

**CO₂ Corrosion Study by Electrochemical Impedance Spectroscopy (EIS) and
Linear Polarization Resistance (LPR)**

by

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Mechanical Engineering**

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the requirements for the
Bachelor of Engineering (Hons)
(Mechanical Engineering)**

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Mechanical Engineering Programme
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(MECHANICAL ENGINEERING)

Approved by,

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January 2008

CERTIFICATION OF ORIGINALITY

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



MOHD FIRDAUS BIN BESAR

ABSTRACT

Corrosion is a phenomenon where metals deteriorate to their natural oxide states after undergoing an electrochemical process in the presence of electrolyte and oxygen. The process takes place where the electron leaves the metal in an oxidation reaction and enters the solution at an area known as anode. Cathode is the area where the electrons return and react with the electrolyte compounds depending on the environment and type of electrolyte. The electron path, which could be the base metals between different metals complete the electronic circuits. CO₂ corrosion is one of corrosion type and can be measured by a lot of measurement techniques. Common types of measurement technique are Electrochemical Impedance Spectroscopy (EIS) and Linear Polarization Resistance (LPR) techniques. The environmental factors such as pH, temperature, oxygen content and percentage of electrolyte can affect the corrosion rate.

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CHAPTER 1

INTRODUCTION

1.1 Problem Statement

One type of corrosion commonly occurs in the oil and gas production field is CO₂ corrosion. Dissolved CO₂ in water or aqueous solutions is known to cause severe corrosion of the mild steel in many industries. Thus it is crucial to carried out study on the effectiveness of the CO₂ corrosion measurement technique in order to investigate this long term corrosion behavior.

There are many types of electrochemical measurement techniques that can be used to study CO₂ corrosion such as Linear Polarization Resistance (LPR) and Potentiodynamic Polarization. This project will focus on Electrochemical Impedance Spectroscopy (EIS) technique and Linear Polarization Resistance (LPR) in order to investigate and study of CO₂ corrosion. There are many environment factors influence the CO₂ corrosion that are oxygen content, pH of the environment, temperature, flow, CO₂ content and percentage of electrolyte. This project focuses on the effect of pH and effect of different percentage of electrolyte on the corrosion rate using EIS and LPR.

1.2 Objective

- To measured the CO₂ corrosion rate using the Electrochemical Impedance Spectroscopy (EIS) technique and Linear Polarization Resistance.
- To study the effect of pH, effect of different percentage of electrolyte and different measurement techniques using EIS and LPR on the CO₂ corrosion rate.

1.3 Scope of Study

The scope of this project is to conduct the laboratory experiment on mild steel in CO₂ environments. The environment conditions for all experiment were:

- Used NaCl as the electrolyte and the concentrations were 1%NaCl and 3%NaCl
- The test temperature was 70°C
- The pH of the concentration were pH 4.0 and pH 5.5

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Carbon Dioxide Corrosion

2.1.1 Overview

The composition of the oil or gas sources is the main contributor to the corrosion of oil and gas pipelines and associated equipments. Carbon dioxide (CO_2) is one of the primary constituent of the gas sources other than hydrogen sulphide (H_2S), dissolved oxygen, organic acid and other impurities. The major form of corrosion encountered in oil and gas production is the one caused by CO_2 . Dissolved carbon dioxide in the produced brines is very corrosive to mild steel tubular and the process equipment used in the industry. Approximately 60% of oilfield failures are related to CO_2 corrosion mainly due to inadequate knowledge capability and the poor resistance of mild steels to this type of corrosive attack. CO_2 can produce not only general corrosion but also localized corrosion, which is a much more serious problem.

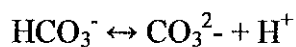
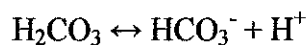
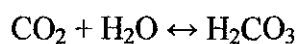
CO_2 combines with water to form carbonic acid that lowers the pH of the water. Carbonic acid is very aggressive to steel and results in large areas of rapid metal loss that can completely erode sucker rods and couplings [2]. The increasing of CO_2 partial pressure and temperature contribute to the increasing of the corrosion severity. CO_2 corrosion pits are round based, deep with steep walls and sharp edges. The pitting is interconnected in long lines but will occasionally be singular and isolated. The pit bases will be filled with iron carbonate scale, a loosely adhering gray deposit generated from CO_2 [2]. Carbon dioxide forms a weak acid known as carbonic acid (H_2CO_3) in water, a relatively slow reaction.

However, CO₂ corrosion rates are greater than the effect of carbonic acid alone. Cathodic depolarization may occur, and other attack mechanisms may also be at work. The presence of salts is relatively unimportant. When CO₂ is present, the most common forms of corrosion include uniform corrosion, pitting corrosion, wormhole attack, galvanic ringworm corrosion, heat affected corrosion, mesa attack, raindrop corrosion, erosion corrosion, and corrosion fatigue. [3]. The presence of carbon dioxide usually means no H₂ embrittlement. As stated before, CO₂ corrosion is one of the most common environments where corrosion occurs, and exists almost everywhere. Areas where CO₂ corrosion is most common include flowing wells, gas condensate wells, areas where water condenses, tanks filled with CO₂, saturated produced water and flowlines, which are generally corroded at a slower rate because of lower temperatures and pressures.

2.1.2 Morphology of CO₂ Corrosion

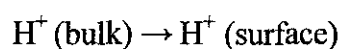
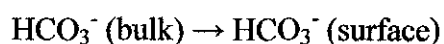
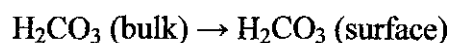
B.R Linter [11] proposed a mechanistic model for the carbon dioxide corrosion of carbon steel in single-phase full pipe flow. He suggested that the overall corrosion process could be divided into four steps. The first step is the dissolution of carbon dioxide in the aqueous solution to form the various reactive species, which takes part in the corrosion reaction.

- Formation of reactive species in the bulk



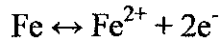
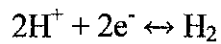
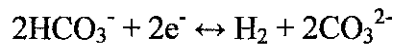
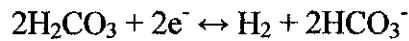
The second step is the transportation of these reactants to the metal surface.

- Transportation of reactants (bulk to surface)



The third step involves the electrochemical reactions (anodic and cathodic) taking place at the metal surface.

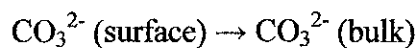
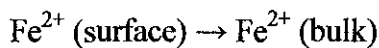
- Electrochemical reactions at the surface



The fourth step is the transportation of the corrosion products to the bulk of the solution.

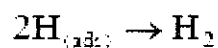
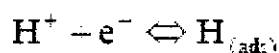
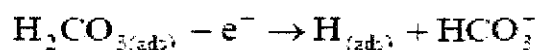
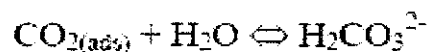
These can be shown as:

- Transportation of products (surface to bulk)



Most researchers agree that, in the practical situation, carbon dioxide corrosion takes place under mixed control, namely, the corrosion is neither completely mass transfer controlled nor completely reaction controlled.

Different mechanisms have been proposed to account for the enhanced corrosion rates in CO₂ systems. These models include other cathodic reactions leading to hydrogen evolution, which are in addition to the pH dependent proton discharge. Nestor Perez [12] proposed the chemical-electrochemical mechanism for cathodic reaction:



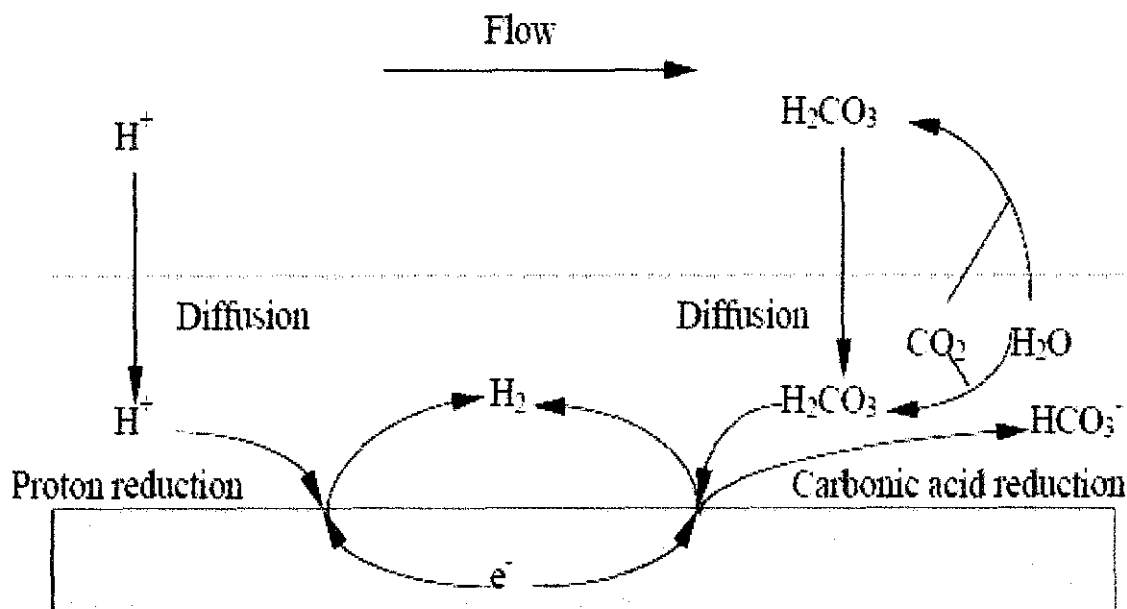


Figure 2.1: Simple model for CO₂ corrosion

In this model, the electrochemical reduction of carbonic acid molecules at the electrode surface followed a heterogeneous CO₂ hydration reaction. Thus carbonic acid and the hydrogen ion are reduced at the electrode surface with the former being rate determining. Both activation and diffusion effects are rate controlling, with the former exerting a dominant effect at the open circuit potential. To determine this model, EIS and polarization techniques were used in rotating disc electrode (RDE) experiments. However, the study was carried out for pure ion in CO₂ saturated brine solutions without consideration of the effect of corrosion product layer. It is thermodynamically more difficult to decrease H₂CO₃ and HCO₃⁻ to hydrogen than to have hydrogen evolution through the more classical cathodic reaction at the surface of metal. This can be explained by comparing the Gibbs free energy (ΔG) of the two reactions. Ketil Videm [13] had approached to this situation and theory and he conclude that both anodic and cathodic reactions are affected by CO₂.

Carbon steel and mild steel in the aqueous CO₂ environment could be susceptible to general corrosion and localized forms of attack depending on various parameters. Kermani [17] categorized the localized corrosion as pitting, mesa attack and flow-induced.

1. Pitting

Pitting is the main corrosion failure in CO₂ environments. There are no conclusive findings on the initiation and propagation of this failure for this environment. Nonetheless, in the field, some failures have been observed adjacent to non-metallic inclusion or incipient mesa attack. Schmitt et al. [18] studied the effects of temperature, chloride concentration, nature of anions and cations and corrosion inhibitors on the pit initiation.

2. Mesa type attack

This localized corrosion is prone to occur in low medium flow conditions where the protective iron carbonate film is unstable. Higher temperatures promote corrosion by elongated corrosion areas (mesas) oriented in the direction of flow. The most severe metal loss often occurs at areas of high fluid turbulence, such as welds, tubing joints, or ends/constrictions in piping. It is rare to lose significant amounts of metal uniformly.

3. Flow-induced localized corrosion

This is an extension of pitting and mesa attack by local turbulence created by the protrusions.

2.1.3 Environmental Factors Influence CO₂ Corrosion

There were several factors that influence the rate of corrosion in the CO₂ environment. The chemistry of both the formation and dissolution of the corrosion products, the rates of chemical reactions and the rates of transport of species involved in the corrosion can be manipulated by these factors. The main factors are:

1. pH of the environment

Uniform corrosion rate in CO₂ saturated brines decreases as pH increases because they are inversely proportional. This is related to the formation of the bicarbonate and carbonate salts and also to the decrease in the solubility of the FeCO₃ which turn makes the formation of a protective film more feasible. It is

known that the pH in the water analysis, usually measured at atmospheric conditions after depressurisation, is most often totally useless for a corrosion prediction [14]

2. Oxygen content

FeCO₃ is unstable in the presence of oxygen, thus passive FeCO₃ films normally form under anaerobic conditions. In addition to the modification of film stability, a higher oxygen concentration contributes to an increase in the rate of the cathodic reaction (oxygen reduction)

3. Iron content

The content of ferrous cation in the solution determines if it possible to form FeCO₃ or not, as it is necessary to exceed the solubility limit in order to precipitate iron carbonate.

4. Flow

Usually corrosion rate increase with flow velocity due to one or more of the following reasons: preventing formation of passive FeCO₃ films; removing existing films or retarding the growth of such film by enhancing mass transfer of reactants near the surface.

5. CO₂ content

The uniform corrosion rate increases with higher CO₂ partial pressure because solution pH decreases and the rate of reduction of carbonic acid increase.

6. Temperature

At low temperature (i.e. less than 60°C), the uniform corrosion rate increases with temperature when no protective corrosion products are formed.

2.2 Electrochemical Impedance Spectroscopy (EIS)

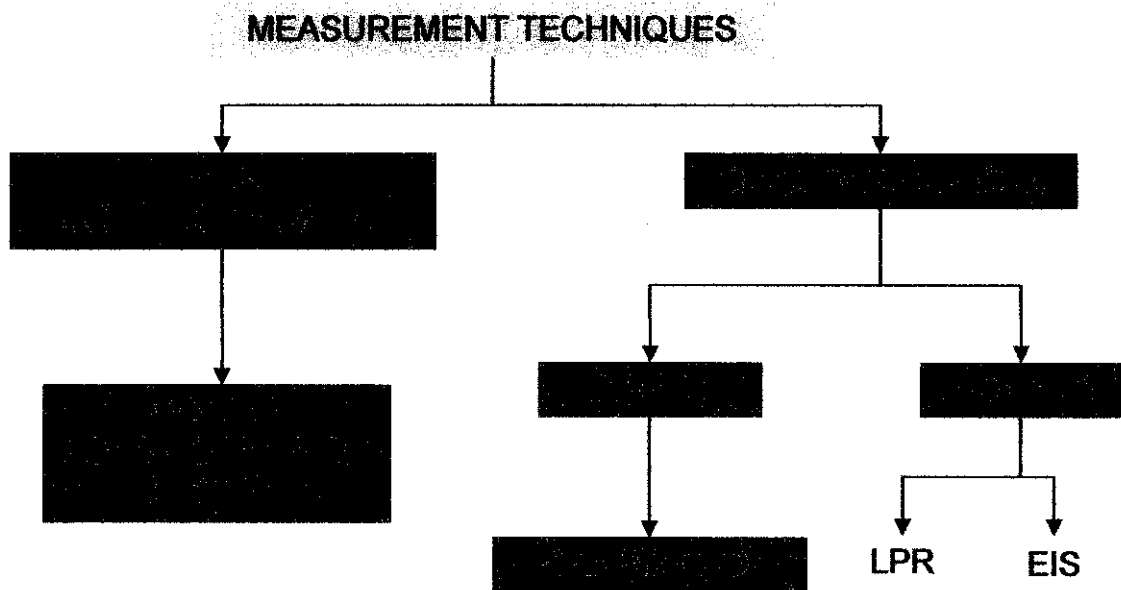


Figure 2.2: Types and classes of measurement technique

EIS is one of indirect electrochemical measurement technique. Understanding the basic concept of Electrochemical Impedance Spectroscopy Technique is important before further investigation about the CO₂ corrosion study based on EIS. After some literature review about this electrochemical technique by referring to ASTM Standard Practice [4], some of important concept or idea must be understand and recognized. There are:

- Electrochemical Impedance Spectroscopy Background
- Simple Corrosion Process
- Diffusion Control
- Inductance
- Depression of Nyquist Semicircle

2.2.1 Electrochemical Impedance Spectroscopy (EIS) Background

EIS is capable of accessing relaxation phenomena in corrosion and passivation processes as well as active pitting of the material [15]. Commonly, linear circuit elements such as resistors, capacitor, and inductor will be combined to model an electrochemical process. For example, the corrosion reaction itself can be modeled by one or more resistors. The ability to model a corrosion process in this manner contributes to the new technique of corrosion measurement like the electrochemical impedance technique. Simple AC circuit theory in terms of circuit analogues can be used to model the electrochemical corrosion process. Such modeling makes better understanding of the EIS concept and directly leads to better investigation of corrosion rates and overall corrosion behavior. Direct current can be viewed as current generated in the limit of zero frequency. Under conditions of direct current, for example zero frequency, Ohm's law can be written as:

$$E = I \times R \quad (1)$$

An imposition of a frequency dependent voltage or current will form non zero frequency, so Ohm's law becomes:

$$E = I \times Z \quad (2)$$

Z is the proportionality factor that is the total of all elements that can against the current. The magnitude of the resistance is dependent on the frequency and formed by these elements such as capacitors and inductors. The resistor created the magnitude of the opposition that is independent of frequency. The technique can be described in terms of a response to a frequency dependent input signal. When a voltage sine or cosine wave is applied across a circuit composed of a resistor only, the resultant current is also a sine or cosine wave of the same frequency with no phase angle shift but with an amplitude which differs by an amount determined by the proportionality factor. The values of the input voltage and output current are related by equation, ($E = I \times R$). Meanwhile, if the circuit consists of capacitors and inductors, the resulting current not

only differs in amplitude but is also shifted in time. It has a phase angle shift. This fact is shown in Figure 2.3.

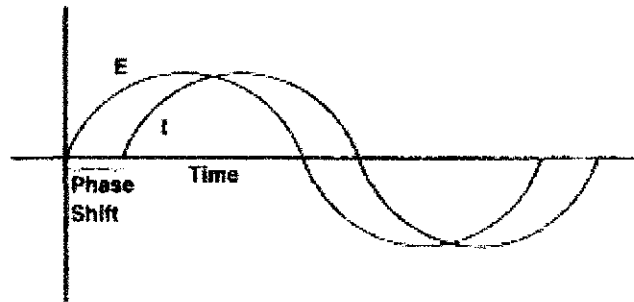


Figure 2.3: Sinusoidal AC voltage and current signals

Vector analysis can be used to describe the equivalent circuit in mathematical terms. The relationship between such vector analysis and imaginary or complex numbers provides the basis for electrochemical impedance analysis. A sinusoidal current or voltage can be shown as a rotating vector in Figure 2.4.

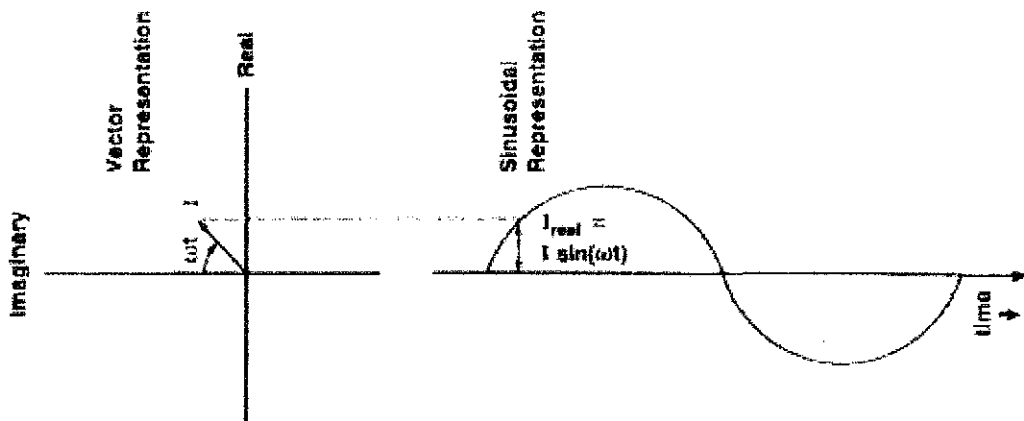


Figure 2.4: Relationship between sinusoidal AC current and rotating vector representation

In the above figure, the current vector rotates at a constant angular frequency f (hertz) or ω (radians/s = $2\pi f$).The x component defines the in-phase current. Therefore, it becomes the “real” component of the rotating vector. The y component is shifted out-of-phase by 90° . By convention, it is termed the “imaginary” component of the rotating vector. The mathematical description of the two components is

$$\text{Real current} = I_x = |I| \cos(\omega t)$$

$$\text{Imaginary current} = I_y = |I| \sin(\omega t)$$

$$|I|^2 = |I_x|^2 + |I_y|^2$$

The voltage can be pictured as a similar rotating vector with its own amplitude E and the same rotation speed ω . As shown in Figure 2.5, when the current is in phase with the applied voltage, the two vectors are coincident and rotate together. This response is characteristic of a circuit containing only a resistor. When the current and voltage are out-of-phase, the two vectors rotate at the same frequency, but they are offset by an angle called the phase angle, θ . This response is characteristic of a circuit which contains capacitors and inductors in addition to resistors.

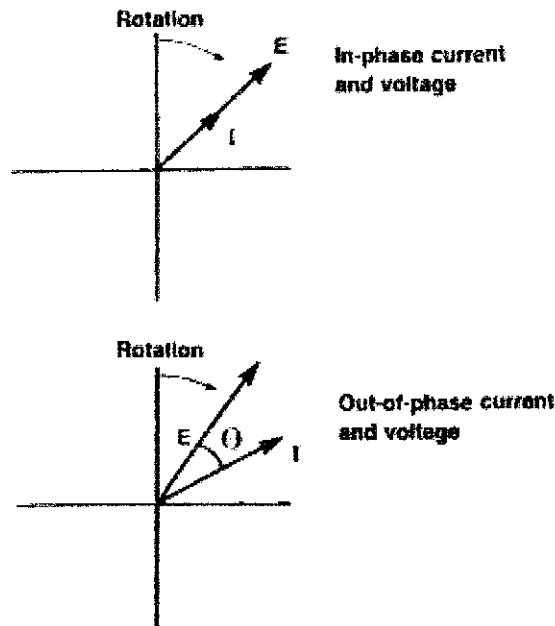


Figure 2.5: In-phase and out-of-phase rotation of current and voltage vectors

In electrochemical impedance analysis, one “views” one of the vectors from the frame of reference of the other. Thus, the reference point rotates and the time dependence of the signals (ωt) is not viewed. In addition, both the current and voltage vectors are referred to the same reference frame. The voltage vector is “divided” by the current

vector to yield the final result in terms of the impedance as shown in Figure 2.6. The impedance is the proportionality factor between the voltage and the current.

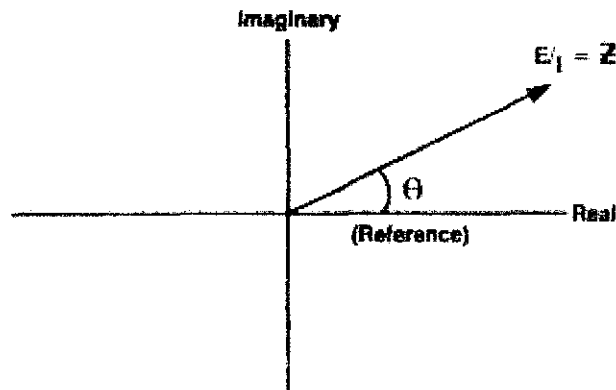


Figure 2.6: Impedance vector

The mathematical convention for separating the real (x) and imaginary (y) components is to multiply the magnitude of the imaginary contribution by j and report the real and imaginary values as a complex number. The equations for electrochemical impedance become:

$$E = E_{\text{real}} + E_{\text{imaginary}} = E' + jE''$$

$$I = I_{\text{real}} + I_{\text{imaginary}} = I' + jI''$$

$$Z = Z' + jZ'' = \frac{E' + jE''}{I' + jI''}$$

$$\tan \theta = \frac{Z''}{Z'}$$

$$|Z|^2 = (Z')^2 + (Z'')^2$$

The goal of the electrochemical impedance technique is to measure the impedance Z (Z' and Z'') as a function of frequency and to derive corrosion rate or mechanism information from the values. Use of simple circuit analogues to model the response is one methodology to achieve this goal. The amplitude of the excitation signal must be small enough so that the response is linearly related to the input, that is, the response is independent of the magnitude of the excitation.

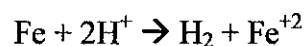
Table 2.1: Circuit elements

Element	Equation
Resistor	$Z = R$
Capacitor	$Z = -1/(i\omega C) = Z\pi f(C)$
Inductor	$Z = i\omega L = Z\pi f$

The three basic circuit elements can be written as shown in above table. Table 2.1 show that a resistor has a real contribution only. That is, the response of a resistor would be a point on the real axis, independent of frequency. Both the capacitor and inductor have purely imaginary contributions. These would appear on the imaginary axis only. One method of electrochemical impedance analysis is to model the corrosion process in terms of circuit elements such as those shown in Table 2.1 and from that model to make conclusions about the physics of corrosion process.

2.2.2 Simple Corrosion Process

The simplest type of corrosion process would be a combination of a corrosion reaction consisting of two simple electrochemical reactions and a double layer. Corrosion would proceed uniformly on the surface. For example, the corrosion of carbon steel in 1 M sulfuric acid can be considered to fall into this category [3]



This equation describes the corrosion reaction. This reaction may be represented by a simple resistor. The double layer is created by the voltage change across the interface. On the metal side of the interface, there may be an excess (or deficiency) of electrons. This excess (or deficiency) is balanced on the solution side by oppositely charged ions. Some are specifically adsorbed at the surface (inner layer). Others are nonspecifically adsorbed and are hydrated. They extend out into the solution in the diffuse layer. The response of this interfacial structure to varying voltage (for example sinusoidal excitation) can be modeled by a capacitor, the double layer capacitance.

For this simple process, the model circuit is that shown in Figure 2.7. The circuit has a resistor R_p in parallel with a capacitor C . The entire parallel circuit is in series with another resistor R_s . The utility of this model for the frequency response lies in the fact that R_s equals the solution resistance not compensated by the potentiostat and R_p equals the polarization resistance as long as the measurement is made at the corrosion potential. By combining R_p with the Tafel slopes for the half-cell reactions by an equation such as the Stern-Geary equation [3], the corrosion rate can be estimated. Thus, analysis of electrochemical impedance enables the corrosion rate to be estimated rapidly in the absence of uncompensated solution resistance when the measurement is made at the corrosion potential

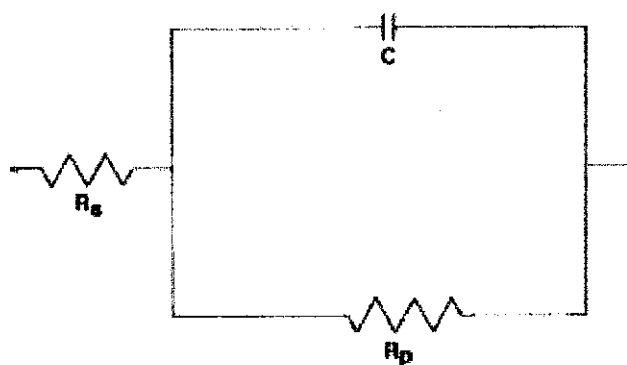


Figure 2.7: Circuit that models simple impedance response

2.2.3 Diffusion Control

Sometimes the rate of a chemical reaction can be influenced by the diffusion of one or more reactants or products to or from the surface. This situation can arise when diffusion through a surface film or hydrodynamic boundary layer becomes the dominating process. Examples are the surface being covered with reaction products of limited solubility. An example of this type of corrosion process that has extreme practical importance is the corrosion of carbon steel in concentrated sulfuric acid in which the product FeSO_4 has limited solubility. Such corrosion has been shown to be controlled by the diffusion of FeSO_4 from a saturated film at the surface to the bulk fluid [7]. Another example is corrosion of steel in water in which the mass transfer of dissolved oxygen can control the corrosion rate [6].

Very often, electrochemical impedance data for such systems has a unique characteristic known as the Warburg impedance. In the low frequency limit, the current is a constant 45° out-of-phase with the potential excitation [6]. The impedance response should ultimately deviate from this relationship. It will return to the real axis at very low frequencies that may be impossible to measure [8]. The equivalent circuit is shown in Figure 2.8. The term W is the Warburg impedance. By appropriate manipulation of the data, the values of the circuit elements can be evaluated [6]. These circuit elements can be used to obtain a value for a resistance (charge transfer resistance) that can sometimes be related to a corrosion rate [9].

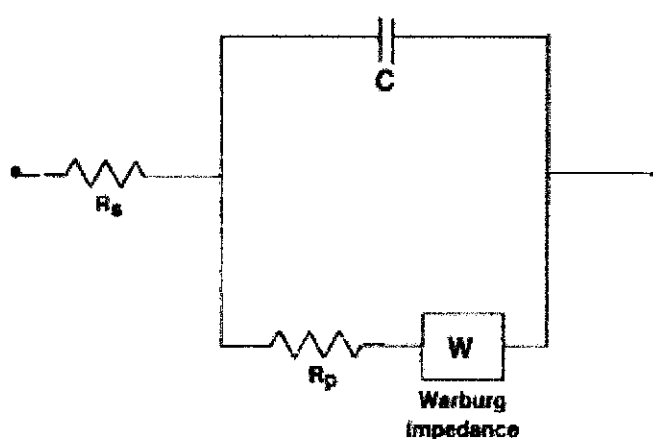


Figure 2.8: Circuit that models impedance in the presence of diffusion

2.2.4 Inductance

Sometimes, the Nyquist type plot exhibits a low frequency portion lying in the fourth quadrant. This behavior seems to have one of a number of causes [6], for example, some type of equilibrium adsorption of a reaction intermediate followed by a rapid desorption of the product. This inductance may be named pseudo-inductance because the processes giving rise to this response are not necessarily the same as those in a real inductor [10]. Indeed, sometimes the behavior is caused by the response not being linearly related to the excitation. Decreasing the amplitude of the excitation might eliminate the pseudo-inductive behavior. Care must be exercised when this behavior is observed. If there is one time constant, the circuit giving rise to the response might be modeled as shown in Figure 2.9. Such a circuit can be solved as long as R_p can be

estimated [9]. The accuracy of the values of R_p and R_L so calculated can be ascertained by comparing the calculated Nyquist and Bode plots with the measured Nyquist and Bode plots. Thus the corrosion rate may be estimated in the presence of inductance.

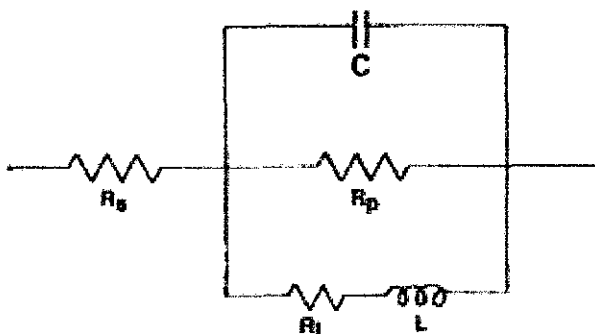


Figure 2.9: Circuit that models impedance in the presence of pseudo-inductance

2.2.5 Depression of Nyquist Semicircle

In real systems, the Nyquist type of semicircle for a simple corrosion process often exhibits some depression below the real axis. An example is shown in Figure 2.10. This behavior has a number of potential causes. Some are improper cell design, surface roughness, dispersion of the time constant caused by the reaction having more than one step, surface porosity, and so forth. Examples that can fit this characteristic are carbon steel in 1 M sulfuric acid and carbon steel in water. Thus, the ability to extract the polarization resistance from this type of curve is important if one is to use the data to estimate corrosion rates, especially when the cause of the depression is unclear. One type of circuit that can model such depression is given by:

$$Z = R_s + \frac{R_p}{1 + (j\omega\tau)^\alpha}$$

In the above equation, the phenomenological term $(j\omega\tau)^\alpha$ replaces the term $j\omega R_p C$ when $\alpha < 1$. In the simple response described by the circuit in Figure 2.4, $\alpha = 1$. The exponent α accounts for the depression below the real axis. The value of R_p can still be estimated by curve-fitting the semicircle and by allowing both the radius and origin to vary [9]. Thus,

corrosion rates can still be estimated even in the presence of such depression, whatever its cause.

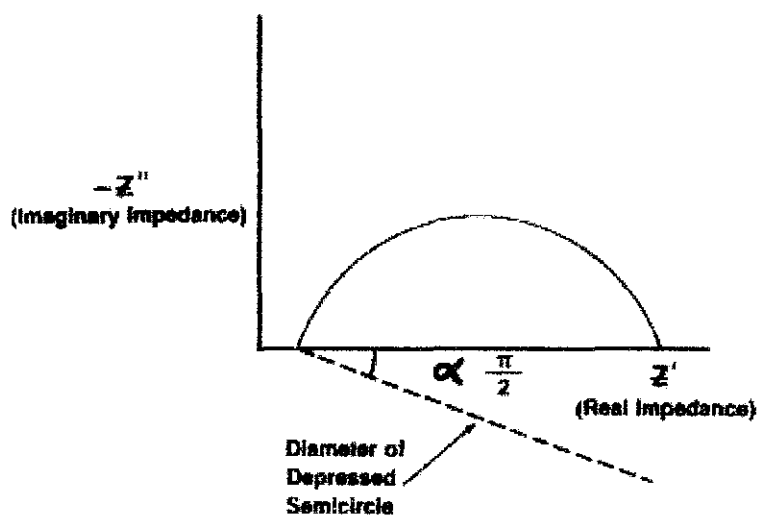


Figure 2.10: Nyquist type of plot showing depression below the real axis

2.3 Linear Polarization Resistance (LPR)

The LPR technique is based on complex electrochemical theory. For purposes of industrial measurement applications it is simplified to a very basic concept. The linear polarization resistance (LPR) technique is an electrochemical method that uses either three or two sensor electrodes. In this technique, a small potential perturbation (typically of the order of 20 mV) is applied to the sensor electrode of interest, and the resulting direct current is measured. The ratio of the potential to current perturbations, known as the polarization resistance, is inversely proportional to the uniform corrosion rate. The accuracy of the technique can be improved by measuring the solution resistance independently and subtracting it from the apparent polarization resistance value. The technique is well known (its theoretical basis had already been developed in the 1950s), and it is widely used under full immersion aqueous conditions.

The advantage of the LPR technique is that the measurement of corrosion rate is made instantaneously. This is a more powerful tool than coupons where the fundamental measurement is metal loss and where some period of exposure is required to determine

corrosion rate. The disadvantage to the LPR technique is that it can only be successfully performed in relatively clean aqueous electrolytic environments. LPR will not work in gases or water/oil emulsions where fouling of the electrodes will prevent measurements being made.

2.3.1 Linear Polarization Method

Electrochemical studies were performed under stagnant condition with the use of static electrodes. The types of electrochemical measurement were used in the study was Linear Polarization (LPR) Test.

2.3.2 Linear Polarization Test

This method is based on the linear approximation of polarization behavior at potentials near the corrosion potential. R_p is given by Stern and Geary equation as below:

$$R_p = \frac{\Delta E}{\Delta t} = \frac{B}{i_{corr}} = \frac{b_a b_c}{2.3(b_a - b_c) i_{corr}} \quad (4)$$

Where, b_a , b_c = Tafel slopes for anodic and cathodic reactions

For the project, The Stern-Geary constant, $B = 25\text{mV}$, was used for all pH. This is in agreement with the available data. R_p can be obtained from the experiment. The corrosion current can be related to Faraday's Law as given below:

$$\text{Corrosion Rate } \left(\frac{\text{mm}}{\text{year}} \right) = (3.27 \times 10^{-3}) \times [(i_{corr} \times EW) \div \rho] \quad (5)$$

Where, EW = Equivalent weight of iron, 27.92

$$i_{corr} = \text{Corrosion current density, } \frac{\mu\text{A}}{\text{cm}^2} = \frac{B}{R_p} \times 10^{-6}$$

$$\rho = \text{iron density, } 7.8 \text{ g/cm}^3$$

CHAPTER 3

METHODOLOGY

3.1 Flow Chart

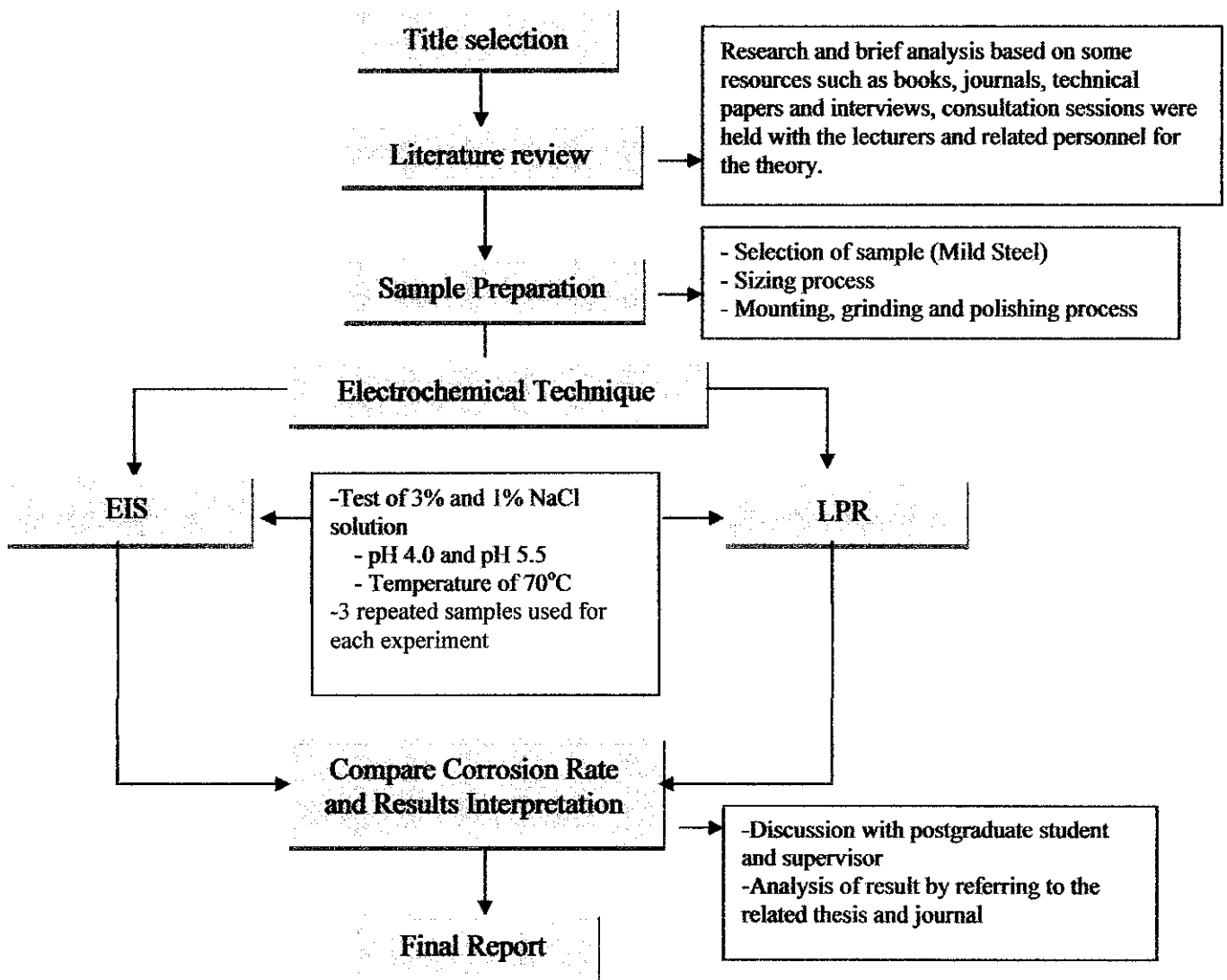


Figure 3.1: Project Flow Chart

3.2 Electrochemical Impedance Spectroscopy and Linear Polarization Resistance

3.2.1 Material / Sample Selection

The main function of this procedure is to find out which material offers the best solution of the project. In most cases, the design of CO₂ corrosion involves an evaluation of the suitability of using mild steel. These two steel types have several advantages:

- Satisfactory performance predictions
- Life cycle costs
- Easy of fabrication / installation

For this corrosion project, all the samples were mild steels.

Table 3.1: Composition of Mild Steels

Samples	Mild Steels	
	Min (%)	Max (%)
Carbon	0.35	
Silicon	0.10	0.35
Manganese	0.45	0.70
Sulphur		0.05
Phosphorus		0.05
Nickel	1.30	1.80
Chromium	0.90	1.40
Molybdenum	0.20	0.35

3.2.2 Sample Preparation

The sample was fabricated from the mild steels plates of 2cm x2cm into the cylindrical shape that having the radius of 0.8cm and the thickness of 0.5cm. All the samples acted as the working electrode and the exposed area was about 2.01cm² as showed in Figure 3.2 and Figure 3.3. Firstly, these samples were spot welded with copper wire with certain length. The weld must be spotted tight and welding carefully to the sample without harmed it. Then, it was mounted with epoxy by cold mounting and then polished to 1200-grade finish using silicon carbide paper (SiC). Finally, it was degreased and rinsed with deionizer water and ethanol. In this way, the polished surface acquired reproducibly bright appearance.

The samples were made in two groups and each group contained 3 samples. The first one was for the test with solution of pH 4 and the second group was for the test with solution of pH 5.5.

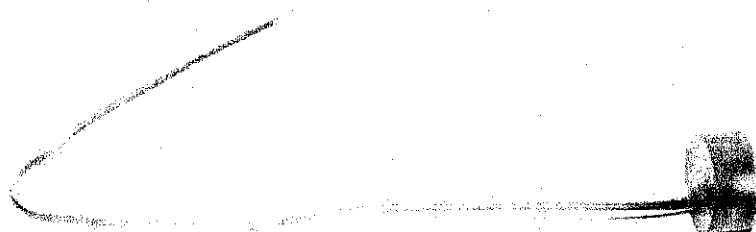


Figure 3.2: The working electrode of Mild Steel sample

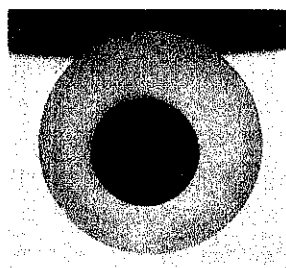


Figure 3.3: The exposed area of Mild Steel sample

3.2.3 Solution Preparation

EIS and LPR experiment conducted using same solution. The solution needed to keep saturated by purging CO₂ gas continuously. The same solution used to obtain a consistent result for the comparison work.

- 1- 1%NaCl and 3% NaCl solution were prepared for the experiment.
 - a. Fill 1 liter of distil water into a beaker.
 - b. Pour 800ml of the distil water from the beaker into another beaker.
 - c. Add 10g/30g of NaCl into the 800ml distil water beaker and stir the solution.
 - d. Pour the remaining distil water into the beaker until get the 1liter of 1%/3% NaCl solution.
- 2- Pour the 1%/3% NaCl solution into the experiment container or apparatus.

3.2.4 Experiment Setup

- 1- Bubble CO₂ gas through 1 liter of 1%/3% NaCl solution for 1 hour to make the solution saturated with CO₂.
- 2- Adjust pH of the solution to 4.0 and 5.5 by adding an amount of 1 molar of Na(HCO)₃ solution.
- 3- Set the temperature at 70°C using hot plate and maintain with an accuracy ±5°C.
- 4- Insert the polished sample to the apparatus and run the experiment.
- 5- For LPR, take readings automatically by the computer that connected to the potentiostats every 5 minutes for the time interval of 1 hour.
- 6- For EIS, take readings automatically by the computer that connected to the potentiostats after 1 hour.
- 7- Repeat the procedures for all the samples.

3.2.5 Apparatus Setup

Electrochemical Impedance Spectroscopy and Linear Polarization Resistance were used in this project to measure the corrosion rate. EIS and LPR needed to be run with three electrodes system known as working electrode (test specimens), counter electrode and reference electrode. These electrodes connected to a potentiostats were put in the solution that stimulated the actual field environment. The function of potentiostats was to verify electric potential difference. A beaker and a bubbler that supplied the CO₂ gas from its cylinder on a hot plate needed to be used for this experiment. The electrodes were connected to the potentiostats with a computer control system.

The impedance measurements were performed using the IM5d system which is based on the universal data and data analysis system AMOS-ANDI (Zahner Elektrik GmbH &Co., Kronach,Germany). Excitation amplitude of 10mV peak to peak was used. Excitation wave forms of these amplitudes caused only minimal perturbation of the electrochemical system, reduced the error caused by the measuring system. The method involved direct measurement of the impedance of the electrochemical system in the frequency range 0.1 to 10⁵ Hz. At lower frequency, no reproducible data could be obtained [16]. The open-circuit potential of the working electrode was recorded every 5 minutes over 60 minutes/1 hour from electrode immersion in the test solution of different pH and different NaCl concentration. All measurements were carried out at temperature 70°C. Reproducibility of the result was ensured by accurate preparation of the test sample and the solutions. The test was repeated for three times to ensure the reliability of the result obtained.

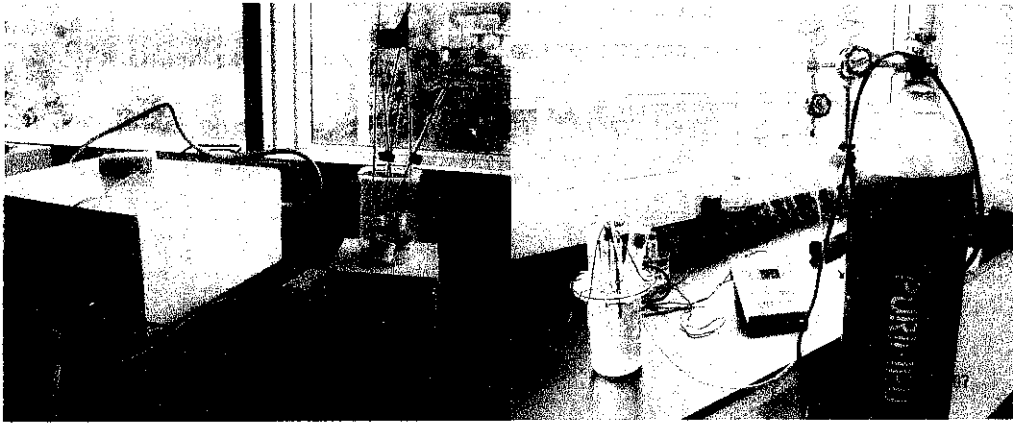


Figure 3.4: Apparatus use in the EIS and LPR experiment

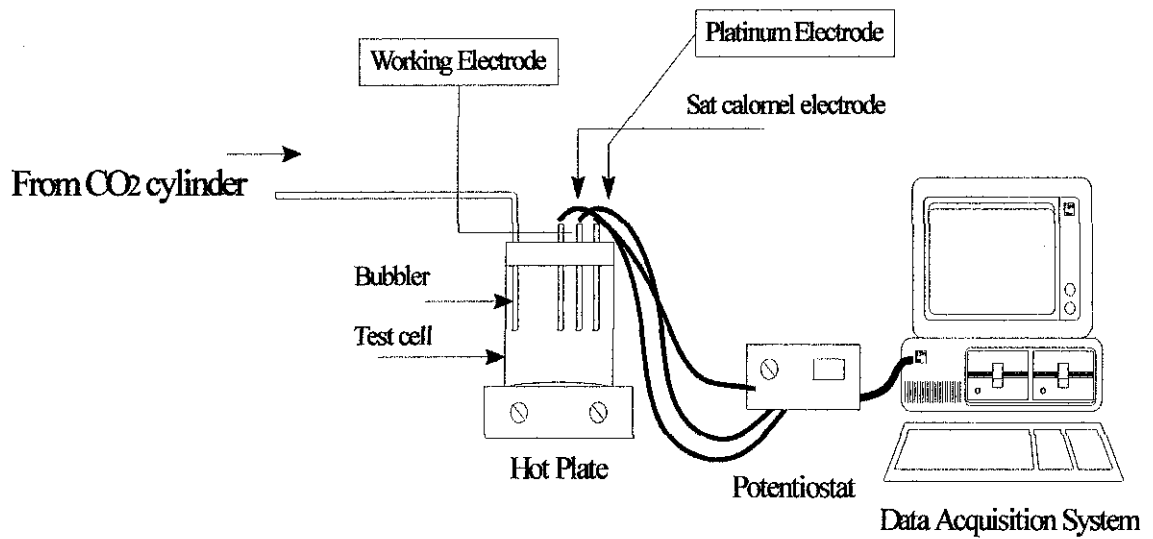


Figure 3.5: Schematic diagram for experimental set-up

CHAPTER 4

RESULT AND DISCUSSION

4.1 Experimental Result by Linear Polarization Resistance

The average corrosion rate was obtained for the time interval of 1 hour the samples exposed to the CO₂ corrosion environment. The reading was taken automatically every 5 minutes. The results of three repeated samples for pH 4.0 and pH 5.5 experiments were compiled into Table 4.1 and 4.2(appendix B). The average corrosion rate of mild steel in the 1% NaCl solution for pH 4.0 and pH 5.5 were 3.160 mm/year and 2.061 mm/year respectively. The average corrosion rates of the mild steel in the 3% NaCl solution for pH 4.0 and pH 5.5 were 1.588 mm/year and 1.284 mm/year. Figure 4.1 showed that the corrosion rate of mild steel in the pH 4.0, 1% NaCl solution were higher than the corrosion rate of mild steel in the pH 5.5, 1% NaCl solution. Figure 4.2 also showed the same situation for corrosion rate in 3% NaCl solution. The corrosion rates for the samples in pH 4.0, 1% NaCl solution increased with increasing in time but the corrosion rates for the samples in pH 5.5, 1% NaCl solution decreased with increasing in time as showed in the Figure 4.1. However, the corrosion rates for the samples in both pHs in 3% NaCl solution decreased with increasing in time as showed in the Figure 4.2.

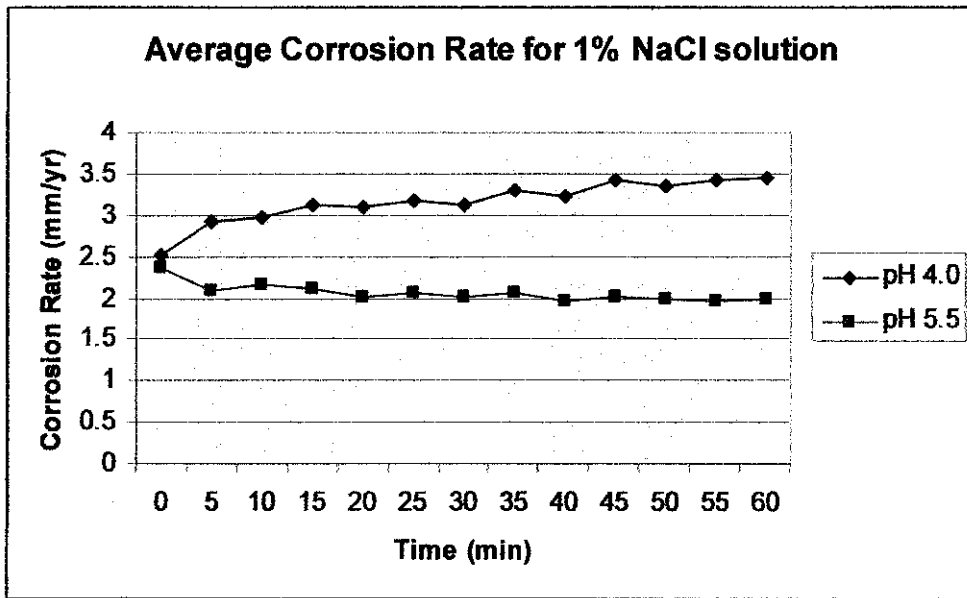


Figure 4.1: Average corrosion rate of mild steel in the 1% NaCl solution of pH 4.0 and pH 5.5 using LPR technique.

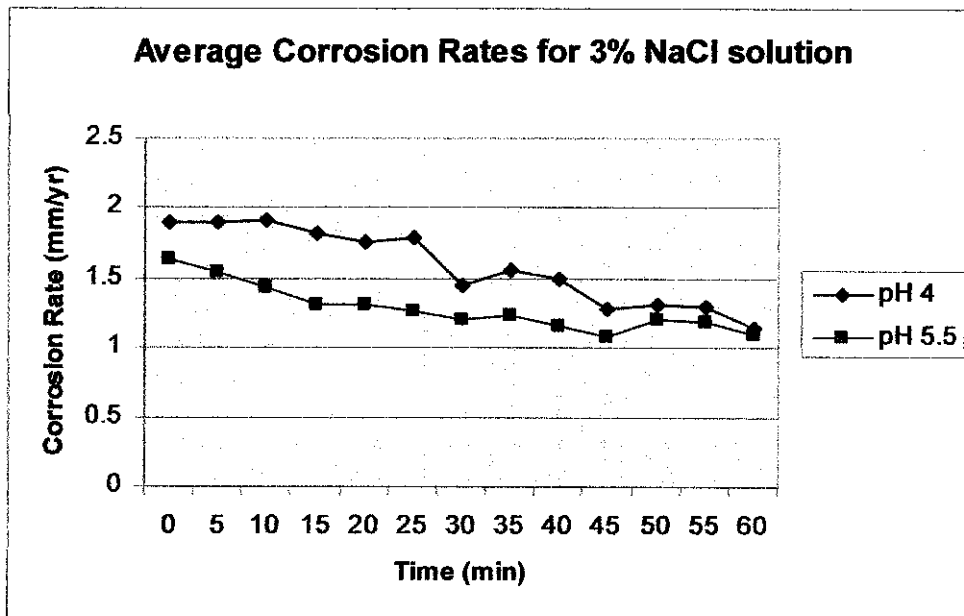


Figure 4.2: Average corrosion rate of mild steel in the 3% NaCl solution of pH 4.0 and pH 5.5 using LPR technique.

4.2 Experimental Result by Electrochemical Impedance Spectroscopy

The readings were taken automatically by the computer after 1 hour of samples immersion in each solution for both pH and different NaCl solution. The results were taken and shown in the Bode plots (Figures 4.3, 4.5, 4.7, 4.9) and Nyquist diagrams (Figures 4.4, 4.6, 4.8, and 4.10). The polarization resistance, R_p got from the Nyquist diagram and the average corrosion rate (CR) can be calculated using the given formula.

$$\blacksquare \quad CR = (315 \times Z \times i_{\text{corr}}) / (\rho \times n \times F) \text{ where } i_{\text{corr}} = B / R_p \quad (5)$$

- Z , atomic weight for iron = 56 g/mol

- ρ , density of iron = 7.8 g/cm³

- n , no. of electron transfer = 2

- F , Faraday's constant = 96500 C/mole

- R_p , polarization resistance = 74.27 Ohm, 108.4 Ohm, 214.7995 Ohm, 241.493 Ohm

- B , Stern-Geary constant = 26 for all pH

$$\blacksquare \quad CR (\text{pH } 4.0, 1\% \text{ NaCl}) = 11.6 \times 26 / 74.27 = 4.061 \text{ mm/year}$$

$$\blacksquare \quad CR (\text{pH } 5.5, 1\% \text{ NaCl}) = 11.6 \times 26 / 108.4 = 2.782 \text{ mm/year}$$

$$\blacksquare \quad CR (\text{pH } 4.0, 3\% \text{ NaCl}) = 11.6 \times 26 / 214.7995 = 1.404 \text{ mm/year}$$

$$\blacksquare \quad CR (\text{pH } 5.5, 3\% \text{ NaCl}) = 11.6 \times 26 / 241.493 = 1.249 \text{ mm/year}$$

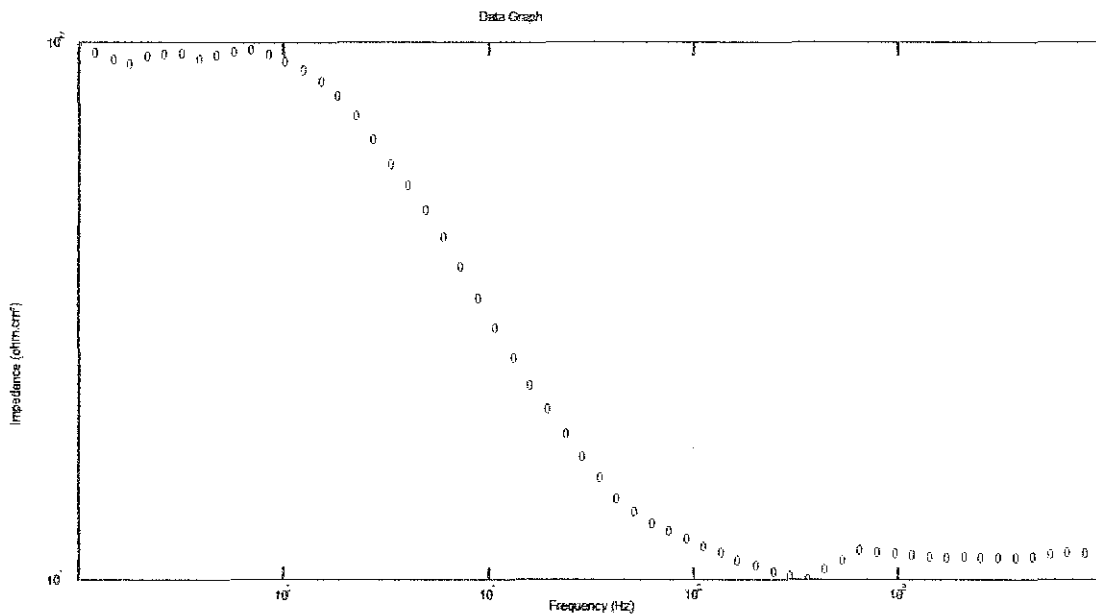


Figure 4.3: Bode plot for mild steel in pH 4.0, 1% NaCl solution using EIS

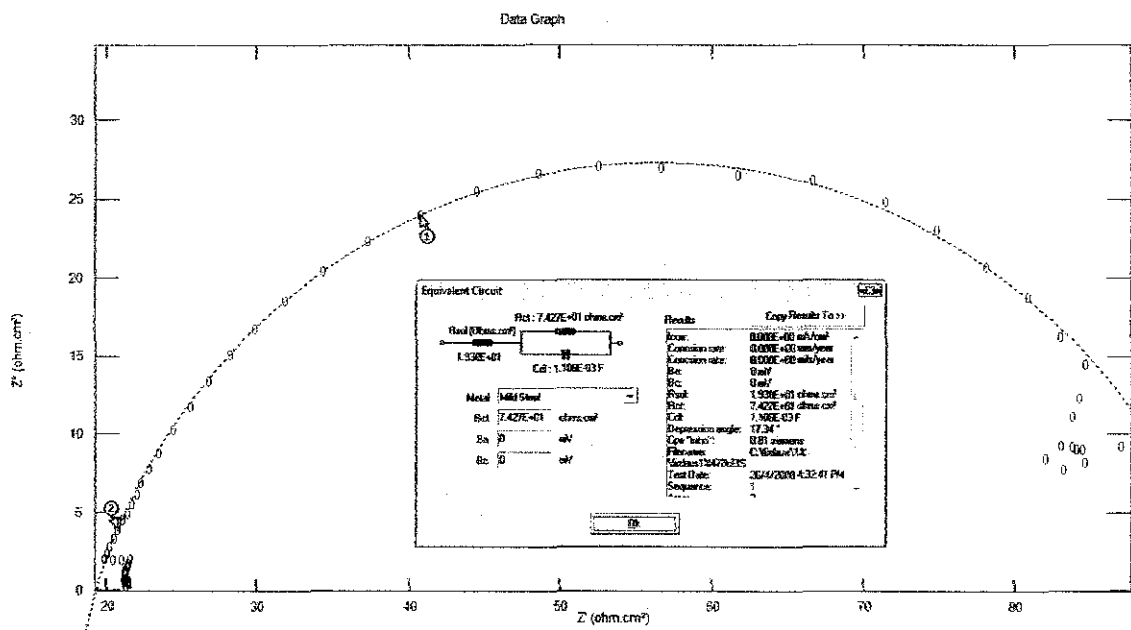


Figure 4.4: Nyquist diagram for mild steel in pH 4.0, 1% NaCl solution using EIS

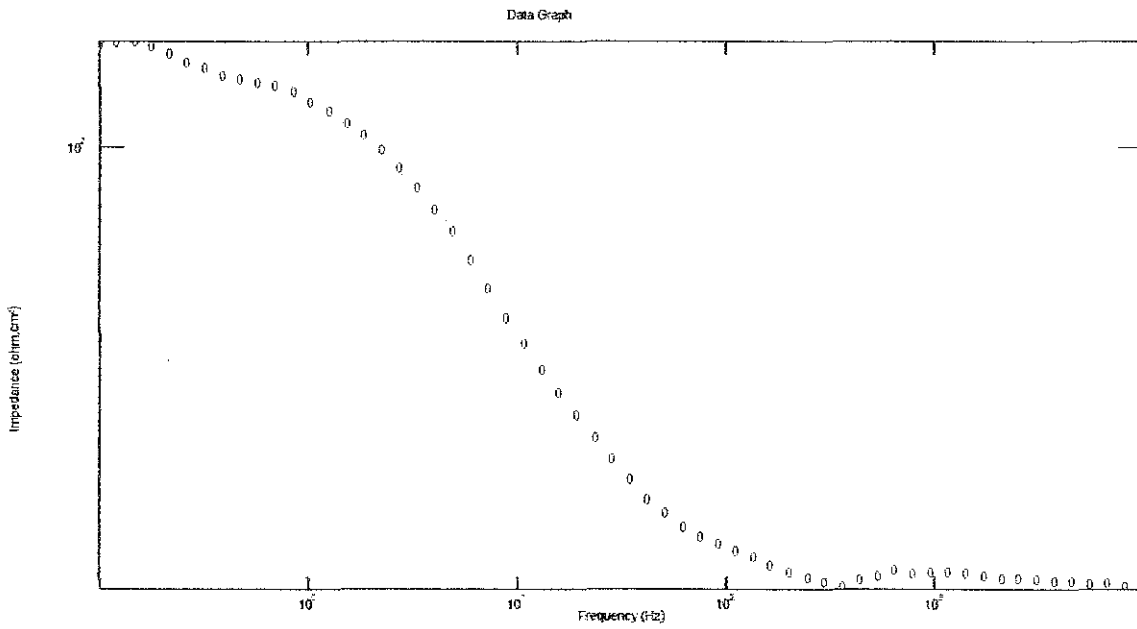


Figure 4.5: Bode plot for mild steel in pH 5.5, 1% NaCl solution using EIS

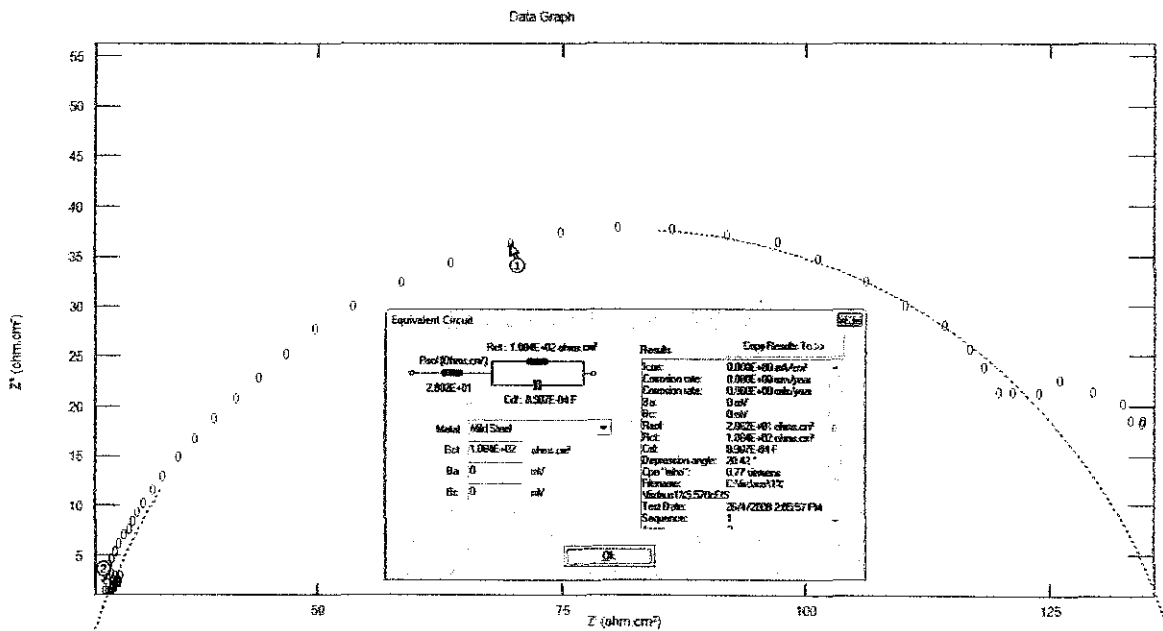


Figure 4.6: Nyquist diagram for mild steel in pH 5.5, 1% NaCl solution using EIS

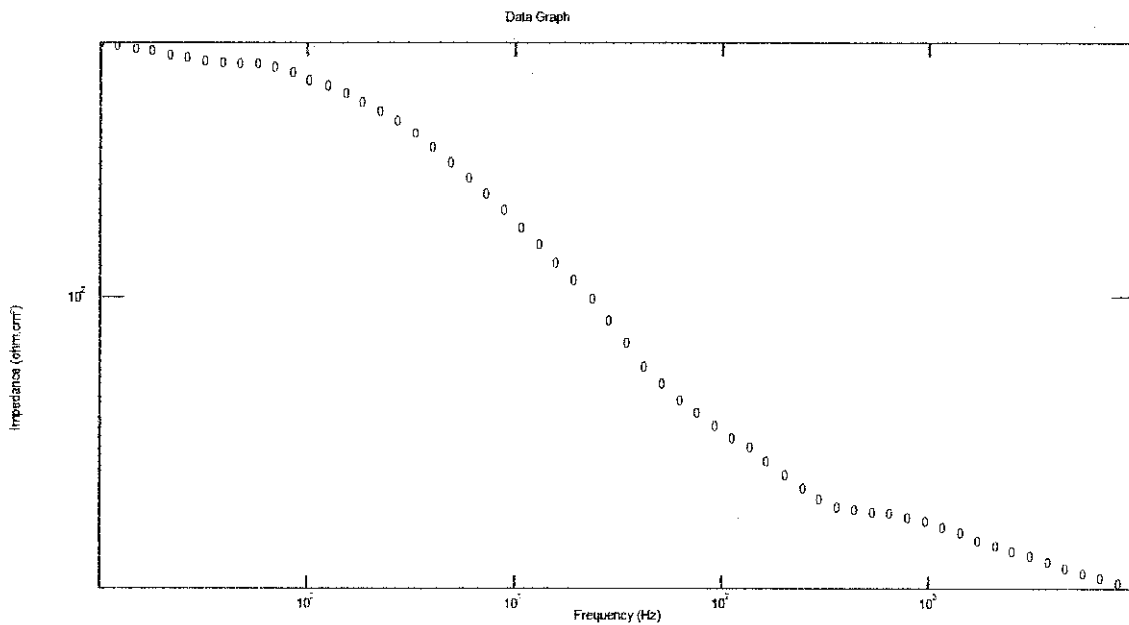


Figure 4.7: Bode plot for mild steel in pH 4.0, 3% NaCl solution using EIS

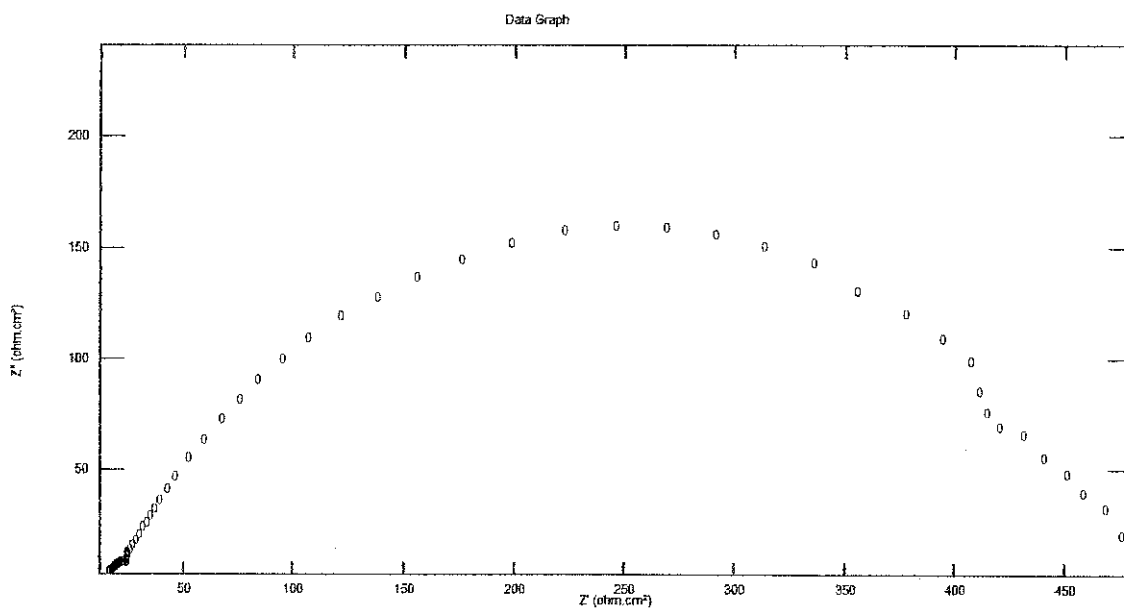


Figure 4.8: Nyquist diagram for mild steel in pH 4.0, 3% NaCl solution using EIS

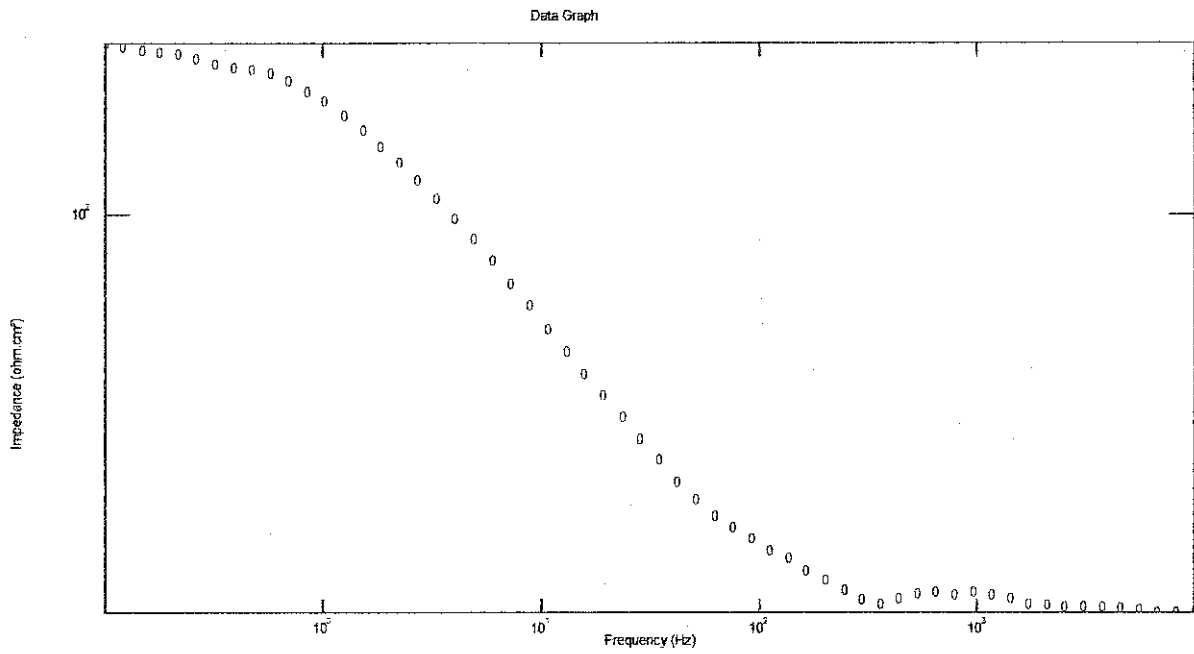


Figure 4.9: Bode plot for mild steel in pH 5.5, 3% NaCl solution using EIS

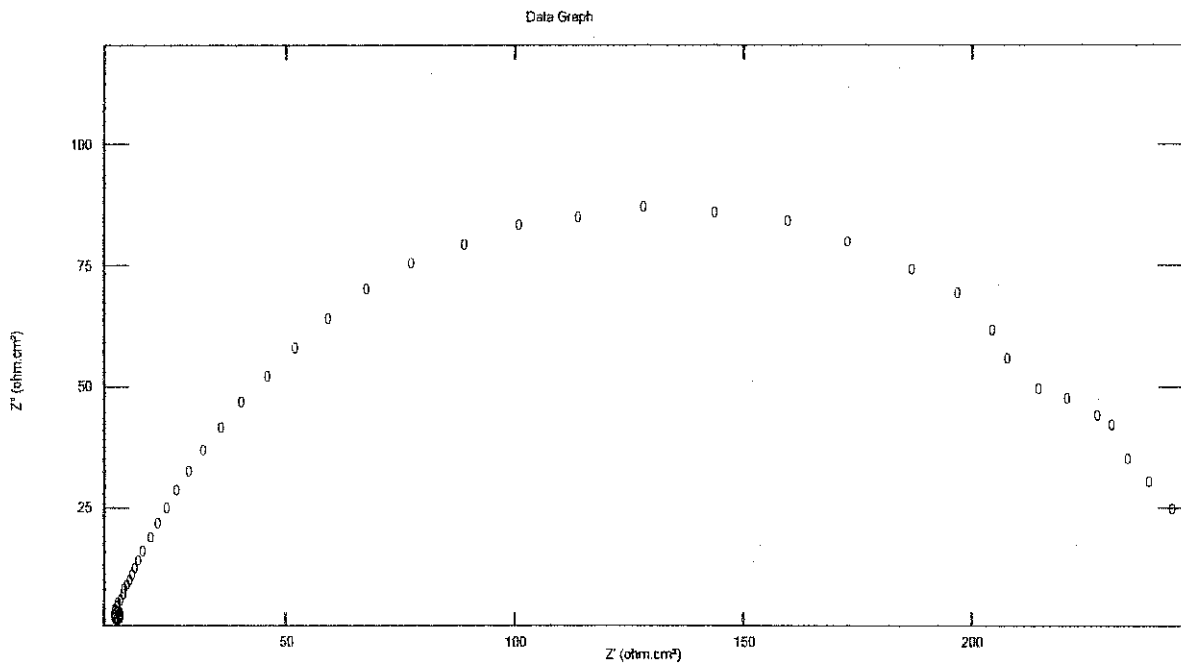


Figure 4.10: Nyquist diagram for mild steel in pH 5.5, 3% NaCl solution using EIS

4.3 Analysis and Discussion

Table 4.3: Final results of the experiments

Conditions \ Results	Average Corrosion Rate (mm/year)			
	LPR		EIS	
Technique				
pH	pH 4.0	pH 5.5	pH 4.0	pH 5.5
1% NaCl	3.160	2.061	4.061	2.782
3% NaCl	1.588	1.284	1.404	1.249

All the experimental results of Electrochemical Impedance Spectroscopy and Linear Polarization Resistance technique had been compiled in Table 4.3. All average corrosion rates using same technique and same solution decreased with the increasing in pH. The corrosion rates of 1% NaCl solution were higher than corrosion rates of 3% NaCl solution for both techniques. There were a large different between corrosion rate of LPR for 1% NaCl solution and the corrosion rate of EIS for 1% NaCl solution by compared with same pH. However, the results of LPR and EIS for 3% solution were approximately same within same pH. The analysis was done after the compilation of the result and followed by the discussion

4.3.1 Effect of pH

Table 4.3 showed that the average corrosion rates of pH 4.0 were higher than average corrosion rates of pH 5.5 for both solutions. pH contributed to the results because pH was the measure of the acidity or basicity of a solution. It was formally a measure of the activity of dissolved hydrogen ions (H^+), but for very dilute solutions, the molarity (molar concentration) of H^+ may be used as a substitute with little loss of accuracy. In solution, hydrogen ions occur as a number of cations including hydronium ions (H_3O^+). In pure water at 25°C, the concentration of H^+ equals the concentration of hydroxide ions (OH^-).

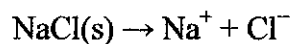
This is defined as "neutral" and corresponds to a pH level of 7.0. Solutions in which the concentration of H^+ exceeds that of OH^- have pH values lower than 7.0 and are known as acids. Solutions in which OH^- exceeds H^+ have a pH value greater than 7.0 and are known as bases. Both pH 4.0 and 5.5 have pH values lower than 7.0, so they are acids but pH 4.0 was stronger than pH 5.5. The formula for calculating pH is:

$$pH = -\log_{10}[H^+]$$

The solution of pH = 4.0 had an $[H^+]$ concentration of 10^{-4} mol/L, or about 1×10^{-4} mol/L. Thus, its hydrogen activity was around 1×10^{-4} . The solution of pH = 5.5 had an $[H^+]$ concentration of $10^{-5.5}$ mol/L the hydrogen activity was 3.163×10^{-6} . The hydrogen activity for pH 4.0 was higher than pH 5.5 and it gave the higher hydrogen evolution reaction for pH 4.0. The decreased in the hydrogen evolution reaction contributed to the decreased of corrosion rates.

4.3.2 Different Percentage of NaCl

An electrolyte is any substance containing free ions that behaves as an electrically conductive medium. Electrolytes are also known as ionic solutions because they generally consist of ions in solution. Electrolytes commonly exist as solutions of acids, bases or salts. Electrolyte solutions are normally formed when a salt is placed into a solvent such as water and the individual components dissociate due to the thermodynamic interactions between solvent and solute molecules, in a process called solvation. NaCl For this experiment, when salt, NaCl, is placed in water, the following occurs:



In simple terms, the electrolyte is a material that dissolves in water to give a solution that conducts an electric current. Originally, a "strong electrolyte" was defined as a chemical that, when in aqueous solution, is a good conductor of electricity. With greater understanding of the properties of ions in solution its definition was gradually changed to the present one.

Most CO₂ corrosion research is done at lower salt concentrations typically from 1 wt% to 3 wt% NaCl. The table 4.3 showed that the corrosion rates of LPR and EIS for 1% NaCl solution were greater than 3% NaCl solution. Experimental results showed that high salt concentrations affect the general CO₂ corrosion rate. It was seen that NaCl significantly reduced the CO₂ corrosion rate. It was obvious that salt retarded both the cathodic and anodic reaction. For the cathodic reaction the presence of salt decreased the magnitude of the charge transfer reactions. On the anodic side, there seems to be a clear retardation of the rate of anodic dissolution of iron which led to an increase of the corrosion potential.

4.3.3 Measurement Technique

Both LPR and EIS got the approximately the same value for same pH in 3%NaCl solution. The percentage of different between the average corrosion rates were about 12% for pH 4.0 and 3% for pH 5.5, so they were small and accepted. However, the results for same pH in 1% NaCl solution showed a large different between EIS and LPR. They also had large percentages of different that were 22% for pH 4.0 and 26% for pH 5.5. The trends of the average corrosion rate were different for LPR in 1% NaCl solution but that did not happened in 3% NaCl solution as shown in figure 4.1 and figure 4.2. The corrosion rate for pH 4.0 increased with increasing in time but corrosion rate decreased with increasing in time in pH 5.5. So, it showed that the LPR result would be unacceptable and LPR had a problem with low conductivity or low concentration of electrolyte. EIS is a sensitive method and it also can be used to measure corrosion rate in low conductivity of electrolyte compared to LPR.

CHAPTER 5

CONCLUSION

The CO₂ corrosion study using Electrochemical Impedance Spectroscopy and Linear Polarization Resistance had been done and the following conclusions were made;

1. EIS can be used to measure corrosion rate for low conductivity and high conductivity of electrolyte but LPR has problem with low conductivity of electrolyte.
2. EIS and LPR successfully showed the effect of pH to the corrosion rate. The increasing of acidity would increase the corrosion rate.

CHAPTER 6

WAY FORWARD

Further analysis can be done to strengthen the result of the study. In determining a realistic result, a comparison study between the experimental works and the calculation from CO₂ corrosion prediction software is required for future study. The purpose of the comparison is to verify the reliability and consistency of the result obtained in the experimental works.

Since the corrosion rate is usually temperature dependent, results will be comparable only for the steel at the process temperature to which the probes are exposed. In heat transfer environments actual plant metal temperatures may be significantly different from that of the test probe. Other than that, this study also can be improved by performing the test at the temperature below and above 70°C to see the effect of the temperature on the corrosion rate in CO₂ environment. The corrosion rate should be varies with the temperature changes. The testing time also need to be much longer to see the effect of time variation.

Corrosion rates may be affected by flow velocity. Consequently, probe electrodes should be used in a velocity typical of the plant conditions. Caution should be exercised in any laboratory tests to reproduce typical velocities and keep the test fluid representative of plant conditions by preventing an unrepresentative build up of corrosion product in solution, or depletion of dissolved oxygen. Where flow dynamics or process fluid separation at a pipe or vessel wall are particularly critical to the corrosion process, a flush-mounted probe may be more desirable than a probe with electrodes positioned near the center of the pipe or vessel.

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APPENDIX A-1

GANNT CHART FOR FIRST SEMESTER OF FINAL YEAR PROJECT

No. Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1 Selection of Project Topic														
-Topic Proposal														
-Topic assigned to students														
2 Preliminary Research Work														
-Introduction														
-Objective														
-Literature Review														
-Project planning														
3 Submission of Preliminary Report				○										
4 Project Work														
-Research: CO corrosion, EIS, Other techniques														
-Laboratory Work: Experiment														
5 Submission of Progress Report								○						
6 Project work continue														
-Practical/Laboratory Work														
7 Submission of Interim Report Final Draft													○	
8 Oral Presentation														○
9 Submission of Interim Report														○



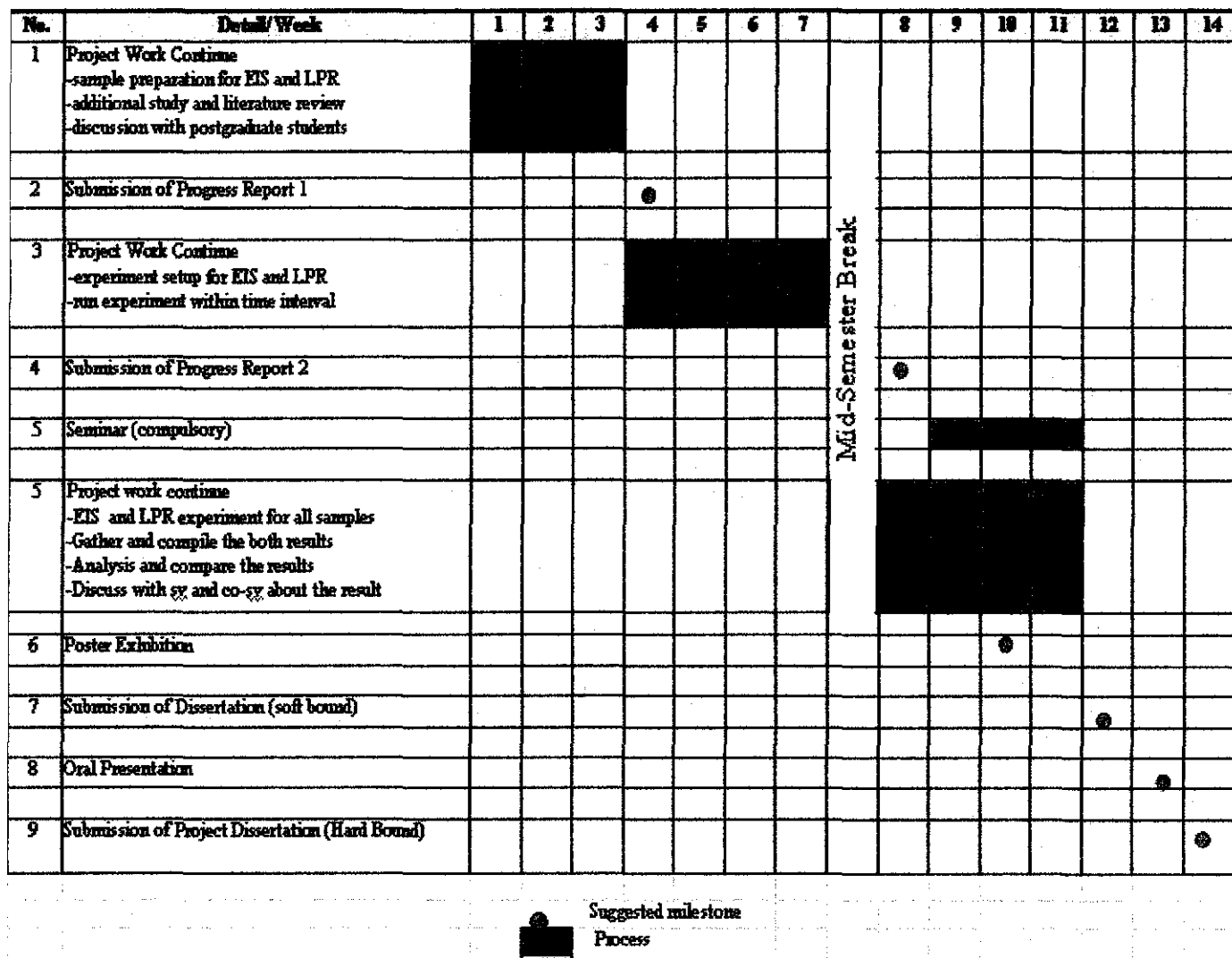
Process



Milestone

APPENDIX A-2

GANNT CHART FOR FIRST SEMESTER OF FINAL YEAR PROJECT



APPENDIX B-1

TABLE 4.1: AVERAGE CORROSION RATE OF 1% NaCl SOLUTION USING LPR

Time (min)	Average CR for pH 4.0 (mm/yr)	Average CR for pH 5.5 (mm/yr)
0	2.52065	2.36445
5	2.9213	2.09735
10	2.98105	2.15785
15	3.11845	2.12025
20	3.0907	2.0187
25	3.16275	2.06435
30	3.10965	2.00195
35	3.3028	2.05605
40	3.2208	1.9548
45	3.4284	2.01045
50	3.3551	1.9883
55	3.41125	1.9735
60	3.45775	1.9808

APPENDIX B-2

TABLE 4.2: AVERAGE CORROSION RATE OF 3% NaCl SOLUTION USING LPR

Time (min)	Average CR for pH 4.0 (mm/yr)	Average CR for pH 5.5 (mm/yr)
0	1.900125	1.6401
5	1.90205	1.5454
10	1.91655	1.43781075
15	1.828275	1.3146767
20	1.762625	1.3108335
25	1.786775	1.26455065
30	1.45585	1.20240905
35	1.561025	1.24142945
40	1.4962	1.161971817
45	1.285425	1.085584283
50	1.30445	1.198939033
55	1.30025	1.190087517
60	1.144075	1.100000549