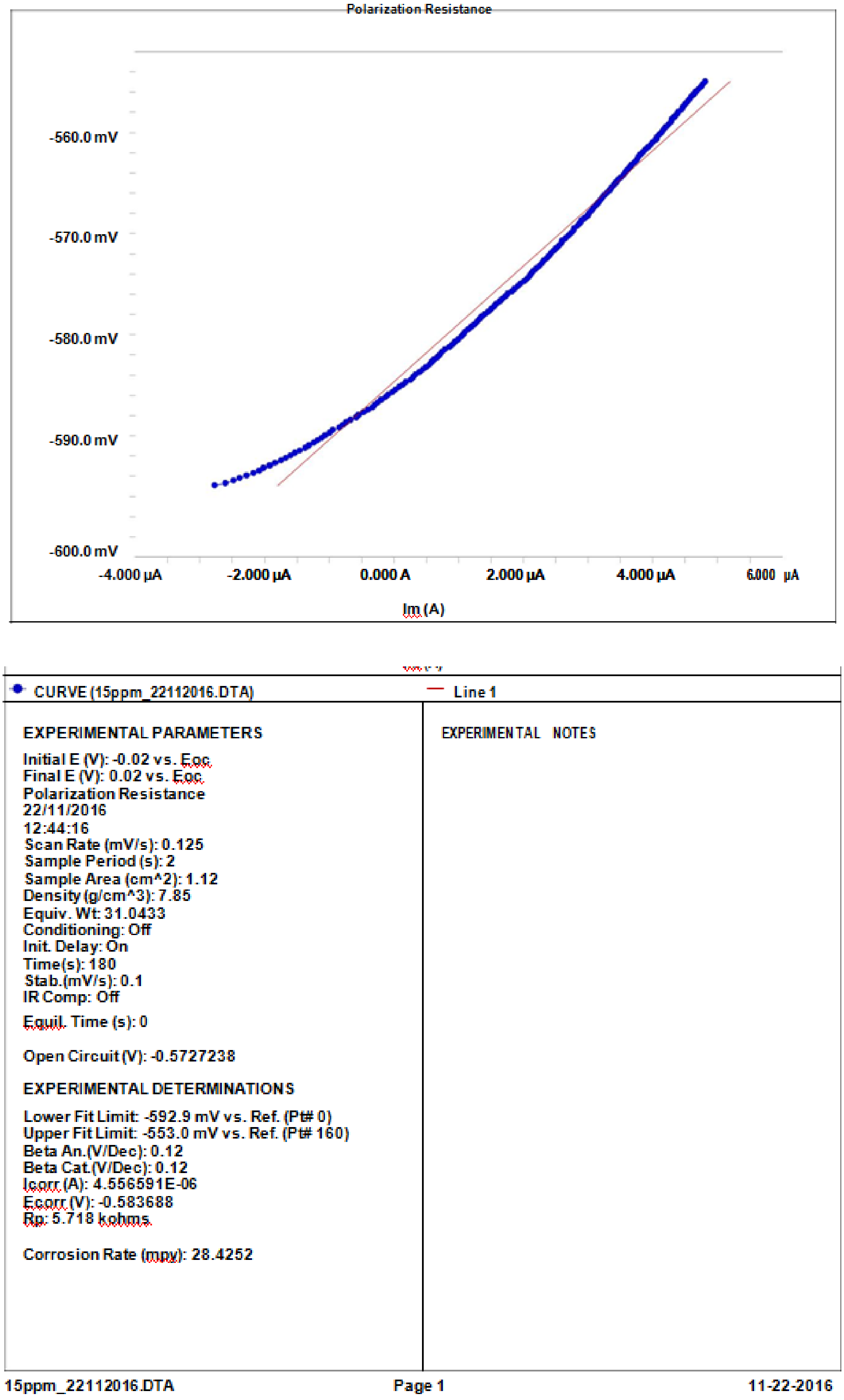
Lower Fit Limit: -544.0 mV vs. Ref. (Pt# 0)
Upper Fit Limit: -504.0 mV vs. Ref. (Pt# 160)
Beta An.(V/Dec): 0.12
Beta Cat.(V/Dec): 0.12
Icorr (A): 3.807919E-06
Ecorr (V): -0.532975
Rp: 6.842 kohms

Corrosion Rate (mpy): 77.1299

EXPERIMENTAL NOTES

10ppm_23112016_2.DTA Page 1 11-23-2016

A.3-3: Result for 10ppm



● CURVE (15ppm_22112016.DTA)

— Line 1

EXPERIMENTAL PARAMETERS

Initial E (V): -0.02 vs. Eoc
Final E (V): 0.02 vs. Eoc
Polarization Resistance
22/11/2016
12:44:16
Scan Rate (mV/s): 0.125
Sample Period (s): 2
Sample Area (cm^2): 1.12
Density (g/cm^3): 7.85
Equiv. Wt: 31.0433
Conditioning: Off
Init. Delay: On
Time(s): 180
Stab.(mV/s): 0.1
IR Comp: Off

Equil. Time (s): 0

Open Circuit (V): -0.5727238

EXPERIMENTAL DETERMINATIONS

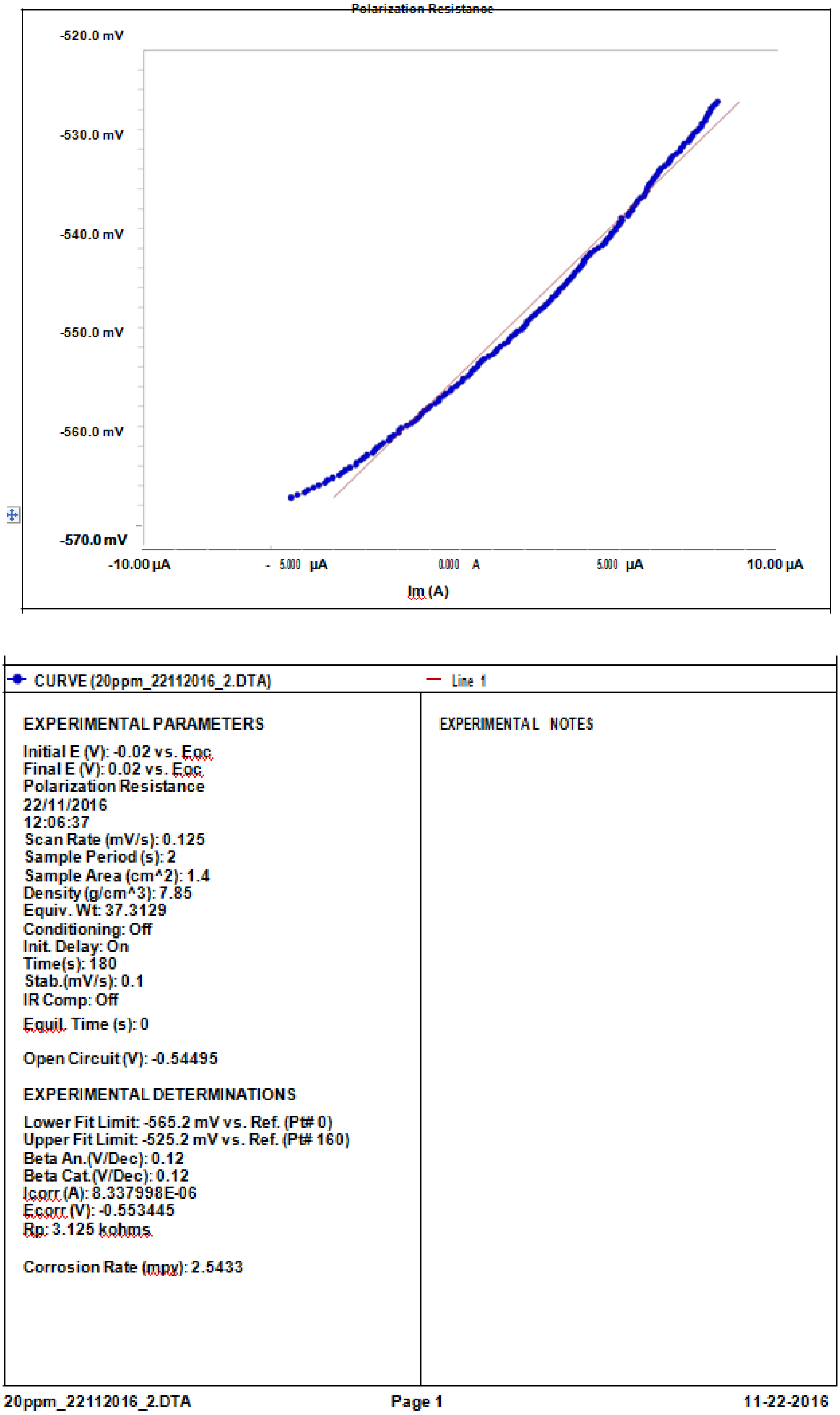
Lower Fit Limit: -592.9 mV vs. Ref. (Pt# 0)
Upper Fit Limit: -553.0 mV vs. Ref. (Pt# 160)
Beta An.(V/Dec): 0.12
Beta Cat.(V/Dec): 0.12
Icorr (A): 4.556591E-06
Ecorr (V): -0.583688
Rp: 5.718 kohms

Corrosion Rate (mpy): 28.4252

EXPERIMENTAL NOTES

15ppm_22112016.DTA Page 1 11-22-2016

A3-4: Result for 15ppm



● CURVE (20ppm_22112016_2.DTA) — Line 1

EXPERIMENTAL PARAMETERS

Initial E (V): -0.02 vs. Eoc
Final E (V): 0.02 vs. Eoc
Polarization Resistance
22/11/2016
12:06:37
Scan Rate (mV/s): 0.125
Sample Period (s): 2
Sample Area (cm^2): 1.4
Density (g/cm^3): 7.85
Equiv. Wt: 37.3129
Conditioning: Off
Init. Delay: On
Time(s): 180
Stab.(mV/s): 0.1
IR Comp: Off

Equil. Time (s): 0

Open Circuit (V): -0.54495

EXPERIMENTAL DETERMINATIONS

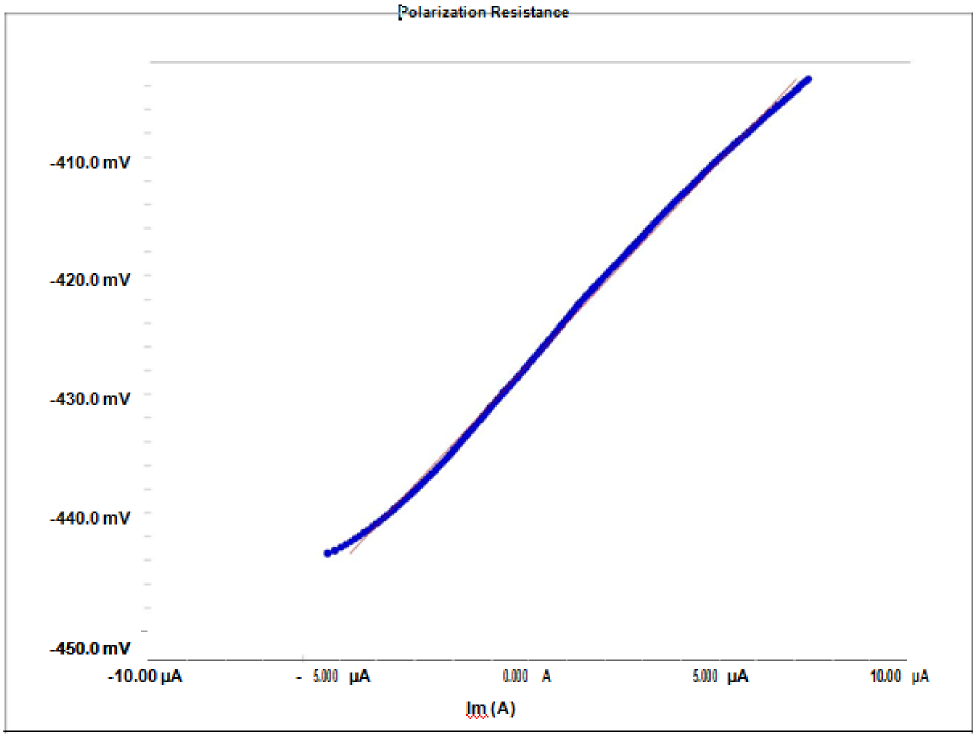
Lower Fit Limit: -565.2 mV vs. Ref. (Pt# 0)
Upper Fit Limit: -525.2 mV vs. Ref. (Pt# 160)
Beta An.(V/Dec): 0.12
Beta Cat.(V/Dec): 0.12
Icorr (A): 8.337998E-06
Ecorr (V): -0.553445
Rp: 3.125 kohms

Corrosion Rate (mpy): 2.5433

EXPERIMENTAL NOTES

20ppm_22112016_2.DTA Page 1 11-22-2016

A3-5: Result for 20ppm



● CURVE (25ppm_23112016.DTA) — Line 1

EXPERIMENTAL PARAMETERS

Initial E (V): -0.02 vs. Eoc
Final E (V): 0.02 vs. Eoc
Polarization Resistance
23/11/2016
10:28:55
Scan Rate (mV/s): 0.125
Sample Period (s): 2
Sample Area (cm^2): 1.12
Density (g/cm^3): 7.85
Equiv. Wt: 29.729
Conditioning: Off
Init. Delay: On
Time(s): 180
Stab.(mV/s): 0.1
IR Comp: Off
Equil. Time (s): 0

Open Circuit (V): -0.4212099

EXPERIMENTAL DETERMINATIONS

Lower Fit Limit: -441.4 mV vs. Ref. (Pt# 0)
Upper Fit Limit: -401.4 mV vs. Ref. (Pt# 160)
Beta An.(V/Dec): 0.12
Beta Cat.(V/Dec): 0.12
Icorr (A): 7.669514E-06
Ecorr (V): -0.425443
Rp: 3.397 kohms

Corrosion Rate (mpy): 1.3386

EXPERIMENTAL NOTES

25ppm_23112016.DTA Page 1 11-23-2016

A3-6: Result for 25ppm