EXPERIMENTAL ANALYSIS OF COMPATIBILITY BETWEEN CORROSION INHIBITOR AND BIOCIDE USING ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

By

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CERTIFICATION OF APPROVAL

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September 2013

CERTIFICATION OF ORIGANALITY

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 here have not been undertaken or done by unspecified sources or persons.

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Muhammad Zul Irfan Bin Mohd Zamri

ABSTRACT

This research is focusing on the experimental study of compatibility between Corrosion Inhibitor (CI) and Biocide that include its behavior towards each other. The corrosion research involves experimental analysis and testing to provide information about the reasons for mechanisms in corrosion process and the determination of corrosion rates and the efficiency of corrosion protection. An electrochemical method, which is Electrochemical Impedance Spectroscopy (EIS) have been used to carry out corrosion testing and data interpretation since this technique offer useful information about the type of corrosion, the kinetics of the corrosion reaction and also the corrosion rate. Six series of experiments (T1,T2,T3,T4,T5A,T5B) have been conducted with different parameter to determine the compatibility effect between the chemicals. EIS analysis provides useful data in the representation of Nyquist Plot. The experimental result shows there are chemical interaction between Corrosion Inhibitor and Biocide. Corrosion Inhibitor was able to perform mitigation role and provide corrosion resistance by forming of protective film. With presence of Biocide, it gives an adverse effect to the corrosion inhibition efficiency.

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CHAPTER 1:

INTRODUCTION

1.1 Project Background

The integrity of carbon steel pipeline is dependent on efficiency of its corrosion protection methods. For controlling corrosion attack due Carbon Dioxide (CO_2) corrosion, addition of corrosion inhibitor is the essential corrosion mitigation technique that been carried out through the industries. Meanwhile, the treat from Microbiologically Influenced Corrosion (MIC) is commonly been controlled by the biocide treatment. The injection of corrosion inhibitor (CI) and biocide will build up a corrosion resistance that responsible to protect the oilfield asset of the pipeline and other equipment.

Corrosion Inhibitor (CI) and biocide are different in its functionality regardless both of the chemicals are apply to resist corrosion attack and provide corrosion control mechanism. Corrosion Inhibitor usually from the Imidazole based while biocide is from Glutaraldehyde and tetrakis hydroxymethyl phosphonium sulfate (THPS).

Most industries add and inject biocide and corrosion inhibitor at the same point and close with each other. It is often not known whether interference between biocide and corrosion inhibitor will lead to an adverse effect. The possible reaction between corrosion inhibitor and biocide can lead to degradation of the chemicals and resulting in inadequate protection of the pipeline. Hence, it is quite essential to study the possible interference between corrosion inhibitor and biocide.

1.2 Problem Statement

In order to provide corrosion resistance in oilfield pipeline both corrosion inhibitor and biocide will been used due to its different in mechanism towards corrosion mitigation. However, the major problem is about the compatibility of these chemicals since review studied had discovered that there are possible reactions between corrosion inhibitor (CI) and biocide chemically that can reduce the efficiency and performance of both chemicals. This can lead to inadequate corrosion protection to the pipeline.

1.3 Objectives

This project aims to:

a) To investigate the compatibility between corrosion inhibitor and biocide relating to the corrosion protection performance of the chemicals.

1.4 Scope of Study

The scope of this study is focused on laboratory testing. Several tests will be conducted during the experimental analysis, including corrosion tests, and compatibility tests which includes effect of corrosion inhibitor on biocide efficiency, effect biocide on corrosion inhibitor efficiency, and corrosion mechanism process.

In addition, an electrochemical method, which is Electrochemical Impedance Spectroscopy (EIS) will be applied to measure the corrosion rate of the sample and provide statistical data on the experimental analysis. The statistical data analysis performed by the EIS is to generate the resistance to polarization and its associated corrosion resistance can also reveal some interesting characteristics of an interfacial behavior.

1.5 Feasibility of Project

The project was planned and reviewed to understand the concept and mechanism of compatibility between two types of chemical that been used in corrosion mitigation method which are corrosion inhibitor and biocide. The project will focus on the experimental analysis in the laboratory by conducting few testing to investigate the efficiency of the chemicals and the reaction effect among each other. Based on the scopes of study done among the published journals and articles, it is feasible to carry out the testing within the given time of project period. Besides that, thorough analysis should be able to provide with the software and machinery aids.

CHAPTER 2:

LITERATURE REVIEW

Corrosion is defined as the destruction or loss of metal through chemical or electrochemical reaction with its surrounding environment. Carbon steel is a commonly used metal in the oilfield pipeline system that is susceptible to corrosion. Other metals in general, such as copper, stainless steel, aluminum alloys also do corrode but the process is slow.

Most corrosion control strategies involve coating the metal with thin films to prevent free oxygen and water from coming into close contact with the metal surface. This breaks the reaction cell, and reduces the corrosion rates. Several major chemical treatment methods can be used to minimize corrosion problems and to assure efficient and reliable operation.

2.1 Corrosion Inhibitor

Corrosion inhibitor is a chemical that react with a metallic surface, or the environment this surface is exposed to, giving the surface a certain level of protection and slow the corrosion process. Inhibitors often work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming a film. Inhibitors are normally distributed from a solution or dispersion. Some are included in a protective coating formulation.

Inhibitors have always been considered to be the first line of defense against corrosion. Inhibitors have been classified to several different groups that indicate their variation in chemical functionality; passivating inhibitors, cathodic inhibitors, organic inhibitors, precipitation inhibitors, volatile corrosion inhibitors.

2.1.1. Passivating inhibitors

Passivating inhibitors cause a large anodic shift of the corrosion potential, forcing the metallic surface into the passivation range. There are two types of passivating inhibitors. Oxidizing anions, such as chromate, nitrite and nitrate, that can passivate steel in the absence of oxygen and non-oxidizing ions such as phosphate, tungstate and molybdate that require the presence of oxygen to passivate steel.

2.1.2. Cathodic inhibitors

Cathodic inhibitors either slow the cathodic reaction itself or selectively precipitate on cathodic areas to increase the surface impedance and limit the diffusion of reducible species to these areas. Cathodic inhibitors can provide inhibition by oxygen scavenger or cathodic poisons. Oxygen scavengers help to inhibit corrosion by preventing the cathodic depolarization caused by oxygen while cathodic poisons are used advantageously as corrosion inhibitors by stifling the cathodic reduction processes that must balance the anodic corrosion reaction.

2.1.3. Organic inhibitors

Organic inhibitors usually designated as 'film-forming' protect the metal by forming a hydrophobic film on the metal surface. Organic inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the surface. The effectiveness of these inhibitors depends on the chemical composition, their molecular structure, and their affinities for the metal surface. Because film formation is an adsorption process, the temperature and pressure in the system are important factors.

2.1.4. Precipitation inhibitors

Precipitation inducing inhibitors are film forming compounds that have a general action over the metal surface, blocking both anodic and cathodic sites indirectly. Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal, thereby providing a protective film. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal and form a protective film.

2.1.5. Volatile corrosion inhibitors

Volatile Corrosion Inhibitors (VCI), also may called Vapor Phase Inhibitors (VPI), are compounds transported in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds, such as morpholine or hydrazine, are transported with steam to prevent corrosion in condenser tubes by neutralizing acidic carbon dioxide or by shifting surface pH towards less acidic and corrosive values.

2.2. Biocide

Many form of corrosion of metals are known based on the principal substance either oxygen, water, carbon dioxide, hydrogen sulphide and microbiologically induced caorrosion (MIC). Hydrogen Sulphide is soluble in water at pressure and temperatures common in oil field operations and when dissolved, behaves as a weak acid and usually causes pitting in a process termed as sour corrosion.

Hydrogen sulphide can be generated by sulphide reducing bacteria (SRB). These bacteria contribute to corrosion due to their ability to flourish in the absence of oxygen and their ability to change sulphide ions into hydrogen sulphide. Microbiologically induced corrosion (MIC) has been identified as one of the major causes of corrosion of oil pipelines.

Technically bocides is any substance that is poisonous to organism and can inhibit their metabolism or annihilate them. Biocides are the most common products to control the growth of micro-organisms. Three general classes of chemical biocides used in microbial control are Oxidizing biocides, Non-oxidizing biocides and Bio-dispersants.

2.2.1. Oxidizing biocides

Oxidizing biocides are powerful chemical oxidants, which kill virtually all micro-organisms, including bacteria, algae, fungi and yeasts. Common oxidizers are chlorine, chlorine dioxide, and bromine, ozone, and organo-chlorine slow release compounds.

2.2.2. Non-oxidizing biocides

Non-oxidizing biocides are organic compounds, which kill micro-organism by targeting specific element of the cell structure or its metabolic or reproductive process. Non-oxidizing biocides are not consumed as fast as the oxidizing types and remain in the system for a significant period of time until they pass out with the blowdown.

2.2.3. Bio-dispersants

Bio-dispersants do not kill organisms, they loosen microbial deposits, which can then be flushed away. They also expose new layers of microbial slime or algae to the attack of biocides. Bio-dispersants are an effective preventive measure because they make it difficult for micro-organisms to attach to equipment or pipe work surfaces to form deposits.

2.3. Compatibility of Chemicals

Based on (Mohanan, 2002), though biocides and inhibitor are used, problems have been noticed in various cooling water systems. The problems included leakage and unacceptable general corrosion rates of the system components.

Compatibility studies have been done by (Hashem, 2000) on the treatment chemicals consist of corrosion inhibitors, scale inhibitors, and biocides. A laboratory performance evaluation was conducted on four corrosion inhibitors in combination with scale inhibitors and biocides, to determine the influence of these other chemicals on the effectiveness of the corrosion inhibitor. The results indicated that in many cases there was an improvement in corrosion inhibition on addition of the scale inhibitor but there was generally a reduction in inhibition on addition of the biocide. Addition of the biocide to the corrosion inhibitor or corrosion/scale inhibitor combinations generally resulted in reduced corrosion inhibitory effect probably related to inhibition of the corrosion inhibitor’s ability to form its protective film under these conditions (Hashem, 2000). The result of combinations of corrosion inhibitor scale inhibitor and biocide are shown in figure below.

CHEMICAL INHIBITORY EFFECTS IN ZUBAIR AQUIFER WATER (RCE TEST)

Corrosion Inhibitor		Corrosion + Scale inhibitors		Corrosion inhibitor + Biocide		Corrosion + Scale inhibitors + Biocide	
Label	Inhibition Effect*	Labels	Inhibition Effect	Labels	Inhibition Effect	Labels	Inhibition Effect
C1	48%	C1 + S1	Similar to C1 alone	C1 + B1	Similar to baseline –B1 reduced C1 effect	C1 + S1 +B1	Similar to baseline – B1 reduced corrosion inhibition
C4	26%	C4 + S3	Better than C4 alone– S3 enhanced corrosion inhibition	C4 + B1	Similar to C4 alone	C4 + S3 + B1	Worse than baseline–B1 reduced corrosion inhibition
C2	66%	C2 + S2	Slightly better than C2 – S2 slightly enhanced corrosion inhibition	C2 + B1	Rises to baseline – B1 reduced C2 effect	C2 + S2 + B1	Similar to baseline – B1 reduced corrosion inhibition
C3	75%	C3 +S1	Similar to C3 alone	C3 + B1	Similar to baseline –B1 reduced C3 effect	C3 + S1 + B1	Similar to baseline – B1 reduced corrosion inhibition
		C3 + S2	Slightly worse than C3			C3 + S2 + B1	Initial reduction but rises to baseline – some reduction in corrosion inhibition due to B1
		C3 + S3	Slightly worse than C3			C3 + S3 + B1	Similar to baseline – B1 reduced corrosion inhibition

Figure 1: Result of chemicals combination

According to (Azmi. A, 2013) the continue studies have been carried out to examines corrosion inhibition using four green corrosion inhibitors in combination with three potential scale inhibitors and biocide. The different inhibitors were separately combined in order to identify synergistic effect between the different chemicals. Laboratary tests used in this study included linear polarization resistance (LPR) measurement, performance in a rotating cylinder electrode (RCE) apparatus and in high pressure stirred autoclaves (AC). The studies conclude that biocides appeared to have an antagonistic effect, preventing the corrosion inhibitor from forming its protective film. (Azmi. A, 2013) Thefore the result from autoclave evaluation were weighted more heavily when ranking the chemical combinations. Visual inspection of the electrode from the autoclave testing also showed that all the electrodes experienced etching in one from or another.

The combinations of corrosion inhibitor, scale inhibitor and biocide are shown in figure below.

RANKING OF CHEMICAL COMBINATION IN ZUBAIR AQUIFER

Rank of Chemical Combination	Chemicals in Combination	Corrosion Rate from Autoclave LPR	Corrosion Rate from Autoclave Weight Loss Data
1st	C1 + S1 + B1	8 mpy	4.8 mpy
2nd	C2 + S2 + B1	~ 20 mpy	11.2 mpy
3rd	C4 + S3 + B1	~ 30 mpy	16.9 mpy
4th	C3 + S1 + B1	Similar to blank rates of 40-60 mpy	About 30 mpy
	C3 + S2 + B1		
	C3 + S3 + B1		

Figure 2: Result of chemical combination and corrosion rate

Phosphonate compounds as the corrosion inhibitors were synthesized and its inhibition efficiency along with biocide (ammonium bromide) action on corrosion of mild steel in natural aqueous solution was investigated (Ramesh. S, 2003).

A triazole phosphonate compounds, namely, 3-benzyledene amino 1,2,4-triazole phosphonate (BATP), 3-cinnamyledene amino 1,2,4-triazole phosphonate (CATP) and 3-anisalidene amino1, 2,4-triazole phosphonate (AATP), were synthesized and its inhibition efficiency along with biocide action on corrosion of mild steel in natural aqueous solution was investigated through weight loss and electrochemical polarization techniques (Ramesh. S, 2003). The result show four different systems been made according to the chemicals used and the condition of applied chemicals.

Table 1

System	Material used	Medium	Parameters of interest
System I	BATP, CATP, AATP with Mo	lake water	Inhibition efficiency
System II	CTAB	lake water	Biocide efficiency
System III	BATP, CATP, AATP with Mo (inhibitors), CTAB (biocide)	lake water	Interference in the inhibitors and biocide (Inhibitors and biocide are added at same time)
System IV	BATP, CATP, AATP with Mo (inhibitors), CTAB (biocide)	lake water	Biocide are added first, after 24 h inhibitors were added

Figure 3: System Classification

The result of the electrochemical studies and polarization parameter of mild steel immersed in lake water for all the systems are given in figure below.

Potentiodynamic polarization parameters of mild steel in lake water with and without inhibitor and biocide (systems I–IV)

Compounds	System	OCP (mV vs. SCE)	E_{corr} (mV)	I_{corr} (mA/cm^2) $\times 10^{-3}$	Corrosion rate (mpy)	Efficiency (I.E.) (%)
Blank	–	− 690	− 695	32.5	14.88	–
BATP	System I	− 720	− 734	12.0	5.49	63.07
CATP	System I	− 736	− 740	12.0	5.49	63.07
AATP	System I	− 756	− 810	4.8	2.19	85.23
BATP + Mo	System I	− 820	− 770	7.4	3.38	77.23
CATP + Mo	System I	− 574	− 769	7.8	3.57	76.00
AATP + Mo	System I	− 510	− 804	4.5	2.05	86.15
BATP + Mo + CTAB	System III	− 733	− 764	5.3	2.42	83.69
CATP + Mo + CTAB	System III	− 723	− 745	5.0	2.28	84.61
AATP + Mo + CTAB	System III	− 665	− 654	2.1	0.99	93.53
CTAB + BATP + Mo	System IV	− 733	− 727	8.5	3.89	73.84
CTAB + CATP + Mo	System IV	− 685	− 680	8.4	3.84	74.15
CTAB + AATP + Mo	System IV	− 700	− 682	2.8	1.32	91.38

Figure 4: Result of electrochemical and polarization parameter

2.4. Electrochemical Impedance Spectroscopy (EIS)

EIS has been successfully applied to the study of corrosion systems for thirty years and been proven to be a powerful and accurate method for measuring corrosion rates. But in order to access the charge transfer resistance or polarization resistance that is proportional to the corrosion rate at the monitored interface, EIS results have to be interpreted with the help of a model of the interface.

An important advantage of EIS over other laboratory techniques is the possibility of using very small amplitude signals without significantly disturbing the properties being measured. To make an EIS measurement, a small amplitude signal, usually a voltage between 5 to 50 mV, is applied to a specimen over a range of frequencies of 0.001 Hz to 100,000 Hz. The EIS instrument records the real (resistance) and imaginary (capacitance) components of the impedance response of the system. Depending upon the shape of the EIS spectrum, a circuit model or circuit description code and initial circuit parameters are assumed and input by the operator.

(Salam. S, 2006) through their study on corrosion behavior shows that electrochemical Impedance Spectroscopy (EIS) is a powerful, rapid and accurate non-destructive method for the evaluation of wide range of materials. It can also provide detailed information of the systems under examination; parameters such as corrosion rate, electrochemical mechanisms and reaction kinetics, detection of localized corrosion, can all be determined from these data. In this work, the corrosion behavior of some austenitic stainless steels was studied in 3.5%NaCl. The effect of Nb content and cold deformation on the corrosion resistance was investigated.

CHAPTER 3:

METHODOLOGY

3.1. Flow Chart of Project Work

Figure shows the summary of work flow that will be conducted throughout the project.

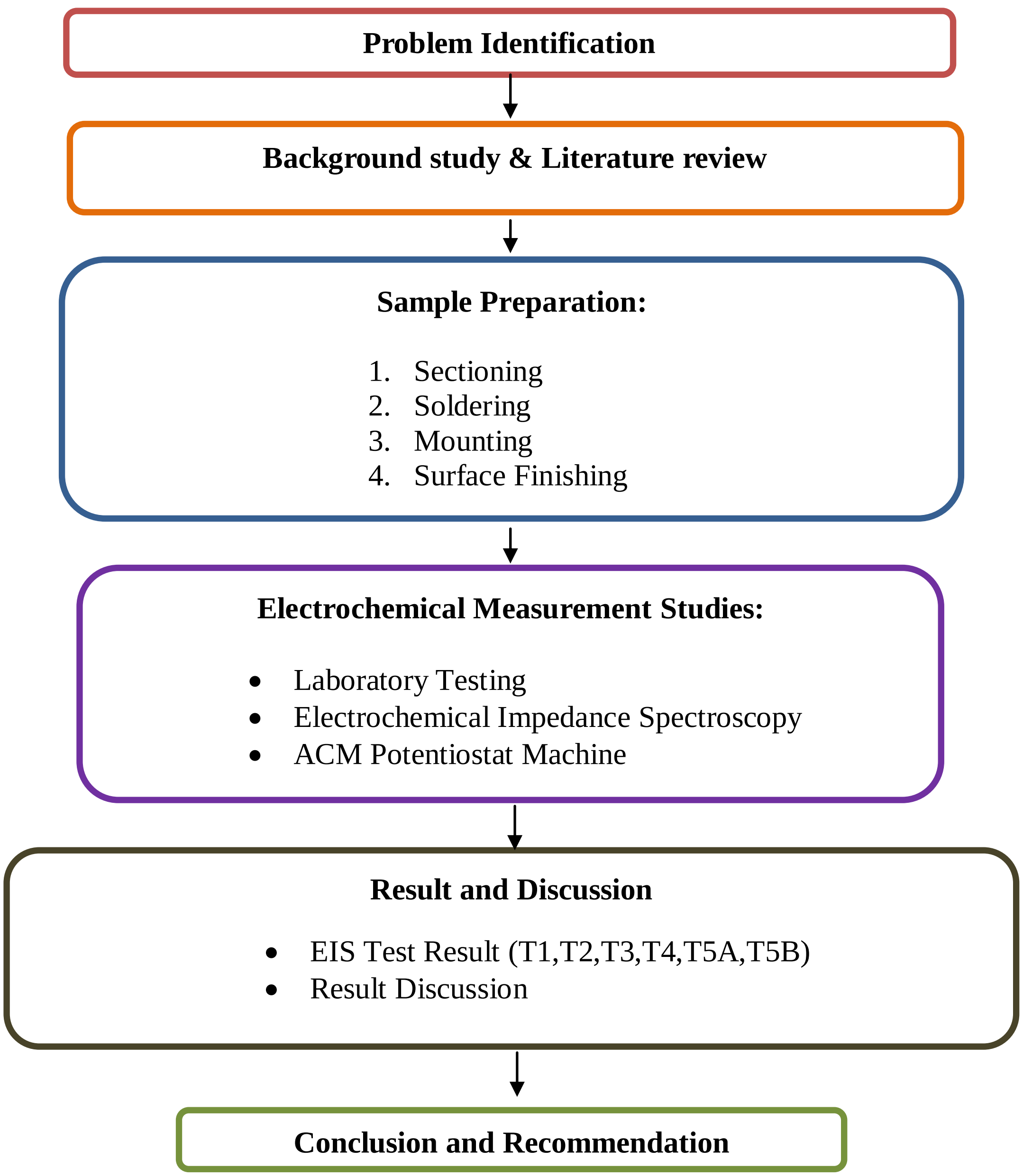

Figure 5: Project Methodology

3.2. Project Activities

3.2.1. Sample Preparation

1. **Sectioning:** Removal of a representative sample from the parent piece by removing a suitably sized specimen at desired location and orientation. The average dimension of each sectioned sample was 1cm length, 1cm width and 0.5cm thickness.

Figure 6: Precision Saw Machine

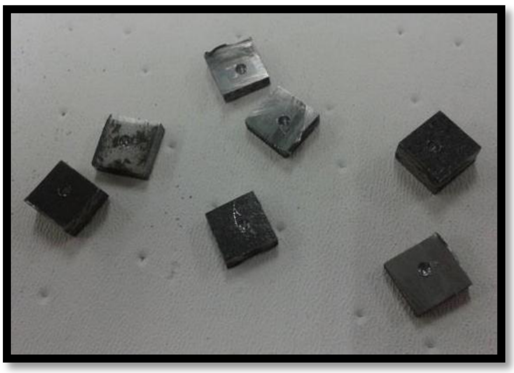

Figure 7: Carbon Steel Samples

2. **Soldering:** Metal joining process in which filler metal is melted to fill the gap between 2 metal pieces, the filler metal having a lower melting point than the work piece.

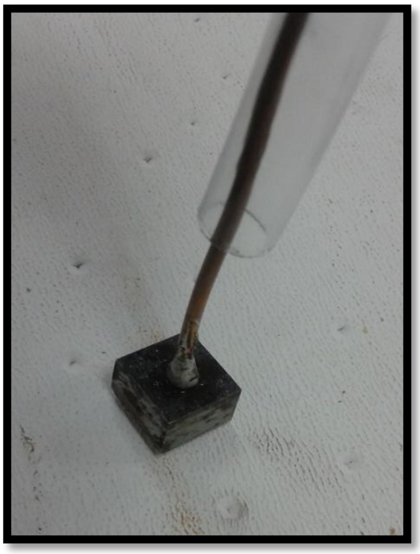

Figure 8: Soldered Sample

3. **Mounting:** Mounting of metallographic specimens for convenience in handling specimens from difficult shapes or sizes during the subsequent steps of metallographic preparation and examination.

Cold mounting parameters:

- Resin: 5 parts
- Hardener: 1 part
- Hardening period: 40 minutes

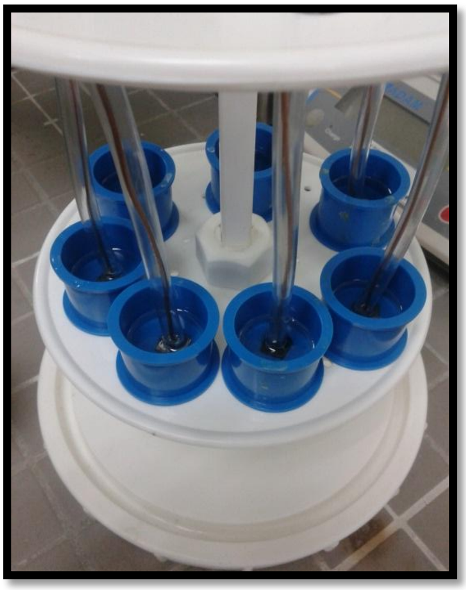

Figure 9: Cold Mounting Process

4. **Surface Finishing:** Surface finish conducted by process of grinding and polishing to produce very fine surface that we call as 'mirror surface'. Grinding been divided into two parts. Coarse grinding produces an initial flat surface and fine grinding remove the zone of deformation due to sectioning and coarse grinding. The depths of deformation during the grinding and polishing stage can be limited by proper abrasive size sequencing.

Figure 10: Grinding of Sample

The samples underwent grinding steps as shown in the Table 1:

Table 1: Grit Size and Wheel Speed for Grinding

SiC Grit Size	**Wheel Speed (RPM)**
120	100 - 250
320	100 - 250
400	100 - 250
600	100 - 250
800	100 - 250
1200	100 - 250

3.2.2. Electrochemical Measurement

Electrochemistry techniques will be applied for studies, monitoring, and prediction of metallic corrosion. EIS measurements can be a very rich source of information for a system where corrosion is a problem which is, type of corrosion, the kinetics of the corrosion reaction, and corrosion rate. The statistical data analysis performed by the EIS data points to generate the resistance to polarization and its associated corrosion resistance are interperate in the nyquist plot and bode plot.

3.3. Gantt Chart and Key Milestone

Table 2: Project Gantt Chart and Milestone

Activities		FYP 1															FYP 2													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	Topic Selection																													
2.	Preliminary research and feasibility																													
3.	Literature review studies																													
4.	Determine the project methodology																													
5.	Proposal Defense																													
6.	Literature Review Enrichment																													
7.	Interim report preparation																													
8.	Material gathering																													
9.	Sample preparation																													
10.	Laboratory testing																													
11.	Electrochemical studies																													
12.	Material and surface characterization																													
13.	Data and result analysis																													
14.	Result validation																													
15.	Thesis preparation																													

FYP 2 Key Milestone

Activities	FYP 2 Schedule													
	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14
Material Gathering														
Sample Preparation														
Laboratory Testing (EIS)														
Material and Surface Characterization														
Data and Result Analysis														
Result Validation														
Thesis Write-up														

Completed Work

Test Matrix and Experimental Progress

Table 3: Test Matrix

TEST	CONDITION	TEMPERATURE	CORROSION INHIBITOR	BIOCIDE	TEST STATUS
1	CO_2 Pressure -1 BAR	60^{o}c	-	-	**DONE**
2	CO_2 Pressure -1 BAR	60^{o}c	Optimum dosage	-	**DONE**
3	CO_2 Pressure -1 BAR	60^{o}c	Half of optimized dosage	-	**DONE**
4	CO_2 Pressure -1 BAR	60^{o}c	-	500ppm	**DONE**
5A	CO_2 Pressure -1 BAR (Inject Biocide First)	60^{o}c	Optimum dosage up to 500ppm	500ppm	**DONE**
5B	CO_2 Pressure -1 BAR (Inject CI first)	60^{o}c	Optimum dosage up to 500ppm	500ppm	**DONE**

3.4. Experimental Setup

Electrochemical Impedance Spectroscopy Test had been carried out to analyze the corrosion mechanism on the carbon steel sample. Electrochemical testing been conducted through set up of experimental apparatus as follow:

Glass cell

The basic solution is prepared by dissolving 10 gram of sodium chloride (NaCl) into 1 liter of distilled water and purged for one hour with carbon dioxide (CO_2). The solution then stirred until the sodium chloride completely dissolved. Temperature in the glass cell have been set up at 60’C for all the testing that been carried out.

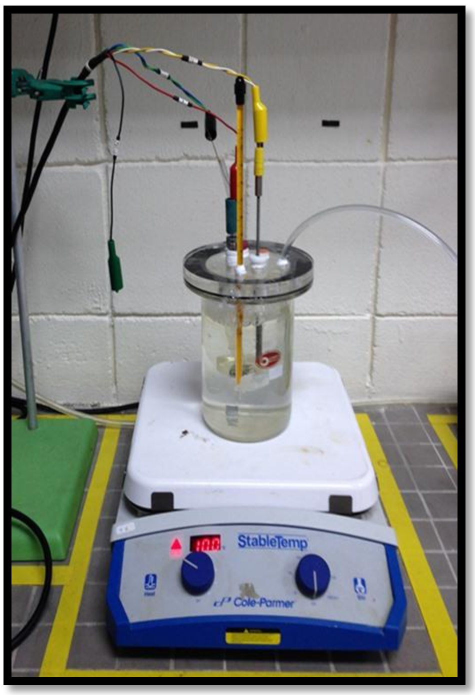

Figure 11: Glass Cell and Experimental Setup

Electrode

Three type of electrode that connected and immersed into the glass cell which are working electrode, auxiliary electrode and reference electrode. The carbon steel sample is act as working electrode while Silver Chloride (AgCl) is used as the reference electrode and stainless steel electrode is used as auxiliary electrode.

ACM Potentiostat Instrument

Testing is set with specific parameter in the ACM Potentiostat Analyzer:

- AC Impedance
- Current amplitude at 10 Mv
- Frequency Range from 5mHz – 100kHz

Figure 12: ACM Instrument Potentiostat

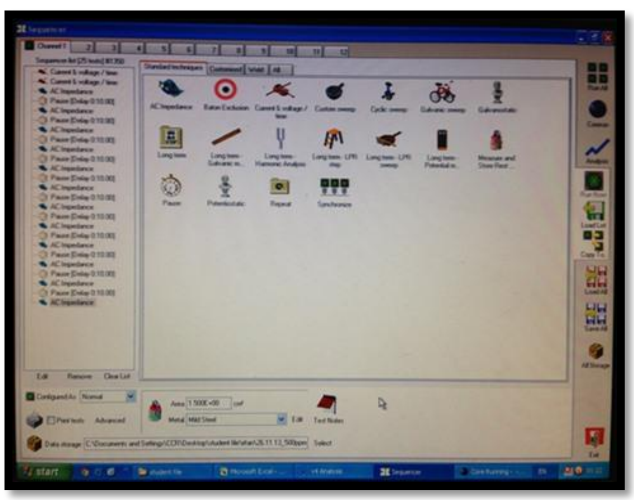

Figure 13: Monitor Display of ACM Potentiostat Software

CHAPTER 4:

RESULT AND DISCUSSION

4.1 Experimental Result

Electrochemical Impedance Spectroscopy Test have been carried out in six series of experiment namely as Test 1,Test 2, Test 3, Test 4, Test 5A, and Test 5B. All the results were tabulated in Nyquist Plot as the function of frequency response to indicate corrosion process and mechanism.

A sinusoidal voltage signal of 10mV was applied thus both real and imaginary part of the impedance were determined and plotted as Nyquist Plot. From nyquist plot it shown three sequences data indicate the time interval between each measurement which been taken at the beginning of the experiment (Sequence 1), middle of the experiment (Sequence 2) and at the end of the experiment (Sequence 3).

Frequency response reaches its highest limit at the left end of the semicircle and the lowest limit at the right side of semicircle. Presence of the semicircle shape of spectra in the nyquist plot determines the indication of time constant and reaction process that occur.

Test 1: Blank Test

(Corrosion Inhibitor:0ppm Biocide: 0ppm)

Blank Test does not involve any injection of corrosion inhibitor or biocide in the glass cell, act as a parameter for comparison condition with the other testing that been conducted. A carbon steel sample as the working electrode was immersed in the solution and the test was conduct for the period of 24 hours. The plotted data result was given as below:

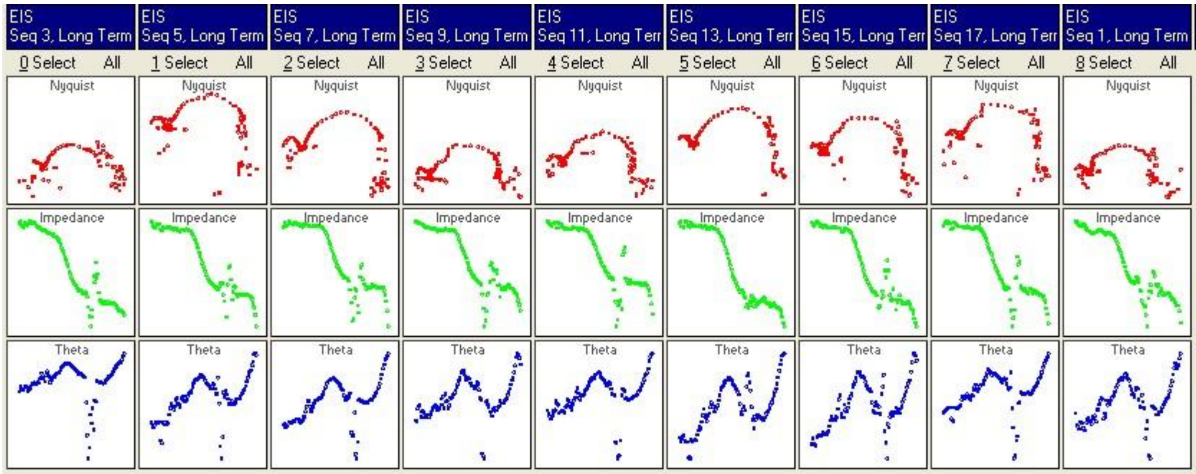

Figure 14: EIS Plotted Data for all sequences of Test 1

<u>Nyquist Plot:</u>

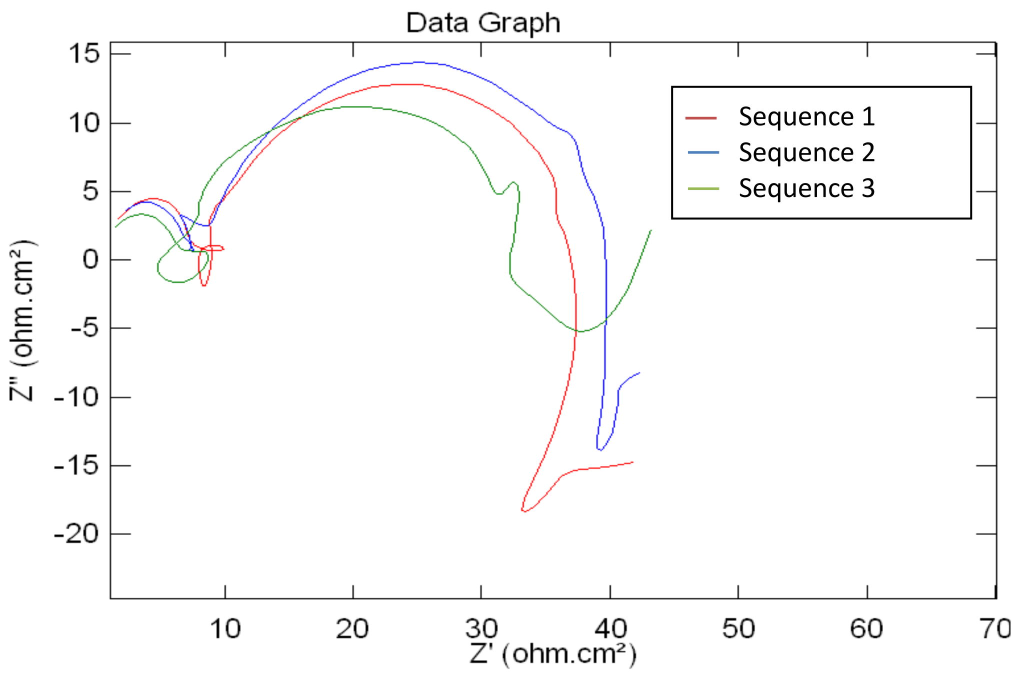

Figure 15: Nyquist Plot Curve of three sequences for Test 1

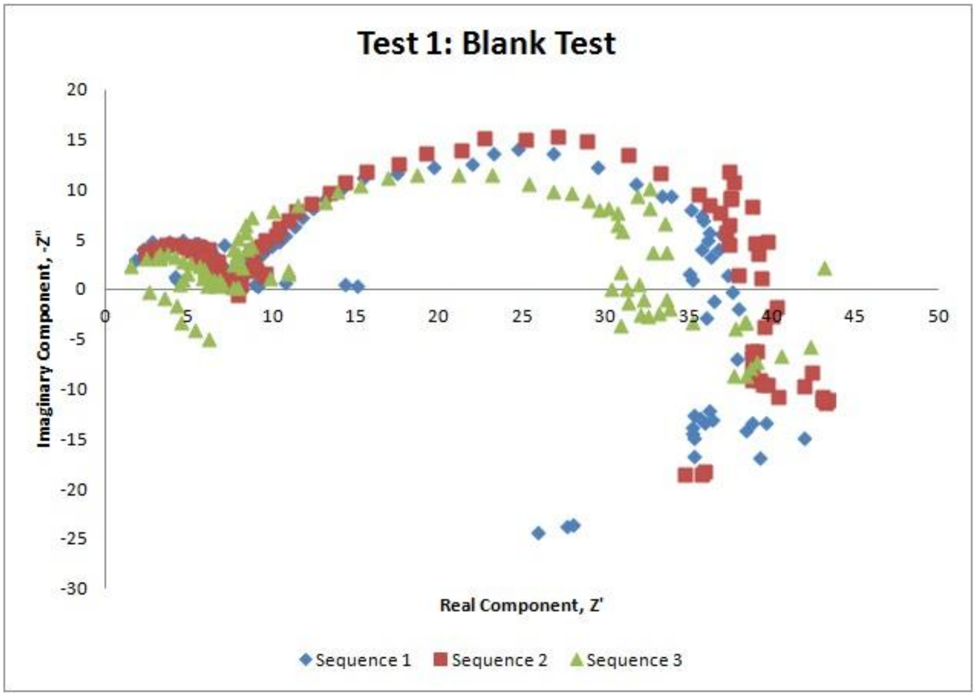

Figure 16: Graph of Nyquist Plot Tabulation Data for Test 1

Figure 15 and Figure 16 show there were two semicircles responses produced through out the frequency range. Two semicircles plotted with an indication of the electrochemical process of interaction between metal surface and solution. A time constant (semicircle) was observed in the low frequency region (right side) which corresponded to charge transfer for the normal corrosion process. Another semicircle that represents time constant was found at the low frequency region (left side) which is related to corrosion product film formation.The plotted data shows that in absence of any corrosion inhibitor or biocide the metal sample was exposed to corrosion process in every sequence of time interval.

As the period of testing longer it was observed there was no changes in the shape of the semicircle during the entire exposure time which indicate the corrosion mechanism do not change significantly.

Comparison in the impedance value between three different sequences which not give a constant changes as the highest at Sequence 2 and lowest at Sequence 3 indicate that the surface is not stable in the solution.

Test 2: Corrosion Inhibitor Test Optimum Dosage

(Corrosion Inhibitor:25ppm Biocide: 0ppm)

Test 2 involves the injection of Corrosion Inhibitor with amount of 25ppm into the glass cell solution and with absence of Biocide. The inhibitor injected at the beginning of the experiment at 0 hour. The plotted data result was given as below:

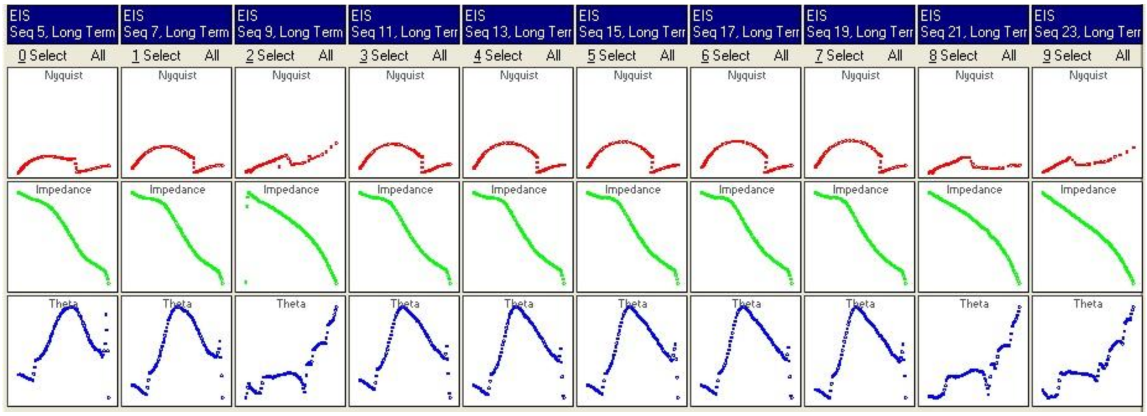

Figure 17: EIS Plotted Data for all sequences of Test 2

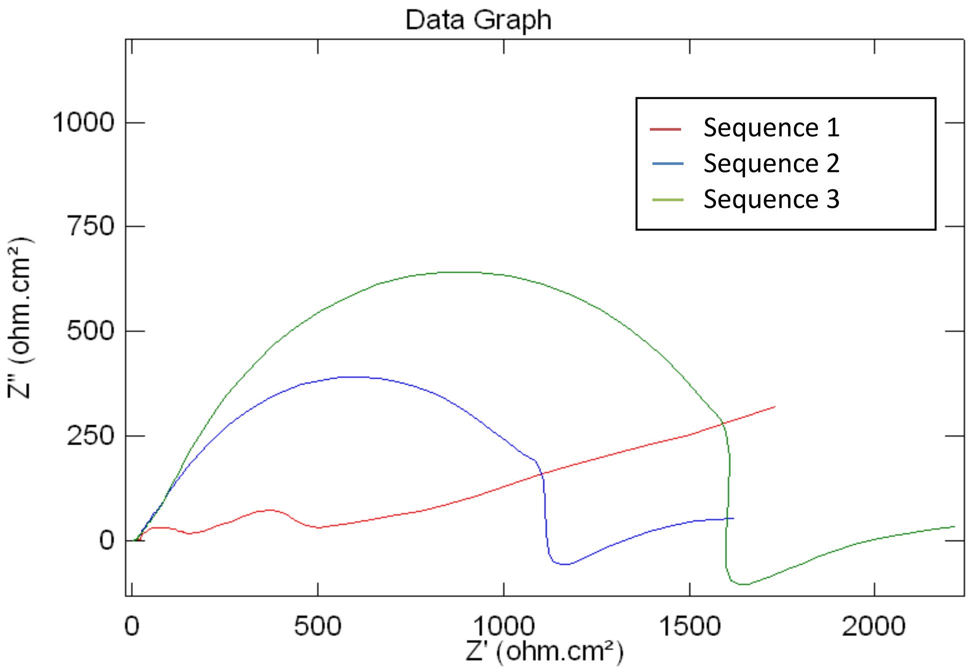

Figure 18: Nyquist Plot Curve of three sequences for Test 2

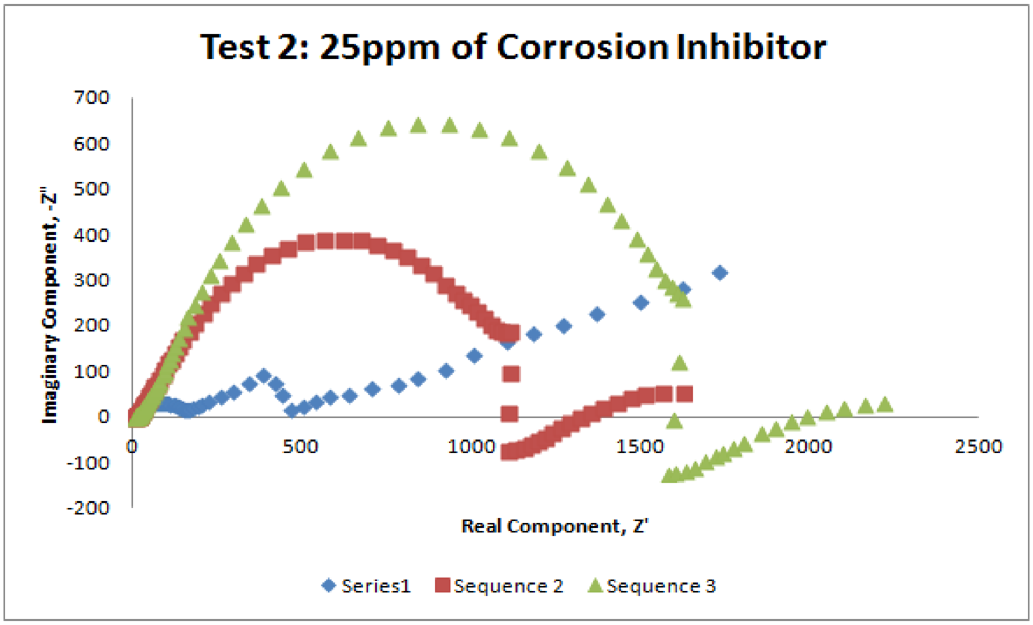

Figure 19: Graph of Nyquist Plot Tabulation Data for Test 2

Figure 18 and Figure 19 show there was a single complete semicircle responses produced at the high frequency region (left side). Single semicircle indicates that one primary reaction mechanism exists which may represent the formation of the inhibitor film. An addition of diffusion tail was found at the low frequency region for all the interval time sequences indicates an effect from the inhibitor film formed on the metal surface. The diffusion element suggests that electrochemical process by the active diffusion of corrosion products away from the metal surface by inhibitor film. The plotted data shows that in the present of corrosion inhibitor metal sample provide formation of film on the surface and as the resistance towards corrosion. As the period of testing longer it was observed that slight changes in the shape of the semicircle at the beginning of the test which indicates the changes in reaction mechanism with injection of Corrosion Inhibitor.

The impedance values between three different sequences constantly increasing indicate that the surface is stabilizing during immersion in the solution. Diameter of the semicircle spectra shape increase gradually corresponds to the increasing on the resistance value.

Test 3: Corrosion Inhibitor Test Half Optimum Dosage

(Corrosion Inhibitor:12.5ppm Biocide: 0ppm)

Test 3 involves the injection of Corrosion Inhibitor with amount of 12.5ppm which is half of the optimum dosage 25ppm into the glass cell solution and with absence of Biocide. The inhibitor injected at the beginning of the experiment at 0 hour. The plotted data result was given as below:

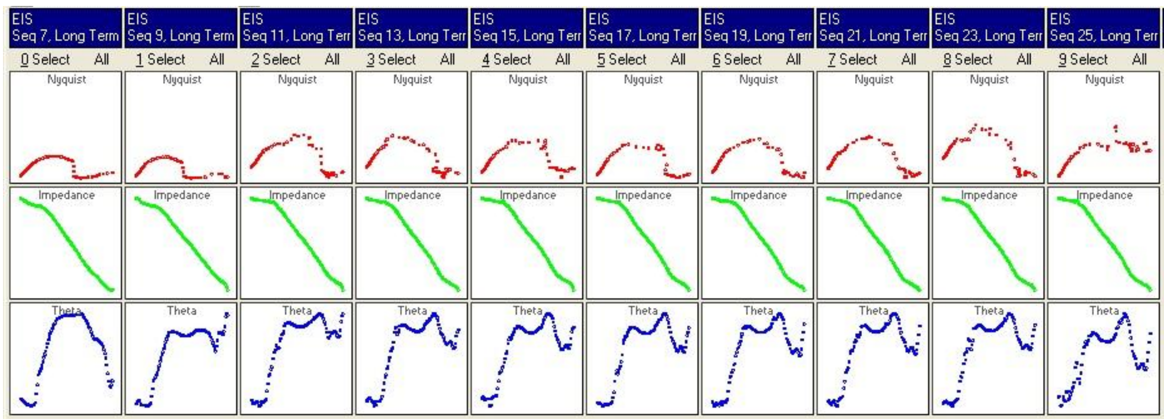

Figure 20: EIS Plotted Data for all sequences of Test 3

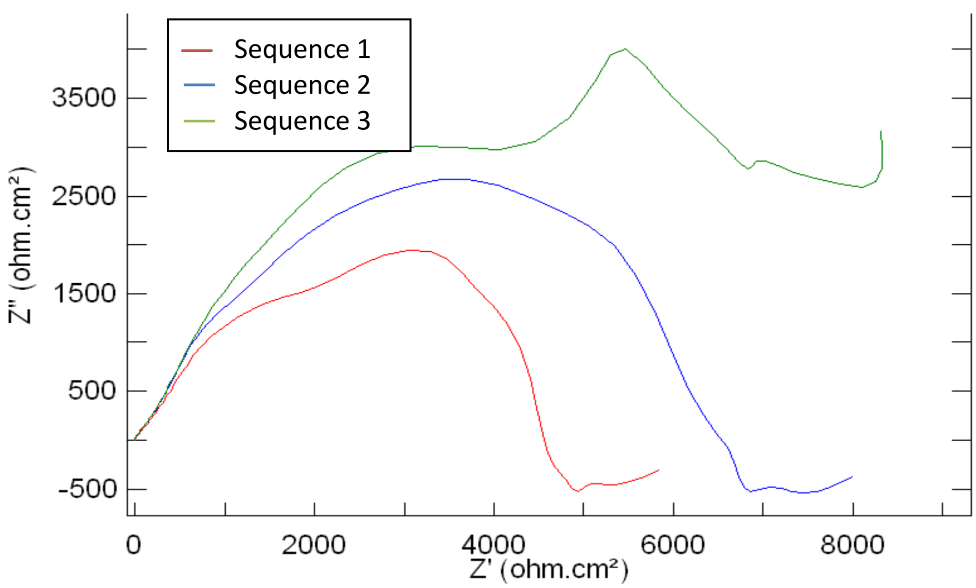

Figure 21: Nyquist Plot Curve of three sequences for Test 3

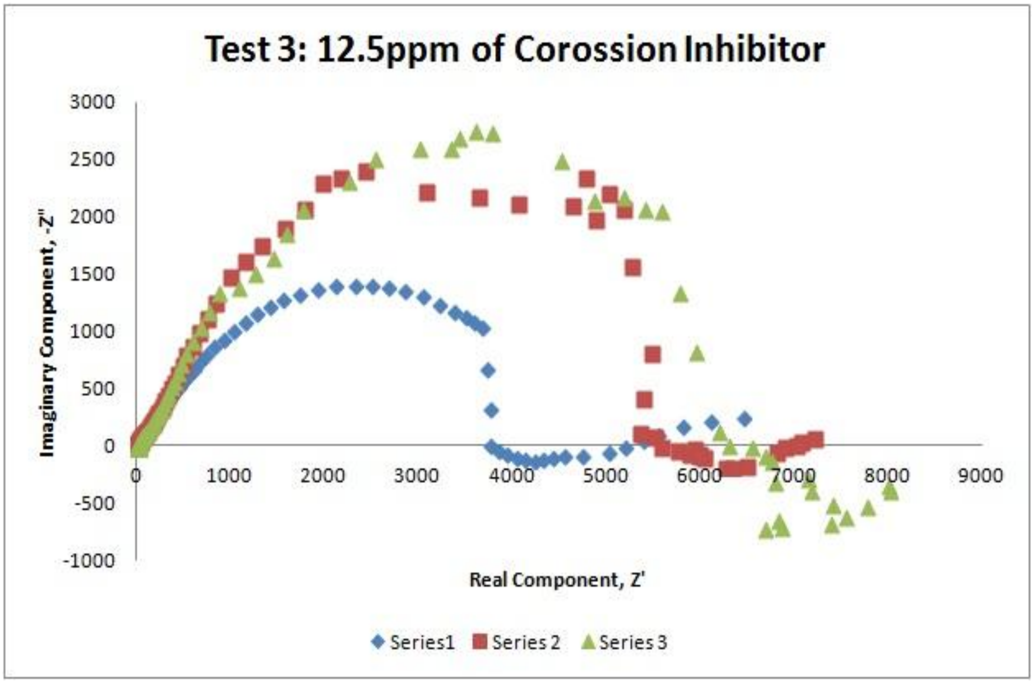

Figure 22: Graph of Nyquist Plot Tabulation Data for Test 3

Figure 21 and Figure 22 show there was a single complete semicircle responses produced at the high frequency region (left side). Single semicircle indicates that one primary reaction mechanism exists which may represent the formation of the inhibitor film. As in the Test 2 there was an addition of diffusion tail found at the low frequency region indicates an effect from the inhibitor film formed on the metal surface. The diffusion element shows that electrochemical process by the active diffusion of corrosion products away from the metal surface through inhibitor film. The plotted data shows that in the present of corrosion inhibitor metal sample provide formation of film on the surface and as the resistance towards corrosion.

The impedance values between three different sequences constantly increasing but not in steady form was shown in Sequence 2 and Sequence 3 which may indicate that the surface not completely stabilizing during immersion in the solution. Diameter of the semicircle spectra shape increase gradually corresponds to the increasing on the resistance value.

Test 4: Biocide Test

(Corrosion Inhibitor:0ppm Biocide: 500ppm)

Test 4 involves the injection of Biocide only with amount of 500ppm into the glass cell solution and with absence of Corrosion Inhibitor. The biocide injected at the beginning of the experiment at 0 hour. The plotted data result was given as below:

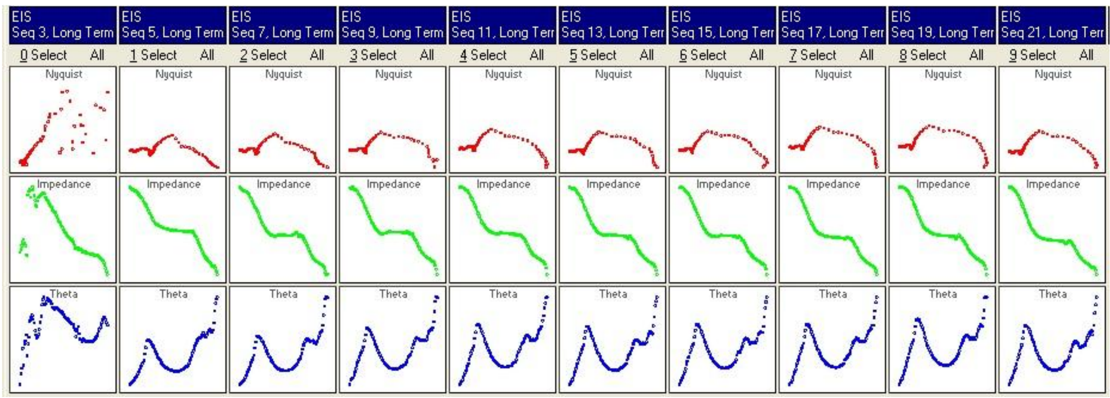

Figure 23: EIS Plotted Data for all sequences of Test 4

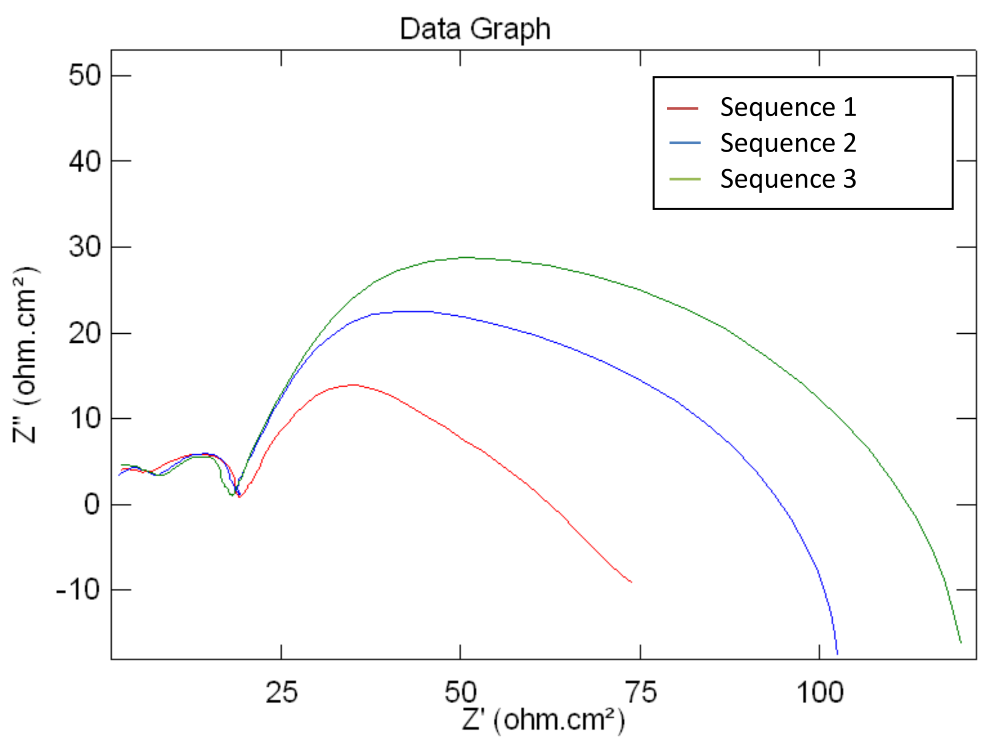

Figure 24: Nyquist Plot Curve of three sequences for Test 4

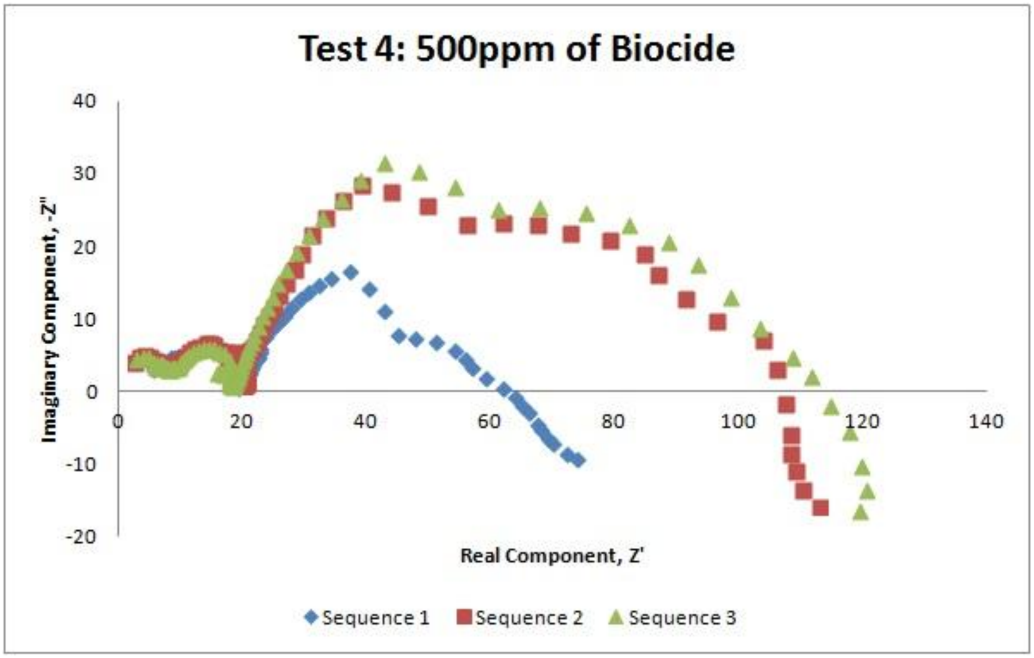

Figure 25: Graph of Nyquist Plot Tabulation Data for Test 4

Figure 24 and Figure 25 show there were two semicircles responses produced through out the frequency range. Two semicircles plotted with an indication of different reaction were generated with electrochemical process of interaction between metal surface and solution. A semicircle was observed in the low frequency region (right side) which corresponded to charge transfer for the normal corrosion process. The low frequency range semicircle dominates the plotted spectra through out the test. Another complete semicircle that represents time constant was found at the low frequency region (left side) which is related to corrosion product film formation in the presence of Biocide. The plotted data shows that with presence of biocide the metal sample was exposed to corrosion process in every sequence of time interval.

As the period of testing longer it was observed there was no changes in the shape of the semicircle during the entire exposure time which indicate the reaction mechanism do not change significantly.

Comparison in the impedance value between three different sequences at the high frequency region which not give any increment value changes indicate that the surface is not stable in the solution with the presence of Biocide.

Test 5A: Compatibility Test Biocide First

(Corrosion Inhibitor:500ppm Biocide: 500ppm)

Test 5A involves the injection of Biocide and Corrosion Inhibitor with amount of 500ppm both. Biocide was injected at the beginning of the experiment (0 hour) with amount of 500ppm once while Corrosion Inhibitor was injected after 2 hour of experimental running with batch injection at interval of 1 hour for every 100ppm dosage up to 500ppm. The plotted data result was given as below:

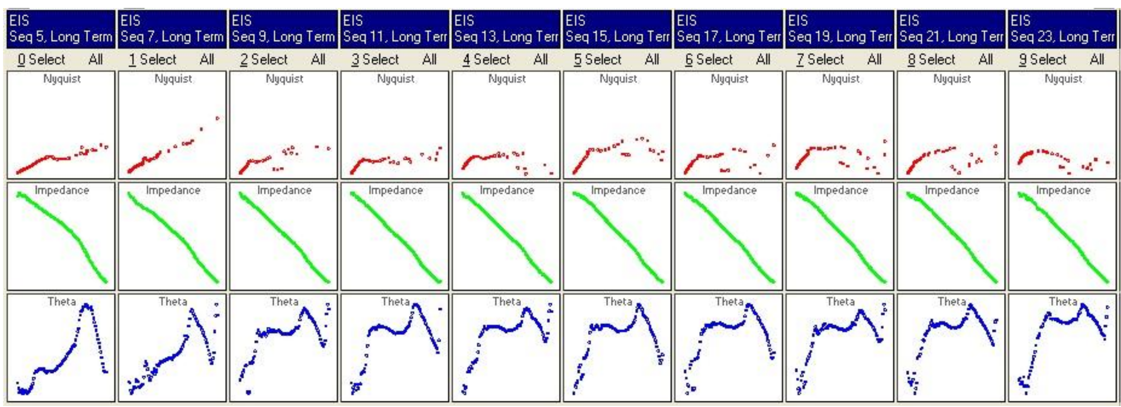

Figure 26: EIS Plotted Data for all sequences of Test 5A

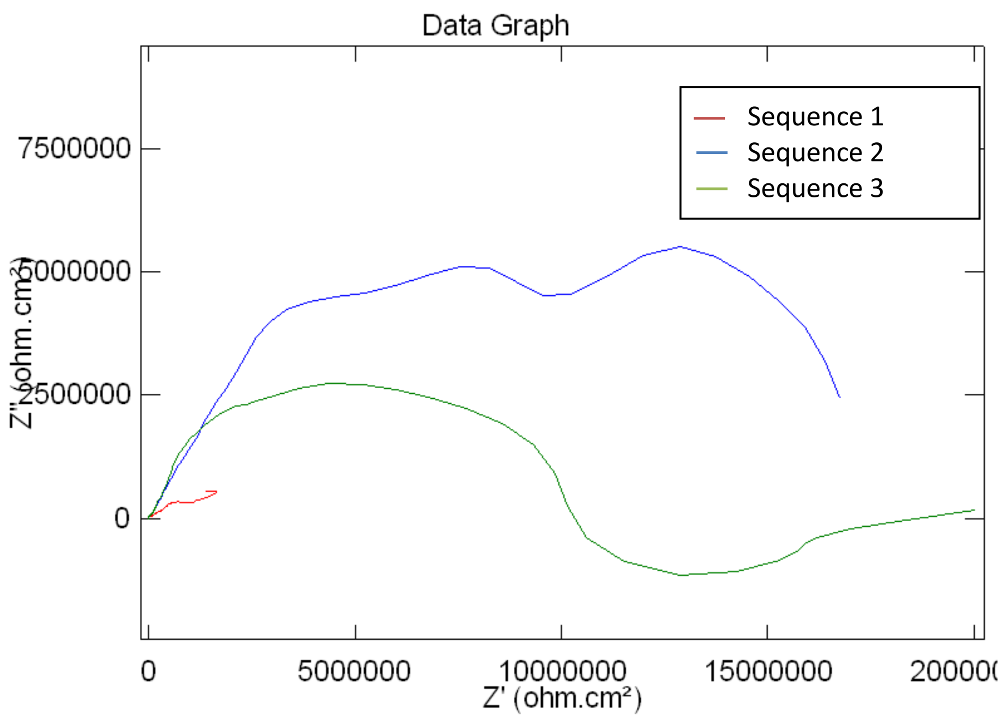

Figure 27: Nyquist Plot Curve of three sequences for Test 5A

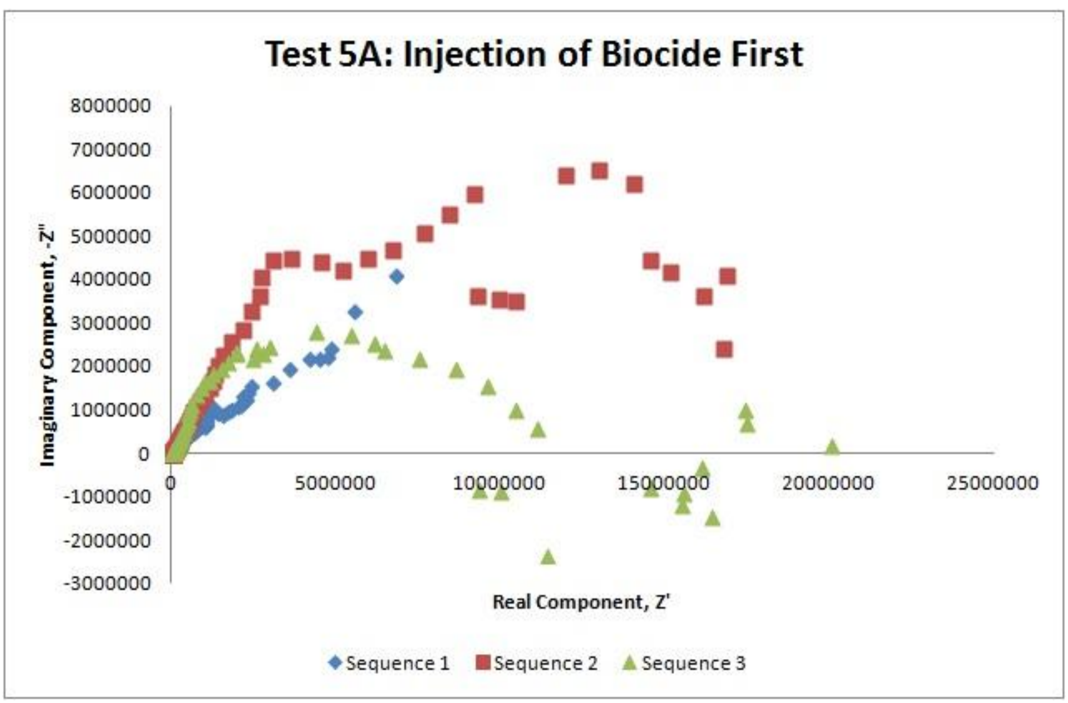

Figure 28: Graph of Nyquist Plot Tabulation Data for Test 5A

Figure 27 and Figure 28 show there are different of spectra shape for all the sequences. Double semicircle responses produced at the Sequence 2 indicate two different of reaction involves which are normal corrosion process and corrosion product film. At the Sequence 2 there was an electrochemical process of interaction between metal surface and solution. However as in the Sequence 3 it shown a huge different in shape of the spectra plotted. The double semicircle gradually disappears and not dominated the response as in Sequence 2 with addition of diffusion tail at the low frequency region. An addition of diffusion tail was found at the low frequency region for all the interval time sequences indicates an effect from the inhibitor film formed on the metal surface. The diffusion element indicates that electrochemical process by the active diffusion of corrosion products away from the metal surface through inhibitor film. The plotted data shows that in the beginning of the experiment the metal surface was exposed to the corrosion process as the presence of Biocide while the presence of corrosion inhibitor provides metal sample with formation of film on the surface and as the resistance towards corrosion.

Diameter of the semicircle spectra shape of Sequence 2 was larger as compare with and Sequence 3 corresponds to the higher on the resistance value was at the time after the inhibitor injection into the solution.

However comparison in the impedance value between Sequences 2 and Sequence 3 which shown not in steady form may due to the alteration of Biocide towards the efficiency and function of inhibitor.

Test 5B: Compatibility Test Corrosion Inhibitor First

(Corrosion Inhibitor:500ppm Biocide: 500ppm)

Test 5B involves the injection of Corrosion Inhibitor and Biocide with amount of 500ppm both. Corrosion Inhibitor was injected at the 0 hour of experiment with batch injection at interval of 1 hour for every 100ppm dosage up to 500ppm. After batch injection of Corrosion Inhibitor, at 6 hour Biocide was injected once with amount of 500ppm. The plotted data result was given as below:

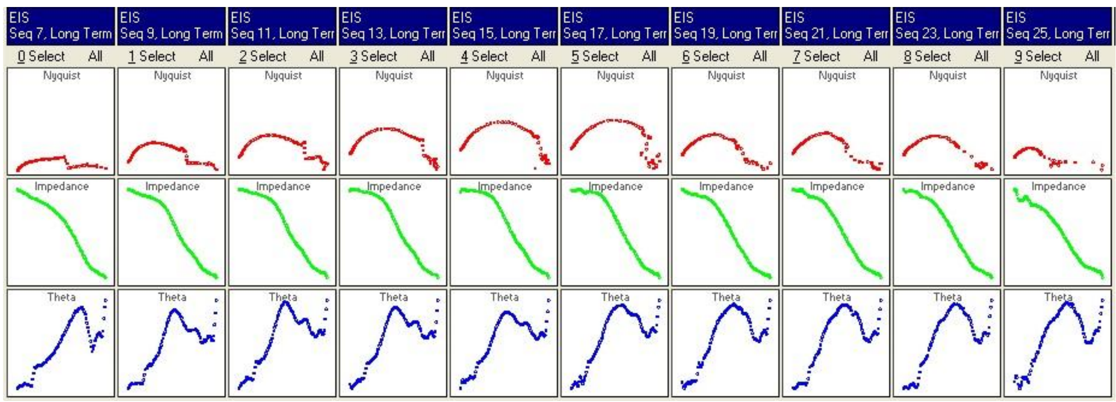

Figure 29: EIS Plotted Data for all sequences of Test 5B

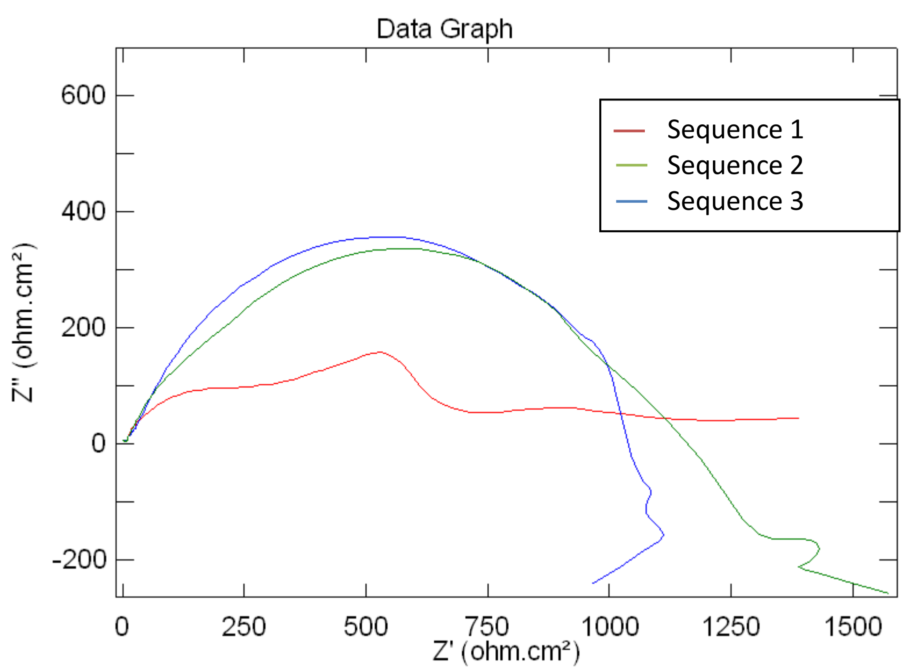

Figure 30: Nyquist Plot Curve of three sequences for Test 5B

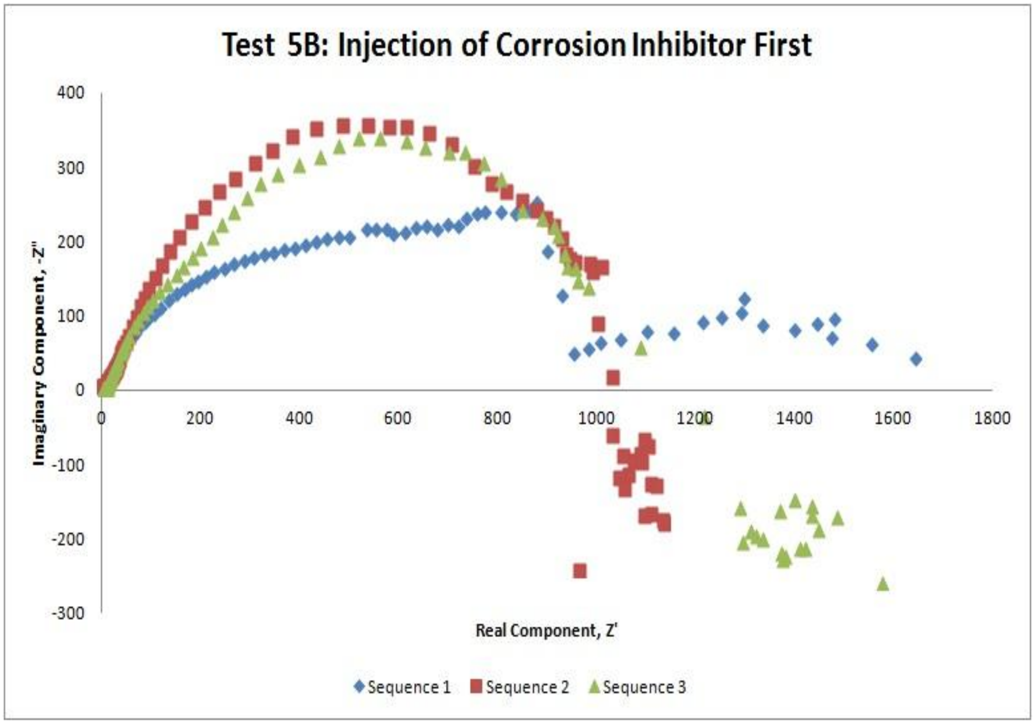

Figure 31: Graph of Nyquist Plot Tabulation Data for Test 5B

Figure 30 and Figure 31 show there were two main different shape of semicircle responses produced where it involve a slight different between Sequence 1 with the Sequence 2-Sequence 3. Double semicircle was found in Sequence 1 represent two different time constant or type of reaction process, where at the high frequency range (left side) it shows a complete single semicircle while at the low frequency range (right side) the was addition an incomplete arc of semicircle of diffusion tail. Diffusion tail was found at the low frequency region indicates an effect from the inhibitor film formed on the metal surface. The diffusion element suggests that electrochemical process by the active diffusion on the metal surface produce inhibitor film. As in the Sequence 2-Sequence 3 the diffusion tail gradually disappear as the result of inhibition film formation decreases as the function of time when there are presence of Biocide in the solution. However at the Sequence 2 and Sequence 3 it shows increment at the diameter of the semicircle response as compare at Sequence 1. Diameter of the semicircle spectra shape corresponds to the increasing on the resistance value. The plot indicates that the metal surface provide a higher resistance due to film formation when Corrosion Inhibitor been injected at the beginning of the experiment.

The impedance values between three different sequences were increase from the Sequence 1 to Sequence 2 and slight decrease from the Sequence 2 to Sequence 3. Impedance value shows that the surface is stabilizing during immersion of Corrosion Inhibitor and the stable condition have minor alteration and affected after injection of Biocide in the solution.

CHAPTER 5:

CONCLUSION

Electrochemical experiment conducted of compatibility testing between Corrosion Inhibitor and Biocide shows a significant chemical interaction between both chemicals. From the result achieved it shows that there are chemical interaction between Biocide and Corrosion Inhibitor. Biocide influences the functionality of the corrosion inhibitor in order to form protective film in the metal surface and enhance corrosion process to occur. Presence of Biocide may give an adverse effect to the corrosion inhibitor efficiency. However with decrease in its efficiency at the present of biocide, corrosion inhibitor still able to perform corrosion mitigation role and provide corrosion resistance by formation of protective film on the metal surface as the corrosion inhibitor was applied first in the solution.

Electrochemical Impedance Spectroscopy provides details of information on the corrosion mechanism and reaction that involve in the solution through a plotted curve of Nyquist Plot. Nyquist Plot shows significant representation of impedance spectra on the time constant of reaction, stability of the interaction, resistance of metals and formation corrosion product on surface.

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