ASSESSMENT OF COATING PERFORMANCE FOR UNDERGROUND PIPELINE

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Supervised by

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Dissertation submitted in partial fulfillment of

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CERTIFICATION OF APPROVAL

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Approved by,

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(Ir. Dr. Mokhtar Che Ismail)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2014

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 the original work contained herein have not been undertaken or done by unspecified sources or persons.

AZMAN BIN IBRAHIM

ABSTRACT

The integrity of underground pipeline relies on the performance of the coating system. In this paper, electrochemical impedance spectroscopy (EIS) was used to evaluate the protective ability of polyamine cured epoxy coating in term of dielectric performance in NS4 simulated soil solution. The objective of this project is to assess the performance of good coating and physically-damaged coating of polyamine cured epoxy by obtaining the dielectric properties in simulated soil solution by using EIS and to determine the effect of coating condition on corrosion rate. The polyamine cured epoxy coating was applied to the carbon steel using airless spray gun. The thickness of coating was set according to the manufacturer specification. For physically-damaged coating, intentional coating flaws were made by stripping the coating. The EIS measurements were conducted by using three-electrode electrochemical cell system; X65 carbon steel samples (WE), a reference electrode and a counter electrode. The cell was filled with simulated soil solution (NS4). The frequency of the EIS measurement was ranged from 0.01 Hz to 100 kHz with an applied AC perturbation of ±10 mV. Based on the Bode plots, the damage coating samples showed low values of impedance compared to good coating. The results show that the damaged coating has reducing the strength of bonding between the coating particles. In term of dielectric properties, it is proposed that a coating system with good performance against corrosion show high values of R_{po} and R_{ct} and low values of C_c and C_{dl}. Based on the results, the values of R_{po} and R_{ct} of good coating is higher than physically-damaged coating while the values of C_c and C_{dl} is lower than physically-damaged coating. After 24 hours of immersion, the corrosion rate obtained from the good coating sample is 0.10×10^{-6} mm/yr which is significantly lower than the corrosion rate of physically-damaged coating sample which is 0.06 mm/yr. The corrosion rate of good coating is considered negligible since the value of charge transfer resistance is very high. Based on the worst case laboratory testing, a good coating can provides acceptable corrosion protection for underground pipeline.

ACKNOWLEDGEMENT

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LIST OF FIGURES

LIST OF TABLES

TABLE OF CONTENTS

CHAPTER 1

INTRODUCTION

1.1 Background of Study

In definition, corrosion is the degradation of a material due to a reaction with environment. According to Chaker and Palmer [**1**], they defined soil-corrosion as the deterioration of metal or any other material due to the reaction of chemical and biological action by soil environment. The interaction between metal and the soil environment can cause the electrochemical process to occur.

Underground steel pipelines are commonly used as a medium to transport gas and crude oil from one place to another. Besides, it is the most economical and safe way of transmitting the resources [**2**]. In Malaysia, Petroliam Nasional Berhad (PETRONAS) is responsible in managing the natural gas transmission under Peninsular Gas Utilization (PGU) project in order to supply piped sales gas to end user in the power, industrial and commercial sector [**3**]. About 1,600 km of the pipelines were installed underground along Peninsular Malaysia. However, corrosion is one of the biggest problems that can occur to the underground pipeline which can lead to high possibility of accidents. Besides, the detection of corrosion for buried pipelines is expensive because its occurrence is difficult to detect.

Peninsular Malaysia consists of different types of soil environment. Different soil environment will result in different level of corrosion dynamic. The aggressiveness of the soil environment is influenced by several parameters such as degree of aeration, pH, moisture, ionic species and microbiological activity [**4**].

In oil and gas industry, carbon steel is the common material in making pipeline. However, carbon steel is not corrosion resistant. In order to ensure the successful use of the carbon steel, the corrosion prevention methods are necessary. The main method to prevent from corrosion of underground pipeline is by application of physical coating [**5**]. The integrity of underground pipeline is depending on the performance of the coating. Thus, it is important to assess the coating performance due to the real economic and environmental issues cause by the deterioration of buried pipeline.

1.2 Problem Statement

Polyamine cured epoxy has been successfully installed for underground pipelines. This is to ensure security supply of gas to the customers. Many studies have been carried out in order to analyze the performance of the coatings in term of physical properties. However, the coatings performance in term of dielectric properties is not widely known. Therefore, it is important to conduct a study to assess the effectiveness of the coatings in term of dielectric properties and determine its capability in reducing the corrosion rate.

1.3 Objectives

The objective of the project is to assess the performance of good coating and physically-damaged coating of polyamine cured epoxy by:

i. Obtaining the dielectric properties in simulated soil solution by using EIS,
ii. Determining the effect of coating condition on corrosion rate.

1.4 Scope of Study

The scope of study includes:

i. Identify the type of coating material for underground pipeline.
ii. Identify the environment for underground pipeline exposed to.
iii. Sample preparation of X-65 carbon steel.
iv. Application of coating system.
v. Analysis of coating performance by using electrochemical impedance spectroscopy (EIS) technique.

1.5 Relevancy of the Project

The project is carried out base on the real industry problem affecting the condition of the underground pipeline due to the acidic soil environment. Knowledge domain of corrosion and materials falls under material specialization.

CHAPTER 2

LITERATURE REVIEW

2.1 Definition of Corrosion

There are many definition of corrosion. However, the most popular definition of corrosion is the deterioration or degradation of a material when it reacts with the environment [**6**]. The environment is considered as corrosive agent. In other words, corrosion is also defined as a natural phenomenon and can be considered as extractive metallurgy in reverse. The extractive metallurgy is obtained from mining activities and refining or alloying them for commercial use. Unfortunately, the refined metal is thermodynamically unstable which can lead toward corrosion process to occur when it reacts with the water and oxygen. For example, in the making of steel, iron will be refined its form from Fe_2O_3 (stable) to Fe (unstable). Due to the unstable energy, Fe will naturally change back to its stable form. Thus, the corrosion process will occur due to corroding/rusting of the steel. The mechanism can be well explained by the figure 2.1 below:

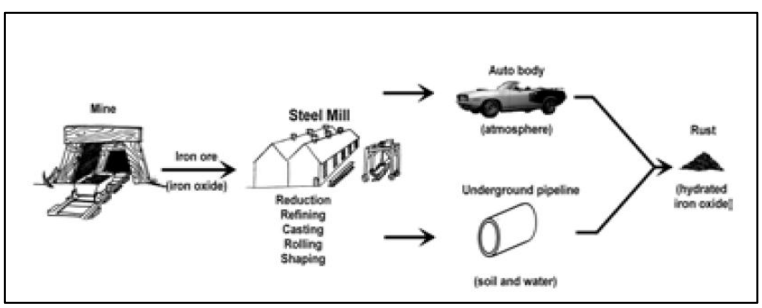


Figure 2.1: Extractive Metallurgy in reverse

Most pure metals are not suitable for underground pipeline construction. In order to make it possible the combination of pure metals with other metal is necessary to form metal alloys (carbon steel). However, carbon steel is not fully corrosion resistance. In order to ensure the successful use of carbon steel, corrosion prevention method is needed. The widely methods used is coating and cathodic protection. Coating is a thin layer which isolates the metal surface from contact with environment. Besides, the cathodic protection is a supplement technique to reduce corrosion by passing sufficient cathodic current for it to cause anodic dissolution rate become negligible during overall stage.

2.2 Peninsular Malaysia Soil Environment

Due to the high demand of natural gas in power sector, PETRONAS has established Peninsular Gas Utilization (PGU) network since 1981. The purpose of the project is to channel the natural gas via pipeline to consuming areas including centralized power station. Besides, the project is an initiative to provide alternative fuel for electricity generation rather than using fuel oil as the primary source of energy [**3**].

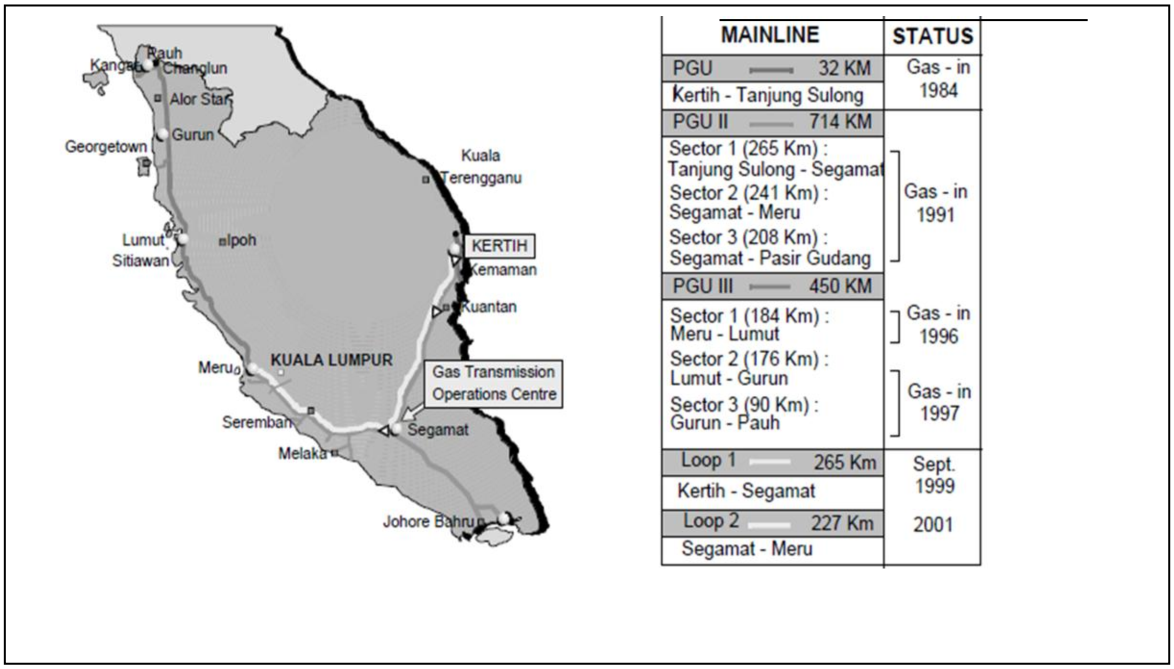


Figure 2.2: Peninsular Gas Utilization Project [**3**]

According to figure 2.2, the length of main and lateral pipelines is more than 1,600 km in order to transmit gas to the end user. Most of the pipelines are made of carbon steel and they were installed underground along the Peninsular Malaysia. Unfortunately, corrosion has become the main problem to the underground pipeline. Thus, these pipelines have high possibilities in contributing to pipelines failures. To analyze the type of corrosion that occurs is a challenge because they are buried in different soil environment. Different soil has different soil resistivity which will result in different level of corrosion dynamic.

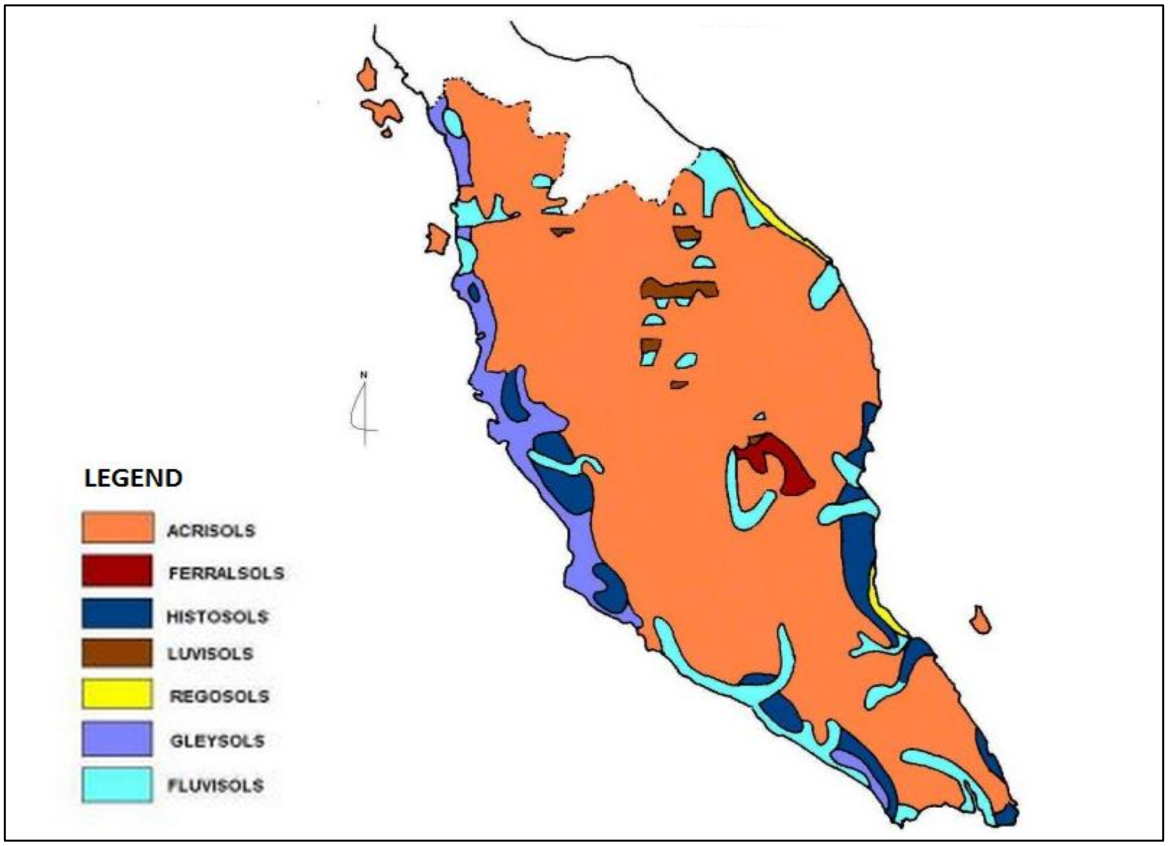


Figure 2.3: Soil map of Peninsular Malaysia [**7**]

According to figure 2.3, more than half of the main soil series in Peninsular Malaysia fall into the Acrisol group. Soil acidity or alkalinity is ranked on a pH scale that runs from zero to 14 as describe in table 2.1 below.

Table 2.1: Soil types of Peninsular Malaysia [**8**]

Soil type	Description
Acrisols	Acidic soils (pH 2.6-3.3) that are typically found in tropical, humid climates. Typically bright coloured with red or yellow.
Ferralsols	Typically red or yellow soils of the humid tropics. Low soil-pH and low concentrations of dissolved weathering products in the soil solution
Histosol	They are found at all altitudes but the vast majority occurs in lowlands and have pH acid comes down to pH 3
Luvisols	Typically a brown to dark brown surface horizon and having alkaline pH values.
Regosols	Their pH is neutral to slightly basic (pH 7.8 to 8.6). Typically found in reddish black to very dark grayish brown depend on the deepness.
Gleysols	It is a wetland soil, occur in nearly all climates. Having a gleyic colour pattern with pH 3.0 to 4.5.
Fluvisols	Occur on all continents and in all climates. They have neutral or near-neutral pH values.

As shown in figure 2.2 and 2.3, mostly the transmission pipeline is operating in acidic soil medium. Carbon steel of buried pipelines is susceptible to degradation by soil corrosivity thus enhance soil corrosion damage. Acidity is the most important chemical property of soils affecting soil corrosivity. Other factors affecting soil corrosion are [**4**];

- Aeration and water-retention (permeability) characteristics of the soil.
- Dissolved salt content and resistivity of the soil.
- Presence of ionic species in the soil for example, chloride or microbiologically active species, such as bacteria.

2.3 Soil Corrosion

Soil corrosion is a complex phenomenon which involves the deterioration of metal or other material toward chemical, mechanical and biological action by soil environment. Carbon steel pipelines are the most preferred medium that have been used for many years to transport large volumes of natural gas, oil and other petroleum product over a long distances. These underground pipelines experienced corrosion attack due to the exposure to the various environment conditions of soil. In order to study the behavior of soil corrosion, it is suitable to use the actual soil extracts or simulated soil solution. Usually, simulated soil (NS1, NS2, NS3, and NS4) is used because of its inorganic characteristic and easy preparation [**9**].

Corrosion of metal is occurred from the electrochemical reaction. The basic representation of corrosion reaction can be expressed on term of iron, water and oxygen. When water and oxygen are present in metal surface, the metal is likely to be in ionic state rather than remain in elemental state [**10**]. The chemical equation for the reaction is:

$$Fe + H_2O + \frac{1}{2}O_2 \rightarrow Fe(OH)_2 \tag{2.1}$$

The formation of ferrous hydroxide is the reaction product of iron and oxygen in pure water. Corrosion is unlikely to occur if one of these elements is absent in the chemical reaction. In corrosion process, there is anodic and cathodic reaction. Both reactions take place simultaneously. The metal dissolution occurs at the anode which can be expressed as:

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{2.2}$$

An oxidation reaction takes place at the anode where the metal releases the electron and change to ionic state. Then, the cathodic reaction consumes electron from the anode and the chemical reaction occurs depends on the type of the environment. In acidic environment the hydrogen evolution reaction will occur due to the presence of hydrogen ions while in near-neutral environment, oxygen reduction reaction will occur.

Cathodic reaction:

(i) Acidic environments:

$$2H^{+} + 2e^{-} \leftrightarrow H_2 \tag{2.3}$$

(ii) Near-neutral and Alkaline environment:

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \tag{2.4}$$

2.4 Parameters Affecting Soil Corrosion

There are several parameters that can affect the soil corrosion. The parameters are:

2.4.1 Soil pH Value

Soil pH value is the main factor that affects soil corrosion. The pH value indicates the level of acidity. The lower the number of pH, the higher the level of acidity. The more acidic the soil, the higher the corrosion rate will be. The pH value of soil usually ranges between 4.5 and 8 [**11**]. In this range, the effect of pH is fairly independent to the corrosion rate, but the corrosion rate will increase quickly when the pH value falls below 4. The soil acidity is usually contributed by industrial waste, acid rain, decomposition of acidic plant and micro-biological activity. The figure 2.4 shows the relationship between pH and corrosion rates for carbon steel.

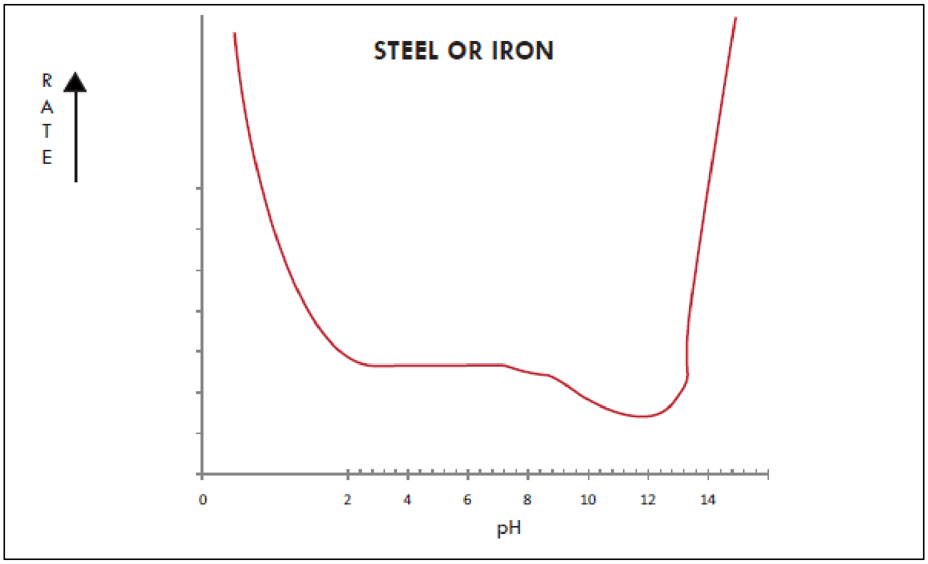


Figure 2.4: Influence of pH towards corrosion rate [**12**]

2.4.2 Soil Resistivity

Soil resistivity depends on the amount of dissolved salt in soil and the content of moisture. Resistivity of soil indicates the level of soil corrosivity since it is correlated with electrochemical reaction. Higher soil resistivity is capable to slow down the corrosion rate. It also can be stated that soil resistivity is reciprocal to the conductivity of particular soil [**11**]. Lower resistivity of soil shows that it will be a good electrolyte in corrosion reaction. Table 2.2 shows the corrosivity index of soil according to the resistivity value.

Table 2.2: Soil corrosivity index [**13**]

Resistivity (ohm.cm)	Category
0 – 2,000	Very corrosive
2,000 – 5,000	Corrosive
5,000 – 10,000	Moderately corrosive
10,000 – 25,000	Mildly corrosive
Over 25,000	Less corrosive

2.4.3 Moisture Content

The moisture of the soil is depending on the water contained in it. Increase in water content will result in high amount of the electrolyte which can trigger the corrosion rate. The moisture content is varies in every type of soil. The table 2.3 shows the influence of moisture content towards corrosion rate. Based on the study that has been carried out by Norhazilan et al. [**14**], the corrosion rate is increase with the amount of moisture content. The result of the research on the correlation between moisture and corrosion rate is shown in figure 2.5.

Table 2.3: Moisture Content Effect on Corrosion rates [**15**]

Soil Type	Moisture	Corrosion (mm/yr)
Sloughs/muskeg/free water accumulation	Always wet	Very corrosive >1.0
Loams/Clays	Mainly wet	Corrosive to moderately corrosive 0.5 – 1.0
Gravels and sandy	Mainly dry	Mildly corrosive 0.2 – 0.5
Arid and sandy	Always dry	Non-corrosive < 0.2

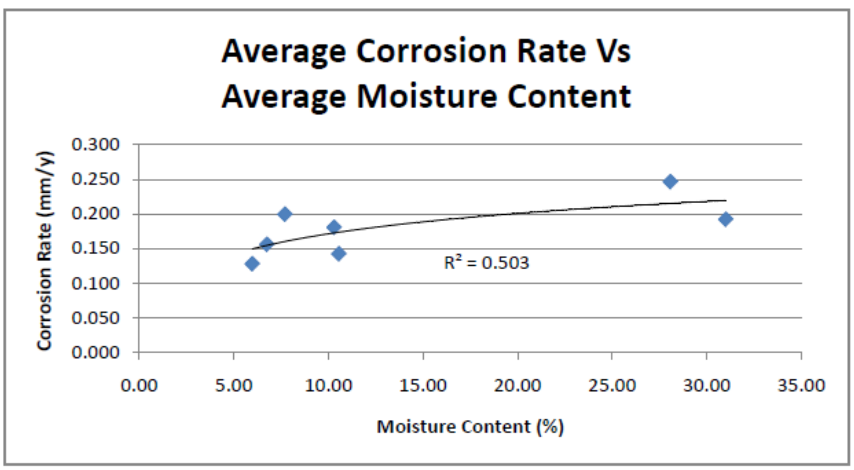


Figure 2.5: Influence of moisture content towards corrosion rate [**14**]

2.4.4 Dissolved Salt Content

The content of dissolved species like chloride ions is significant to the integrity of buried pipeline because they can increase the electrical conductivity of the water so that it can facilitate the flow of corrosion current. The chloride ion is very harmful because it can cause pitting initiation to the carbon steel. Besides, their presence is also capable to reduce the resistivity of the soil. The size of chloride ion is very small which it can penetrate the natural protective film that form on the surface of the metal. Thus, the effectiveness of natural protective layer will be reduced while the corrosion rate will increase.

2.5 Corrosion Testing Method

Many testing methods are available in order to assess the corrosion behavior of metals. For example, adhesion test (pull-off test) and electrochemical test (polarization and impedance measurement). In fact, electrochemical methods are more reliable because they provide both qualitative and quantitative results. For assessment of coating performance, impedance measurement using electrochemical impedance spectroscopy technique (EIS) is crucial.

2.5.1 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical methods have been widely used as a non-destructive technique in order to study the corrosion behavior of coated materials. The electrochemical impedance spectroscopy (EIS) technique is said to be an efficient and convincing tool for assessing the corrosion behavior of coated metals [**16**]. The advantages of using EIS are the possibility of continuous monitoring of the progress of the corrosion with instantaneous corrosion rate measurement and providing information of the electrochemical degradation mechanism. The purpose of using EIS is to determine the resistance of coating towards corrosion attack since impedance is defines as the ability of an electric circuit to resist flow of electrical current.

Generally about EIS measurement, a small AC voltage is applies over a range of frequencies in order to measure the electrochemical response. The response from the electrochemical result will be interpreted in term of an electrical circuit. The equivalent circuit is to quantify the chemical and physical process involved. The circuit consists of electrical components that have the same frequency response with the electrochemical reaction. Two important components that build the circuit are capacitor and resistor. Capacitor has the same frequency response as a reaction step when ions are built on a surface. Besides, the resistor represents the charge transportation through the material.

Many equivalent circuit models that can be proposed for material with coating system applied. However, the most suitable model to describe the corrosion response for polymer coated materials is shown in figure 2.6.

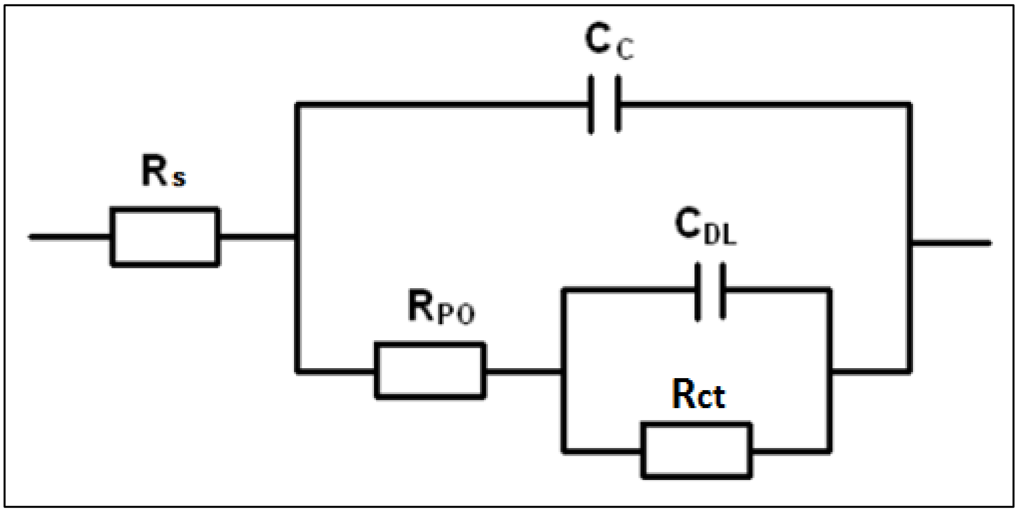


Figure 2.6: A typical equivalent circuit for coated metals [**17**]

R_s - The electrolyte resistance which is the resistance between the working electrode and the reference electrode.

R_{po} - The resistance of the transportation of charge through pores, holiday and other damage in the coating.

R_{ct} - The charge transfer resistance, associated with the kinetic of the corrosion process.

C_c - The capacitance of the polymer coating.

C_{dl} - The double layer capacitance that arise from dipole interaction on the metal surface.

C_c is used to measure the degree of degradation of the paint while R_{po} is related to the absorption of water or to the permeability of the paint. Besides, C_{dl} is the double layer capacity and can be used as a measure of the paint's loss of adhesion.

The coating sandwiched between the coated metal and the electrolyte can be represented as illustrated in figure 2.7 below:

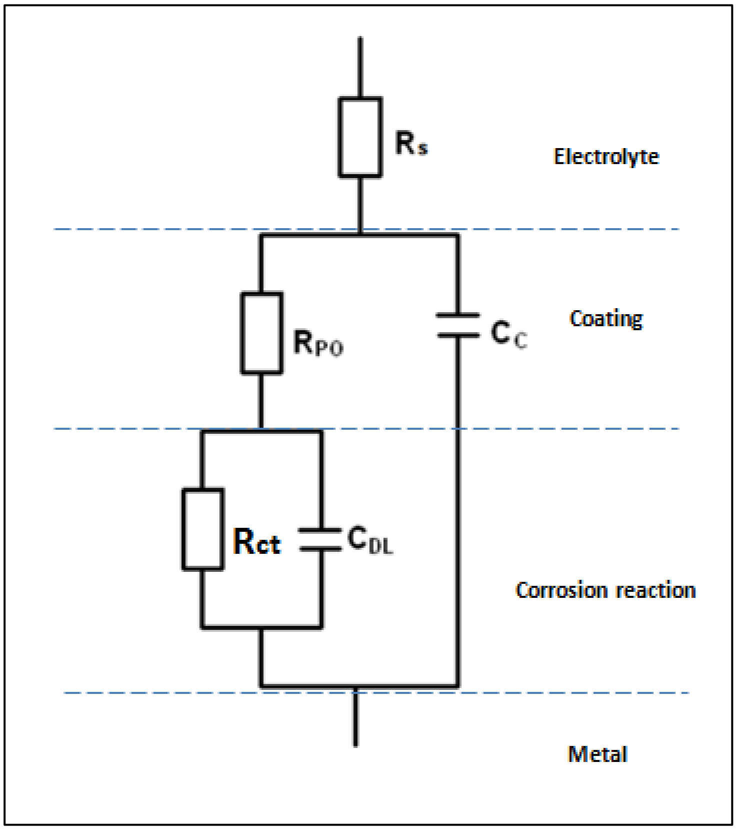


Figure 2.7: Details on equivalent circuit used to described polymer-coated metals [**18**]

Based on figure 2.7, R_{ct} is an important parameter because the value can be used to determine the corrosion rate of the metals. R_{ct} represents the value of double layer that form on the surface of the metal. R_{ct} is always inversely proportional to the corrosion current density. The higher the value of R_{ct} the lower the corrosion rate. This can be explained by the Stern-Geary Equation:

$$i_{corr} = 1/R_{ct}[\beta\alpha/2.303\ (\beta\alpha + \beta c)] \quad (2.5)$$

Where,

βα : The anodic tafel slope

βc : The cathodic tafel slope

After determined the value of R_{ct} the value of corrosion can also be determined by using the Faraday's Law as shown below:

$$CR = [(i_{corr}A)/ nF\rho] \tag{2.6}$$

Where,

n: Number of electron

A: Atomic weight (g/mol)

ρ: Density of the specimens

F: Faraday's constant

CHAPTER 3

METHODOLOGY

3.1 Overall Project Flow

From Figure 3.1, it shows the project flow chart where research is done based on books, journal and technical papers specifically on corrosion of carbon steel in soil environment, evaluation of coating performance, and EIS technique.

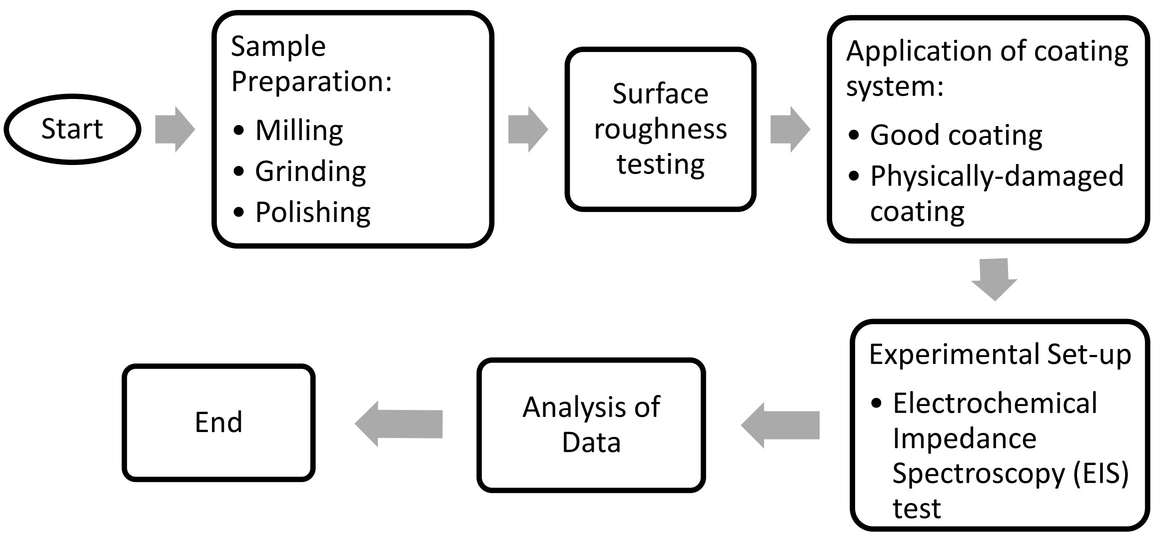


Figure 3.1: Project flow chart

3.2 Project Activities

Simulation of Pipe Samples

The sample is made from X65 carbon steel that has been used for pipeline. It undergoes milling process before a sample of 1cm × 1cm is obtained. The sample is a combination of carbon steel welded to copper wire by conductive silver paste and mounted in hard, cold-curing epoxy resin as figure 3.2. The author has prepared 12 samples from X65 carbon steel material.

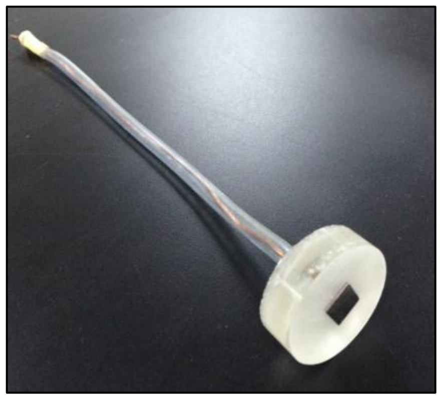


Figure 3.2: Pipe sample

Continuity Testing

The continuity of the sample is tested using Multitester. A small voltage is applied across the chosen path. The purpose of continuity test is to ensure the flow of current through the sample and copper wire after soldering process is carried out. If the current flow across the path, it showed that the soldering between cooper wire and carbon steel is good and connected.

Surface Grinding

The surface grinding was done on samples in order to obtain a smooth and flat surface before they proceed to sand blasting process. Besides, the other purpose of surface grinding is to clean sample surface from dirt and rust. The author used grinding paper with grade 60, 180, 240 and 320 in order to grind the samples.

Figure 3.3: Surface grinding machine

Sand Blasting

The purpose of sand blasting process is to clean the surface of the samples from any contamination. According to BS 4232 standard, the minimum requirement for epoxide and vinyl resin paint is second quality level which is Sa 2.5 (near-white finish).

Figure 3.4: Sand blasting machine

Surface Roughness Testing

After the samples were sand blast, the average roughness of samples is measured using profilometer. Profilometer is a measuring instrument used to measure a surface's profile in order to quantify its roughness. The ideal surface preparation for spray painting should have roughness average, Ra of 18.25μm [**18**].

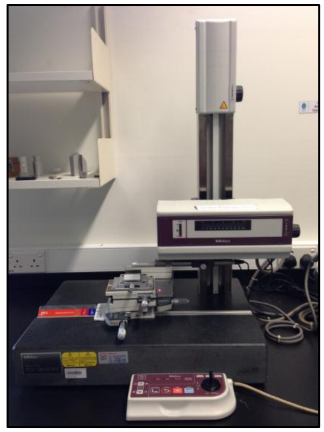


Figure 3.5: Profilometer

The author has done the roughness testing to the sample using profilometer machine and the result is obtained as below:

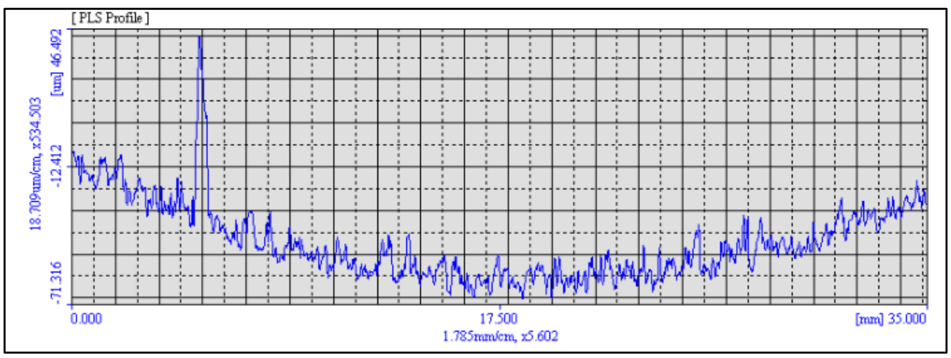


Figure 3.6: Surface roughness graph

Table 3.1: Surface roughness result

Parameter	Result	Judgment	Error Besides Pe...
Ra	12.507um	X	12.507um
Rz	51.253um	X	51.253um

The result of roughness average (Ra) of the samples is about 12.507 which are closed to the ideal surface preparation. Thus, the surface roughness of samples is acceptable.

Coating System

The type of coatings that have been used for the project is polyamine cured epoxy. This coating is manufactured by Jotun Company. The coating was applied to the carbon steel using airless spray gun. The thickness of coatings was set according to the manufacturer specification as shown in the table 3.2

(i) Polyamine cured epoxy (Jotamastic 87)

Table 3.2: Painting specification

	Minimum	Maximum	Typical
Film thickness, dry (μm)	150	300	200
Film thickness, wet (μm)	180	365	245

For physically-damaged coating, standard test for cathodic disbonding of pipeline coating (ASTM G8) was used as reference. Some intentional coating flaws were made by stripping the coating layer.

Electrolyte

In order to study the corrosivity of soil environment by electrochemical method, simulated soil solution is frequently used due to their reproducibility in laboratory and easy preparation [**9**]. For this project simulated soil solution (NS4) is used. In order to achieve an anaerobic condition, the NS4 solution is purged by bubbling 100% N_2. The purging gas is maintained at a positive pressure over the test solution throughout the entire test period. The composition of NS4 solution is stated in table 3.3.

Table 3.3: Composition of NS4 solution [**2**]

Reagents	Composition (g/L)
KCL	0.122
NaHCO3	0.483
CaCl2.2H2O	0.181
MgSO4.7H2O	0.131

The pH value of the NS4 is approximately 7.97.

EIS measurement

EIS measurements were carried out by using three-electrode electrochemical cell system; X65 carbon steel samples (WE), a reference electrode and a counter electrode. The cell was filled with simulated soil solution (NS4). The frequency of the EIS measurement was ranged from 0.01 Hz to 100 kHz with an applied AC perturbation of 10 mV.

3.3 Test Parameters

In order to carry out EIS test, some parameters have to be considered based on the literature review in order to simulate the original condition of the soil environment. Table 3.4 below shows the test parameters that are required.

Table 3.4: Test Matrix

Test Matrix	
Pressure (bar)	1
Temperature (^oC)	Room Temperature
Material	X65 Carbon Steel
Electrolyte	Simulated soil solution (NS4) + HCl
pH	3.3

3.4 Test Setup

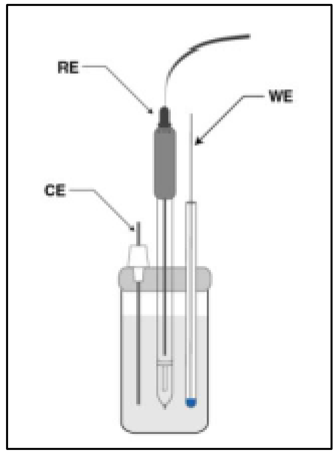


Figure 3.7: EIS setup

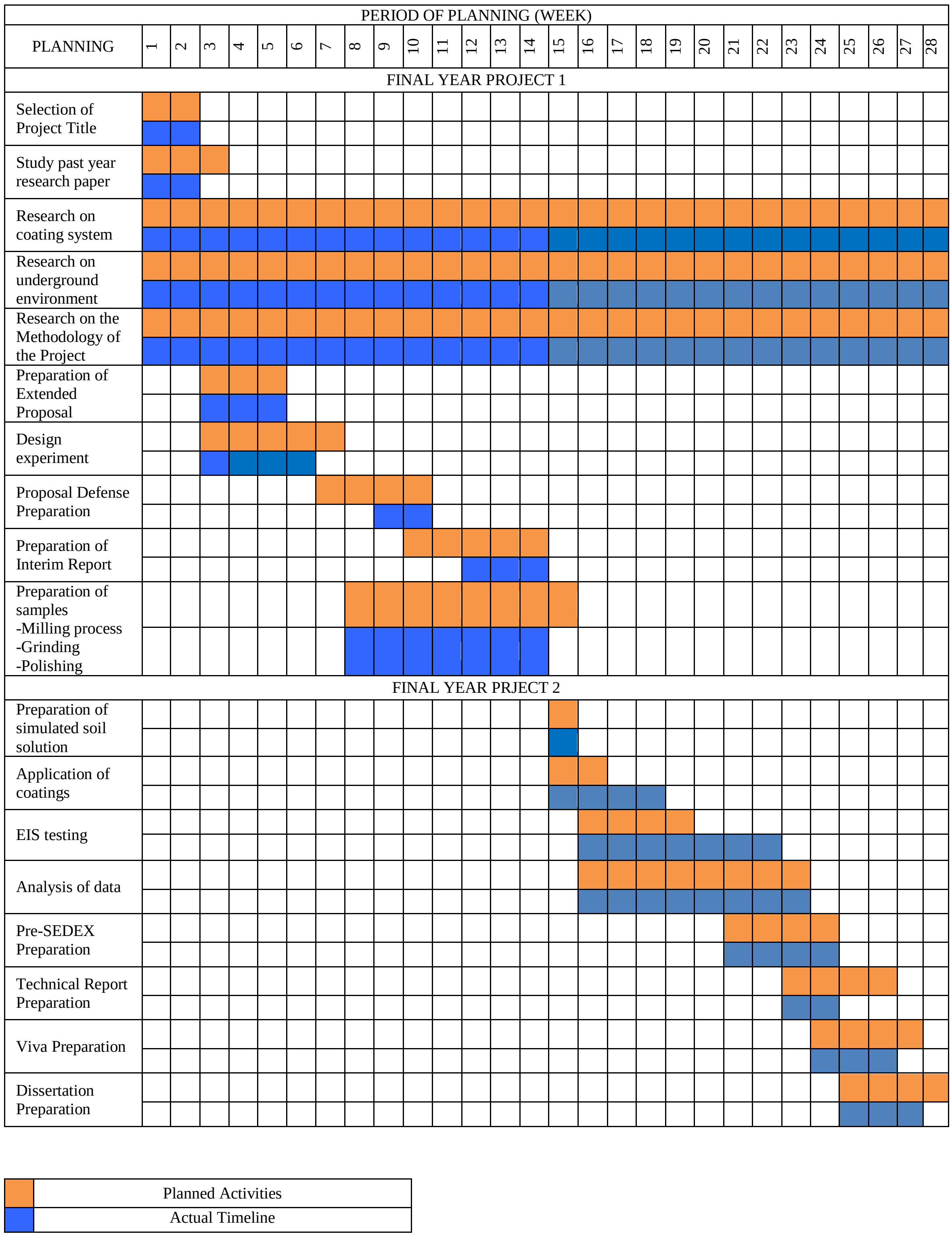
1. Equip a clean electrochemical cell with a RE reference electrode and a CE/ RE auxiliary/ counter electrode.
2. Carefully mount the sample WE working electrode in the cell as well.
3. Fill the electrochemical cell with NS4+HCl solution. Make sure all the electrodes are immersed in the solution.
4. Connect the cell with the potentiostat.
5. Adjust the experiment settings to match the required test parameters.
6. Click on the PERFORM button to initiate the experiment.
7. Let the experiment running for 24 hours to generate result depend on the ability of samples.

3.5 Key Project Milestone

Table 3.5: Key milestone

Activity	Week
Selection project title	2
Extended proposal submission	6
Design the experiment	7
Proposal defense	10
Preparation of samples	14
Preparation of simulated soil solution	15
EIS testing	22
Data analysis	23
Technical paper submission	25
Viva	26
Final dissertation submission	28

3.6 Gantt Chart



3.7 Tools / Method

The methods that were used in this project are milling, surface grinding, sand blasting, spray painting, surface roughness testing, and electrochemical impedance spectroscopy testing.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Evaluation of Coating Performance

Electrochemical impedance spectroscopy analysis of the polyamine cured epoxy coating system obtained during exposure to NS4+HCl solution was performed on the basis of Nyquist plots and Bode plots. The electrochemical elements that related in corrosion process were obtained based on the proposed equivalent circuit. The examples of electrochemical elements are coating resistance, coating capacitance, charge transfer resistance, and double layer capacitance.

4.1.1 Good Coating in Simulated Soil Solution (Baseline measurement)

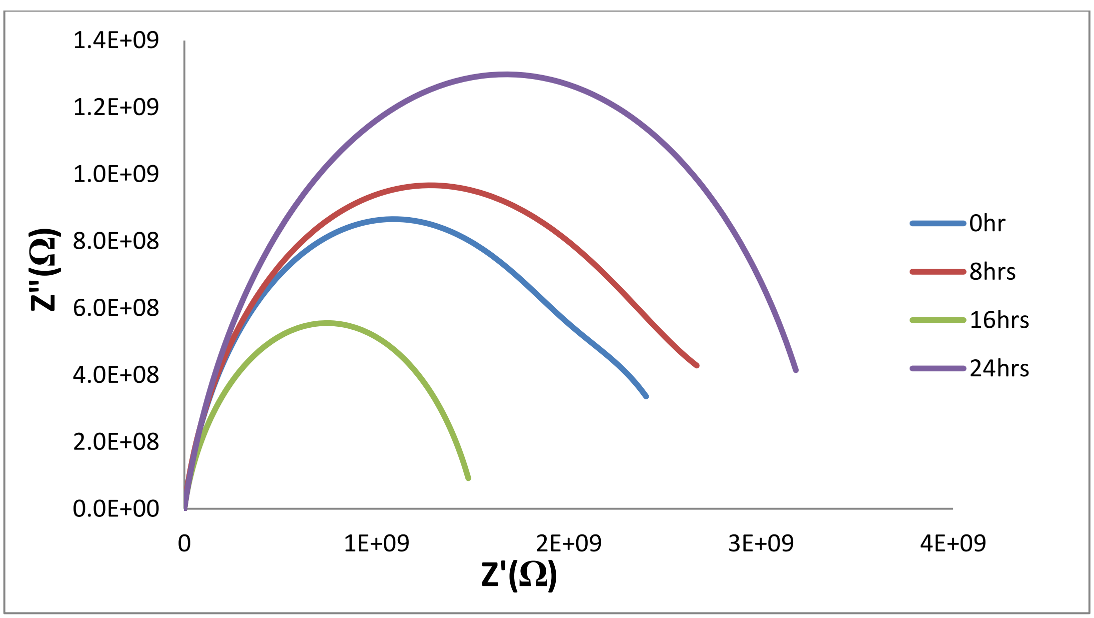


Figure 4.1: Nyquist plots for good coating sample in NS4+HCl.

Figure 4.1 shows the Nyquist plots of good polyamine cured epoxy coating sample at initial time until 24 hours of immersion in NS4+HCl solution. From the figure, it shows that value of impedance is very high after 24 hours of immersion.

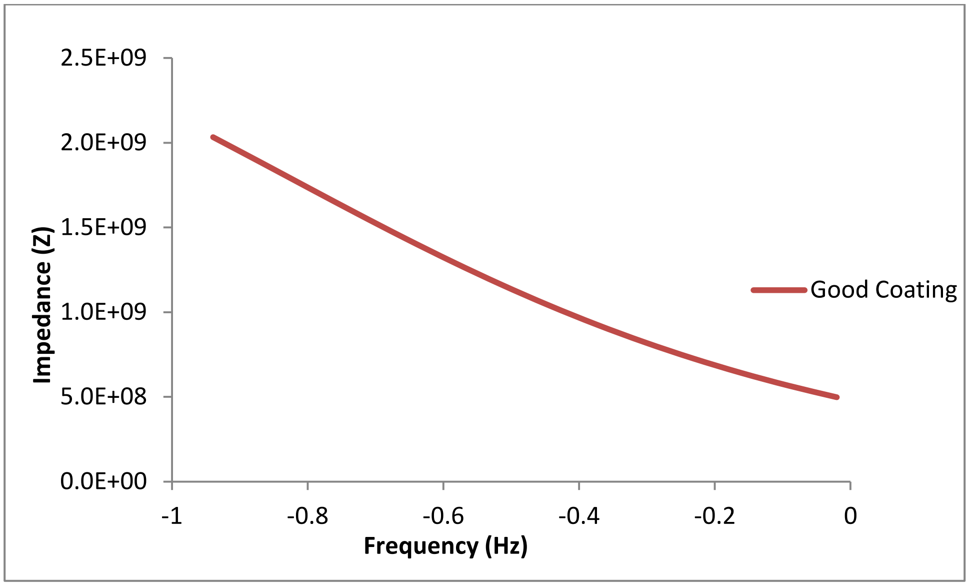


Figure 4.2: Bode plots for good coating sample in NS4+HCl.

Figure 4.2 shows the Bode plots of good polyamine cured epoxy coating sample at 24 hours of immersion in NS4+HCl solution. The impedance value was taken at low frequency domain. From the figure, it shows that the impedance value is very high at low frequency. It indicates that the coating has very high resistance against corrosion.

4.1.2 Physically-Damaged Coating in Simulated Soil Solution

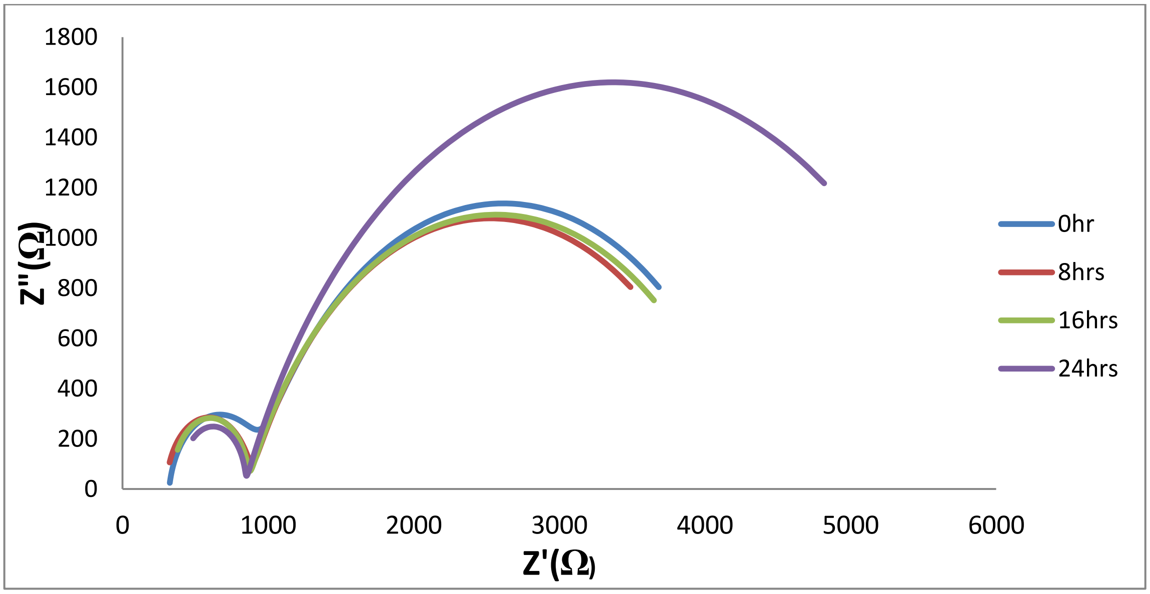


Figure 4.3: Nyquist plots for physically-damaged coating sample in NS4+HCl.

Figure 4.3 shows the Nyquist plot of physically-damaged polyamine cured epoxy coating in NS4+HCL solution. Two semicircles were seen on fully developed plot. The two semicircles represent the coating and the double layer developed on the substrate beneath the coating.

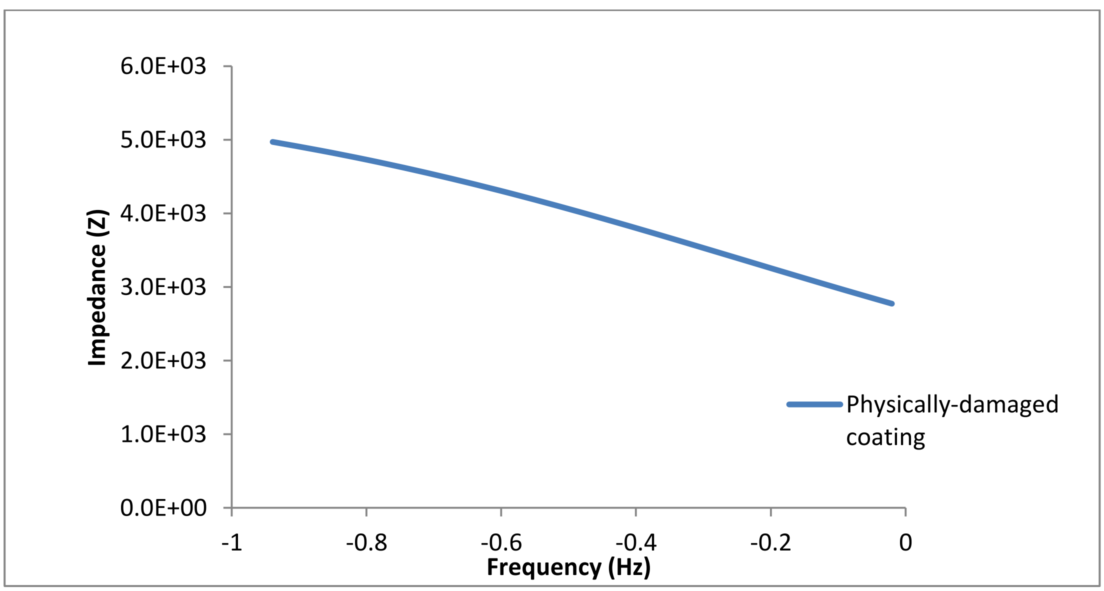


Figure 4.4: Bode plots for physically-damaged coating sample in NS4+HCl.

Figure 4.4 shows the Bode plot of physically-damaged polyamine cured epoxy coating sample at 24 hours of immersion in NS4+HCl solution. The impedance value was taken at low frequency domain. The value of the impedance at is significantly lower compared to the good coating of polyamine cured epoxy.

4.1.3 Discussion

Based on the Bode plots from figure 4.2 and 4.4, the damage coating samples shows low value of impedance compare to good coating. The results show that the damaged coating has reducing the strength of bonding between the coating particles. It means the pore resistance of the coating is weak and water can easily penetrate through the coating thus lead to rusting on metal.

In order to analyze the EIS data in detail, an equivalent circuit can be proposed. Some consideration must be taken in proposing the equivalent circuit. The first thing to be considered is the Nyquist diagram; two semicircles appear in fully developed plot. Further, in coated metal samples, the high frequency interval is usually related to dielectric properties of organic coatings, while the low frequency range corresponds to the metal response during corrosion process [**17**]. Based on these considerations, the equivalent circuit that represents these types of electrochemical behaviors is shown in figure 4.5.

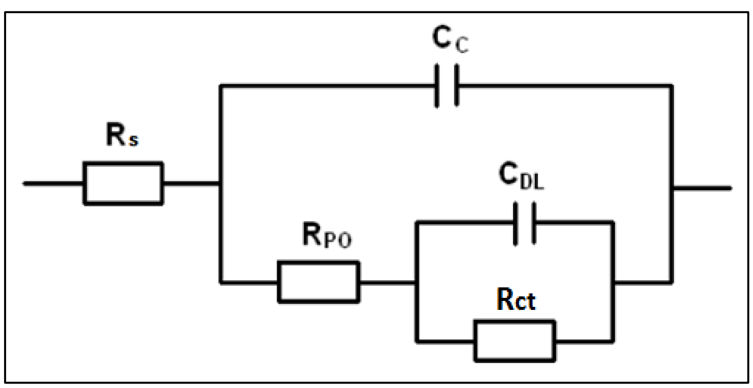


Figure 4.5: Equivalent circuit to simulate the impedance test.

The dielectric properties values for the above equivalent circuit were obtained by using Autolab. Figure 4.6 and 4.7 show the equivalent circuit with dielectric values for 24 hours of immersion.

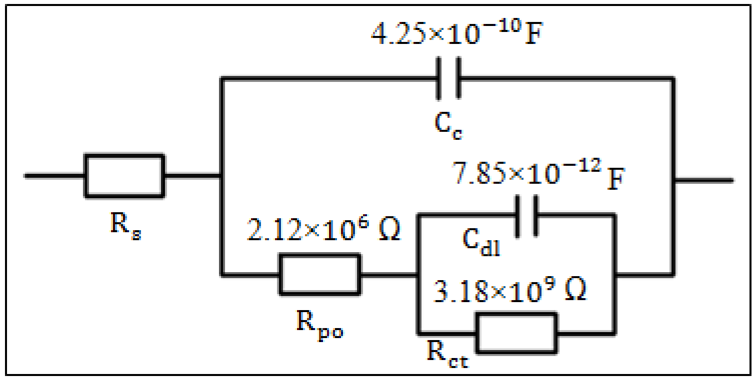


Figure 4.6: Dielectric values of good coating at 24 hours of immersion.

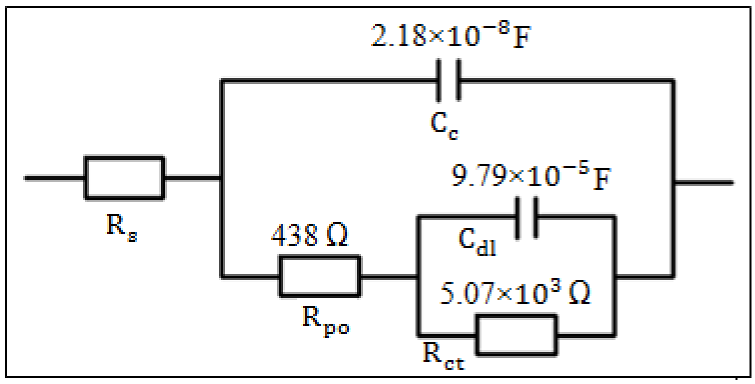


Figure 4.7: Dielectric values of damaged coating at 24 hours of immersion.

All the values for every immersion time are summarized in Table 4.1.

Table 4.1: Dielectric values obtained by simulation of the result in Fig. 4.1 and 4.3

Samples	Time (hours)	R_{po} (Ω)	C_c	R_{ct} (Ω)	C_{dl}
Good coating	0	2.11×10^{7}	3.11×10^{-10}	2.40×10^{9}	1.25×10^{-8}
	8	5.48×10^{6}	2.87×10^{-10}	2.67×10^{9}	5.52×10^{-10}
	16	4.57×10^{6}	8.55×10^{-11}	1.48×10^{9}	3.13×10^{-10}
	24	2.12×10^{6}	4.25×10^{-10}	3.18×10^{9}	7.85×10^{-12}
Physically-damaged coating	0	649	1.36×10^{-6}	3.32×10^{3}	8.08×10^{-5}
	8	576	1.35×10^{-7}	3.31×10^{3}	9.22×10^{-5}
	16	519	4.41×10^{-8}	3.42×10^{3}	9.91×10^{-5}
	24	438	2.18×10^{-8}	5.07×10^{3}	9.79×10^{-5}

Some criteria for the evaluation of coating performance have been reported in some studies on the dielectric properties values of the equivalent circuit. It is proposed that a coating system with good performance against corrosion show high values of R_{po} and R_{ct} and low values of C_c and C_{dl}. Besides, the values of R_{po} lower than 10^6 Ωcm^2 reveal that coatings present poor behavior as metal protection [**17**].

Based on the table 4.1, the value of R_{po} for good coating is higher than 10^6 Ωcm^2. It shows that good polyamine cure epoxy coating has good performance against corrosion. R_{po} is related to the absorption of water or to the permeability of the paint. High value of R_{po} indicates that less water is absorbed through the paint and corrosion process is unlikely to occur on the metal surface.

In term of capacitance, the values of Cc and Cdl for good coating are lower than the values for physically-damaged coating. Thus, the good coating has better performance in term of capacitance.

The charge transfer resistance, R_{ct} associated with the kinetic of the corrosion process and it is inversely proportional to the corrosion rate. The value of the corrosion rate can be obtained by using Stern-Gary Equation (2.5) and Faraday's Law (2.6). The overall values of corrosion rate after 24 hours of immersion for all samples are tabulated in Table 4.2.

Table 4.2: The values of i_{corr} and corrosion rate for all samples

Sample	Time (hours)	R_{ct}	i_{corr}	Corrosion rate (mm/yr)
Blank	24	547	47.62	0.55
Good coating	24	3.18×10^9	8.19×10^{-6}	0.10×10^{-6} (negligible)
Physically-damaged coating	24	5.07×10^3	5.13	0.06

Based on the table 4.2, the corrosion rate of good coating sample and physically-damaged sample are 0.10×10^{-6} mm/yr and 0.06 mm/yr respectively. The corrosion rate of good coating is negligible since the value of R_{ct} is very high. This shows that, the good coating gives the best performance in reducing the corrosion rate of the carbon steel.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

In this paper, EIS technique has been employed to monitor the behavior of good and physically-damaged polyamine cured epoxy coating performance in term of dielectric properties. From the values of the dielectric properties, the capability of the coating in reducing the corrosion rate of the carbon steel is obtained.

Based on the Bode plots, the damage coating samples shows low value of impedance compare to good coating. The results show that the damaged coating has reducing the strength of bonding between the coating particles. It means the pore resistance of the coating is weak and water can easily penetrate through the coating thus lead to rusting on metal.

In term of dielectric properties, the values of R_{po} and R_{ct} of good coating is significantly higher than the physically damaged coating while the values of Cc and Cdl of good coating is significantly lower than physically damaged coating. The high value of R_{po} indicates that less water is absorbed through the paint and corrosion process is unlikely to occur on the metal surface. Meanwhile, the high value of R_{ct} reduces the corrosion rate of metal in soil environment since R_{ct} associated with the kinetic of the corrosion process. Therefore, the good coating condition has better performance against corrosion for underground pipeline.

The corrosion rate obtained from the good coating sample is negligible since the value of charge transfer resistance is very high while the corrosion rate of physically-damaged coating sample is 0.06 mm/yr.

5.1 Recommendations

It is highly encouraged to conduct more tests against coating condition to get wider range of data to increase the data accuracy.

More studies is required against different parameters such as temperature and pH value in order to assess the performance of polyamine cured epoxy coating for underground pipeline.

Detail inspection is recommended before installing the underground pipeline as the pipe performance will eventually reduce when the damage is happened on pipe coating.

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