

# **CERTIFICATION OF APPROVAL**

## **A Study of Chemical Compatibility between Corrosion Inhibitor and Biocide in Offshore Application**

by

Mohammad Faris Al Hanis B Abdul Hamid Albakri

A project dissertation submitted to the

Mechanical Engineering Programme

Universiti Teknologi PETRONAS

In partial fulfillment of the requirement for the

**BACHELOR OF ENGINEERING (Hons)**

**(MECHANICAL ENGINEERING)**

Approved by,

---

(AP Ir. Dr. Mokhtar Che Ismail)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2013

## **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.

---

MOHAMMAD FARIS AL HANIS BIN ABDUL HAMID ALBAKRI

## **ACKNOWLEDGEMENT**

Firstly, the highest gratitude goes to Allah the Al-Mighty. Next, the author would like to express humble gratitude to the author's family, FYP's supervisor, AP. Ir. Dr. Mokhtar Che Ismail , UTP's technicians, Mr. Faisal, research officer, Mr. Izzudin and friends all over. These people have helped the author a lot to successfully complete this project within the time provided. It has been a wonderful time working together and the author has learned a lot in a short period of time.

As an undergraduate, it is important for the author to have a positive mind set during this period so as to avoid bad habits such as laziness and procrastination. Throughout the two semesters, the author has gained a valuable experience in various aspects especially in engineering materials. The exposure to such environment will be very useful to the author's future career. The author hope to make good use of the knowledge gained.

Personally, this is a great experience as the author was allowed to be involved with hands-on tasks throughout these two semesters. The author hope that all the information gained from this project may benefit others especially the UTP's students and staffs as a source of reference.

## ABSTRACT

The main threat to the oil and gas pipeline is due to internal corrosion from corrosive acid gases and microbes. The integrity of offshore pipeline is dependent on successful mitigation of carbon dioxide (CO<sub>2</sub>) corrosion and microbiologically influenced corrosion (MIC) through effective corrosion inhibitor and biocide treatment. Possible reactions between corrosion inhibitor (CI) and biocide can reduce the efficiency and performance of both chemicals. This can lead to inadequate corrosion protection of the pipeline. This research is to study the chemical compatibility between CI and biocide focusing on the performance of the CI. Corrosion simulation was based on 3% NaCl solution saturated with CO<sub>2</sub> at 1 bar and 60°C, with fixed biocide concentration of 500ppm and various CI dosages. The compatibility was studied based on comparison between three injection methods and the individual effect of each chemical. Corrosion measurement was performed in three-electrode glass cell testing by using Linear Polarization Resistance (LPR). Surface film morphology was studied with Scanning Electron Microscope (SEM) and crystallinity structure with X-ray diffraction (XRD). 25ppm CI reduced corrosion rate from 1.4mm/yr to 0.04mm/yr with 97% efficiency. The presence of biocide reduced the performance from 2.5% to 25% significantly depending on the injection method. Thus, dosage of CI more than 500ppm was required to increase inhibition efficiency. By using SEM, the existence of CI layer has been observed by no detection of general corrosion on the inhibited surface. The XRD patterns of inhibited surface shows the presence of iron peaks only, the peaks due to oxide of iron were found to be absent. In conclusion, biocide was found to affect the performance of CI efficiency.

## Table of Contents

ABSTRACT.....	iv
1 INTRODUCTION .....	1
1.1 Background of Study.....	1
1.2 Problem Statement .....	1
1.3 Objective .....	1
1.4 Scopes of Study .....	2
2 LITERATURE REVIEW.....	3
2.1 Corrosion Inhibitor Theory.....	3
2.1.1 Corrosion inhibitor classification.....	3
2.2 Biocides Theory .....	4
2.3 Compatibility Issue.....	4
3 METHODOLOGY & PROJECT WORK .....	8
3.1 Overview .....	8
3.2 Materials - Composition of sample .....	9
3.3 Sample Preparation.....	9
3.3.1 Sectioning.....	9
3.3.2 Soldering .....	10
3.3.3 Mounting.....	11
3.3.4 Grinding and Polishing .....	12
3.4 Experimental procedures .....	13
3.5 Test Matrix .....	15
3.5.1 Test 1 (Blank test without corrosion inhibitor).....	16
3.5.2 Test 2 & 3 (inject corrosion inhibitor only) .....	16
3.5.3 Test 4A & 4B (inject biocide only).....	16
3.5.4 Test 5A, 5B & 5C (Compatibility simulation: corrosion inhibitor + biocide) 16	
3.6 Electrochemical studies - Linear Polarization Resistance.....	17

3.7	Characterization methods .....	19
4	RESULTS AND DISCUSSIONS .....	20
4.1	Baseline corrosion rate .....	20
4.1.1	Test 1 (Blank Test).....	20
4.1.2	Test 2 (25 ppm Corrosion Inhibitor) .....	21
4.1.3	Test 3 (12.5 ppm corrosion inhibitor) .....	21
4.1.4	Test 4A (500ppm biocide) .....	22
4.2	Compatibility mode .....	23
4.2.1	Test 5A (Inject biocide first).....	23
4.2.2	Test 5B (inject simultaneously) .....	25
4.2.3	Test 5C (inject corrosion inhibitor first) .....	27
4.3	Corrosion rate comparison .....	29
4.3.1	Individual effect .....	29
4.3.2	Compatibility effect on corrosion rate .....	30
4.4	Physical interaction of CI and biocide .....	31
4.4.1	Test 1 (Blank Test).....	31
4.4.2	Test 2 (25ppm corrosion inhibitor) .....	32
4.4.3	Test 5B (corrosion inhibitor + biocide).....	32
4.5	Chemical interaction between CI and biocide.....	34
5	CONCLUSION AND RECOMMENDATION.....	35
6	REFERENCES.....	36

## LIST OF FIGURES

Figure 2.1: Effect of Biocides + Inhibitor on Mild Steel Corrosion .....	6
Figure 2.2: Inhibition efficiency of Biocide and Inhibitor on Copper .....	6
Figure 3.1: General overview of the study.....	8
Figure 3.2: Precision saw machine for sectioning purpose.....	9
Figure 3.3: Sectioned samples with average dimension of 1cm (length), 1cm (width) and 0.5cm (thickness).....	10
Figure 3.4: Sample has been soldered to the copper wire.....	10
Figure 3.5: Moulded samples inside cylinder-shape rings.....	11
Figure 3.6: Typical glass cell set up used in the experiment .....	14
Figure 3.7: Step 1 - Open Sequencer software.....	17
Figure 3.8: Step 2 - Click "Current & Voltage/ time" button & click "OK" .....	17
Figure 3.9: Step 3 - Click "Long Term" button and put desired amount of measurement .....	18
Figure 3.10: Step 4 - Click "Long term - LPR sweep" button and click "OK" .....	18
Figure 3.11: Scanning Electron Microscope (SEM) Diffraction (XRD)	19
Figure 3.12: X-Ray	19
Figure 4.1: Average corrosion rate trend curve at 60°C and 1 bar CO <sub>2</sub> .....	20
Figure 4.2: Effect of 25ppm CI injection at 60°C and 1 bar CO <sub>2</sub> .....	21
Figure 4.3: Effect of 12.5ppm CI injection at 60°C and 1 bar CO <sub>2</sub> .....	21
Figure 4.4: The effect of 500ppm biocide injection on corrosion rate at 60°C and 1 bar CO <sub>2</sub> .....	22
Figure 4.5: Effect of injection method of injecting biocide first on the corrosion rate. ....	24
Figure 4.6: Effect of injection method of injecting biocide and CI simultaneously on the corrosion rate.....	26
Figure 4.7: Effect of injection method of injecting CI first on the corrosion rate. ....	28
Figure 4.8: Comparison of corrosion rate trends of test 1, 2, 3 and 4A.....	29
Figure 4.9: Comparison of corrosion rate change curves of test 5A, 5B and 5C over 10 days .....	30
Figure 4.10: General corrosion SEM pictures (front view) of the test 1 specimen at 500 X, blank test, 60°C, 1 bar CO <sub>2</sub> .....	31
Figure 4.11: Pitting corrosion SEM pictures (front view) of the test 1 specimen at 2000 X, blank test, 60°C, 1 bar CO <sub>2</sub> .....	31

Figure 4.12: General SEM pictures (front view) of the test 2 specimen at 500 X, 60°C, 1 bar CO <sub>2</sub> .....	32
Figure 4.13: General SEM pictures (front view) of the test 5B specimen at 500 X, 60°C, 1 bar CO <sub>2</sub> .....	32
Figure 4.14: Crack SEM pictures (front view) of the test 5B specimen at 2000 X, 60°C, 1 bar CO <sub>2</sub> .....	33
Figure 4.15: XRD superimpose results .....	34

## LIST OF TABLES

Table 3.1: SiC grit size and proposed wheel speed for grinding .....	13
Table 3.2: Test Matrix.....	15
Table 4.1: Corrosion rate for Test 5A .....	23
Table 4.2: Corrosion rate for test 5B.....	25
Table 4.3: Corrosion rate for test 5C.....	27

## ABBREVIATION & NOMENCLATURE

Carbon Dioxide - (CO<sub>2</sub>)

Microbiologically Influenced Corrosion - (MIC)

Corrosion Inhibitor - (CI)

Tetrakis hydroxymethyl phosphonium sulfate - (THPS)

Linear Polarization Resistance - (LPR)

Electrochemical Impedance Spectroscopy - (IES)

Energy Disruptive X-ray - (EDX)

Scanning Electron Microscope - (SEM)

X-ray Photoelectron Spectroscopy - (XPS)

Sulfate Reducing Bacteria - (SRB)

3-Benzylidene Amino 1,2,4-Triazole Phosphonate - (BATP)

3-Cinnamylidene Amino 1,2,4-Triazole Phosphonate - (CATP)

3-Anisalidene Amino 1, 2,4-Triazole Phosphonate - (AATP)



# **1 INTRODUCTION**

## **1.1 Background of Study**

In the oil and gas industries – mainly the exploration and production operations, the field operators normally would like to have uninterrupted supply of oil and gas to the export or processing points. However, the main threat to the oil and gas equipment especially pipeline is due to internal corrosion from corrosive acid gases and microbes.

Therefore, the integrity of carbon steel pipeline is dependent on successful corrosion mitigation program. Carbon Dioxide ( $CO_2$ ) corrosion is mitigated by using corrosion inhibitor. The threat from Microbiologically Influenced Corrosion (MIC) is mitigated by mean of biocide treatment.

Both of the oilfield chemicals are of different chemistry, Corrosion Inhibitor (CI) is usually Imidazole-based, and biocide is either Glutaraldehyde or tetrakis hydroxymethyl phosphonium sulfate (THPS).

Due to the small footprint of offshore platform, the injection process of these chemicals is close to each other, which lead to possible reaction between CI and biocide. The possible reaction between CI and biocide can lead to degradation of the chemicals and resulting in inadequate protection of the pipeline.

## **1.2 Problem Statement**

Possible reactions of corrosion inhibitor (CI) and biocide can reduce the efficiency and performance of both chemicals. This can lead to inadequate corrosion protection to the pipeline.

## **1.3 Objective**

The main objective of this project is to study on the chemical compatibility between corrosion inhibitor and biocide focusing on the performance of the corrosion inhibitor by means of effect on corrosion protection performance and surface characterization of chemical reaction between corrosion inhibitor and biocide.

## **1.4 Scopes of Study**

The scopes of study of this project are as follows:

- Compatibility between corrosion inhibitor and biocide
- Corrosion inhibitor protection
- Carbon dioxide (CO<sub>2</sub>) environment
- Nitrogen environment
- Effect of injection method on the final corrosion rate

## **2 LITERATURE REVIEW**

### **2.1 Corrosion Inhibitor Theory**

Corrosion inhibitor is a chemical compound which decreases the corrosion rates of a material such as metal and alloy when added to a liquid or gas. Corrosion inhibitor could be used in all pH (Schweitzer, 2006). The effectiveness of a corrosion inhibitor depends on the quantity of water, fluid composition and flow regime.

Corrosion inhibitor could reduce rate of anodic oxidation or reduce rate of cathodic reduction or both. It forms a protective film on surface of metal. Corrosion inhibitor is adsorbed into metal surface by physical (electrostatic) adsorption and chemisorption (Schweitzer, 2006). Physical adsorption is a result of electrostatic attractive forces between organic ions and electrically charged metal surfaces. Chemisorption is a transfer or sharing of inhibitor molecule's charge to metal surface, forming a coordinate-type bond.

#### **2.1.1 Corrosion inhibitor classification**

There are three classifications of corrosion inhibitors, which are passivation inhibitor, organic inhibitor and precipitation inhibitor (Schweitzer, 2006). Firstly, a passivation inhibitor is a material capable of forming a protective oxide film on metal surfaces. It is the most effective compared to others. It builds a thin protective film along the anode, increasing the potential at the anode and slowing the corrosion reaction. The film is initiated at the anode although it may eventually cover the entire metal surface. Because the film is not visible to the naked eye, the appearance of the metal is left unchanged. However, passivation inhibitor can cause pitting and accelerate corrosion when concentration falls below minimum limit. For this reason, it is essential for a constant monitoring of inhibitor concentration when conducting the testing.

Organic inhibitor is a material builds up a protective film of adsorbed molecules the metal surface. Precipitation inhibitor is a compound causes formation of precipitation on the surfaces of metal and thus, providing protective film.

## **2.2 Biocides Theory**

A biocide is a microorganism or chemical substance, which can exert, render harmless, or deter a controlling effect on any harmful organism by biological or chemical means. It is a bactericide for control of mixed bacteria in both aerobic and anaerobic (including sulphate reducers) in fresh water, seawater and low brines. Examples of biocides are Glutaraldehyde and Tetrakis(hydroxymethyl) Phosphonium Sulfate (THPS).

In (Shanthy, 2009) journal, result from experimental has indicated that the optimum concentration of CTAB (a type of biocide) for destroying bacteria viz., E. coli, Salmonella and Shigella is more or equal to 25 ppm. The formulation consisting of 5 ppm of Zn<sup>2+</sup> and 100 ppm of CTAB exhibits 98% corrosion inhibition efficiency and 100% biocidal efficiency.

## **2.3 Compatibility Issue**

Microbiologically Influenced Corrosion (MIC) and Carbon Dioxide Corrosion are the two important operational problems in offshore pipeline. Pipelines are known to be susceptible, especially to fouling-induced corrosion, due to basic design characteristics and recirculation of water. Based on (Mohan, 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.

Phosphates and chromates have been normally used as scale inhibitor and corrosion inhibitor in cooling water systems. In the late ages of 1970s and 1980s polyphosphates, carboxylic acids, phosphonates and polymeric phosphonates with zinc ions were used as corrosion inhibitors and antiscaulants (Veres, 1992), (Mathiyarasu, 1997), (Rajendiran, 1998), (S. Rajendiran, 1999). These Polyphosphates have simply hydrolysable P-O bonds causing in the formation of orthophosphates. These orthophosphates are not the good corrosion inhibitors but good feed for microorganisms and algae, causing in bio fouling effects. Since phosphates act as good nutrients (Schwanck, 1990) (Maruthamutu, 1996) for microbes and inhibitors such as chromate are contaminated to the environment, the development of right chemicals that are capable of replacing phosphates and chromates has become highly important. Phosphonates are not the good corrosion

inhibitors but in the existence of zinc ions, they functioned better as corrosion inhibitors. Numerous industries are using dissimilar types of biocides to control micro fouling in cooling water systems. Maintenance engineers are identifying suitable biocides for specific microbes like algae, Sulfate Reducing Bacteria (SRB), and iron bacteria to prevent the microbiologically influenced corrosion (MIC). For controlling fouling and corrosion, inhibitors are added constantly and biocides are added once a week or once in fourteen days. Hence, it is quite important to find the interference between biocides and inhibitors in cooling water systems.

Generally, chemists and microbiologists are assessing the efficiency of inhibitors for corrosion control and the efficiency of biocides on biological growth separately. However, there are few studies that concern with the interference between biocides and inhibitor for offshore pipeline application and this subject needs extensive development and research. Though several studies on the use of phosphonates, viz. Aminotrimethylene phosphonate (ATMP) with zinc ion as corrosion inhibitor have been reported in literature (Gunasekaran, 2001), there is no report on the influence of inhibitor (ATMP) with some biocides except that of (Maruthamutu, 1996), (Ramesh, 2003), (A. Rajasekar, N. Muthukumar, 2005) and (Mohan, 2002).

According to the research by (Mohan, 2002), aminotrimethylene phosphonate (ATMP) as inhibitor and cetyl trimethyl ammonium bromide (CTAB) and cetylpyridinium bromide (CPB) as biocides have been selected to study the interaction between biocides and inhibitor. Figure 2.1 shows that in the presence of corrosion inhibitor and biocide, the corrosion inhibition efficiency was almost 58% in the existence of 50ppm and 38% in the existence of 25ppm of cetyl trimethyl ammonium bromide (CTAB). In addition, there are about 45% inhibition efficiency in the presence of inhibitor with 50ppm cetylpyridinium bromide (CPB), zinc ion and aminotrimethylene phosphonate (ATMP) and 31% efficiency in the existence of 25ppm of biocide, cetylpyridinium bromide (CPB).

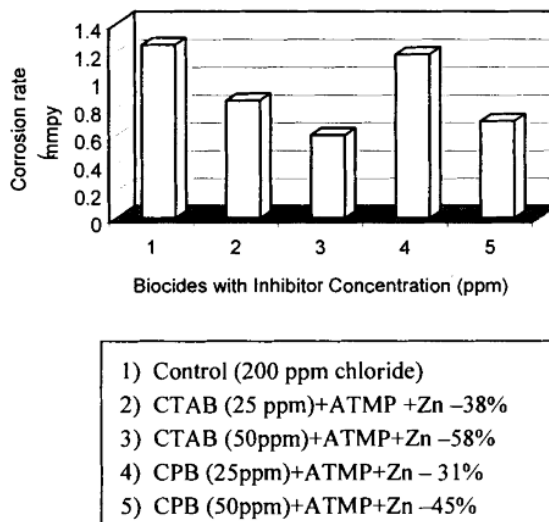


Figure 2.1: Effect of Biocides + Inhibitor on Mild Steel Corrosion

While in copper system (Mohan, 2002), Figure 2.1 shows that the inhibition efficiency of biocides with inhibitor in copper system. In the existence of both inhibitor and biocide system, the inhibition efficiency was approximately 94% at 50pprn and 89% at 25pprn of CTAB. Furthermore, CPB with inhibitor indicated inhibition efficiency of about 88% and 82% in the existence of 50pprn and 25pprn of CPB, respectively.

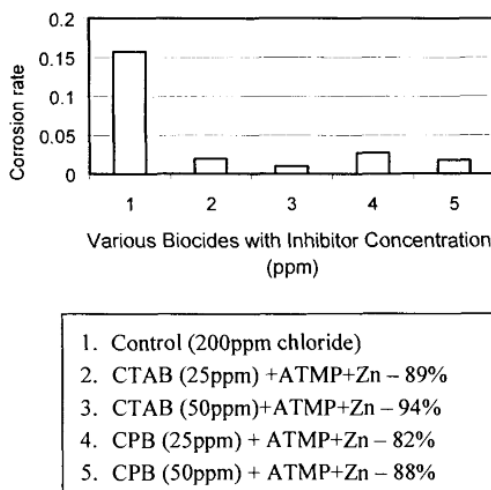


Figure 2.2: Inhibition efficiency of Biocide and Inhibitor on Copper

(Mohan, 2002) concluded that cetylpyridinium bromide (CPB) acts better than cetyl trimethyl ammonium bromide (CTAB), when biocides are taken with inhibitor with respect to both mild steel and copper. He also concluded that copper performs better than mild steel when inhibitor is mixed with biocide.

In (Ramesh, 2003) study, A triazole phosphonate compounds, namely, 3-benzylidene amino 1,2,4-triazole phosphonate (BATP), 3-cinnamylidene amino 1,2,4-triazole phosphonate (CATP) and 3-anisylidene amino 1, 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 studied by using weight loss and electrochemical polarization methods. Results from experimental observation have shown 2,4-triazole phosphonate (AATP), Molybdenum (Mo) and cetyl trimethyl ammonium bromide (CTAB) offered good corrosion inhibition efficiency. Moreover in the existence of cetyl trimethyl ammonium bromide (CTAB) with inhibitor (BATP, CATP and AATP), the efficiency was 71.82%, 72.63%, and 80.52% respectively.

From (A. Rajasekar, N. Muthukumar, 2005) journal, they concluded the selection of inhibitor in petroleum product pipeline is an important factor so the interference between biocide and inhibitor and degradation of inhibitor should be analyzed for effective usage of biocides. For examples, ester acts as a good biocide, but carboxylic acid reduces the pH of the water and boosts the bacterial growth in the pipeline. Therefore, the interference between inhibitor and biocide should be avoided.

### 3 METHODOLOGY & PROJECT WORK

#### 3.1 Overview

The approach of this study is summarized in Figure 3.1. First step is preparing the samples; sample preparation stage consisted of sectioning, mounting, grinding, and polishing processes. The samples will undergo Linear Polarization Resistance method in 8 different conditions. Based on Figure 3.1, test 1 has no corrosion inhibitor and biocide, tests 2 and 3 with corrosion inhibitor only, tests 4A and 4B consist biocide only and tests 5A, 5B and 5C consist both corrosion inhibitor and biocide. Test 1, 2, 3, 4A, 5A, 5B and 5C are simulated under carbon dioxide environment at 1 Bar and 60°C while test 4B is simulated under nitrogen condition at 25°C. All of the tests needed are prepared in the standard glass cell. Next, characterizations of all samples are performed by using Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD).

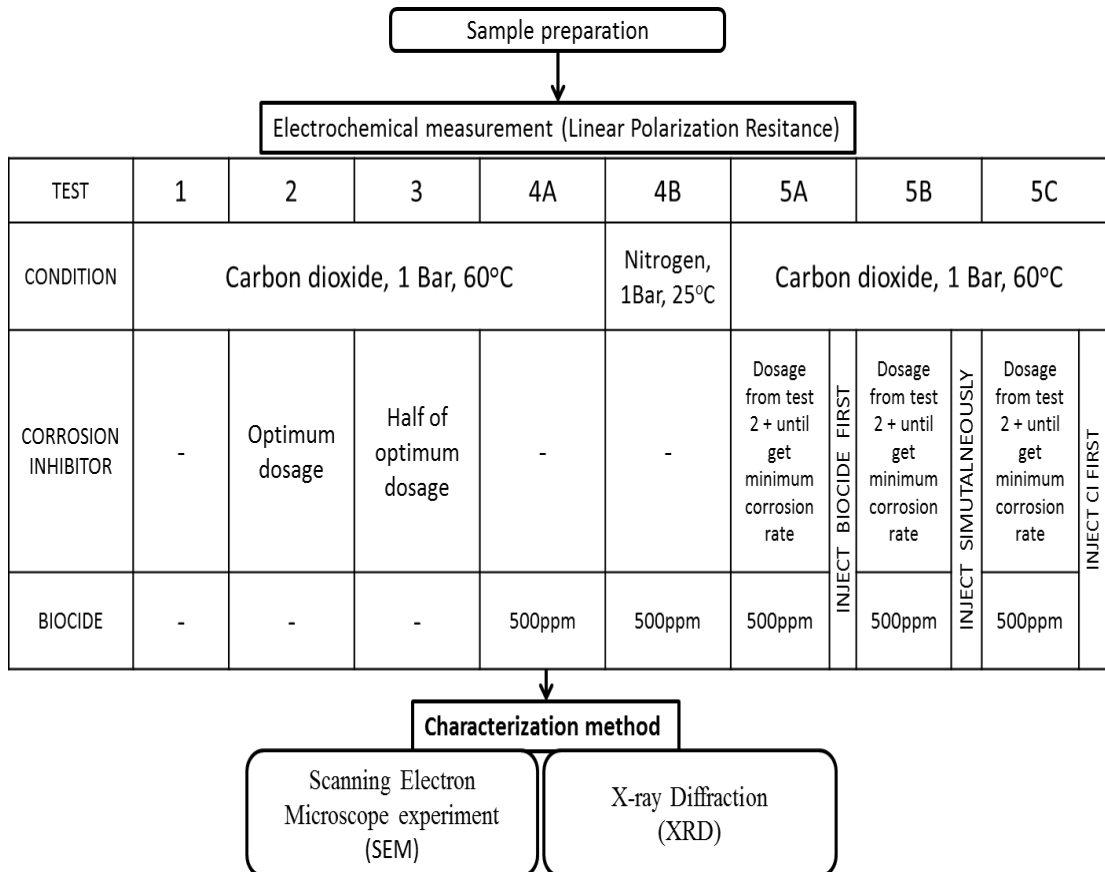


Figure 3.1: General overview of the study



### 3.2 Materials - Composition of sample

Carbon steel ASTM A106 has been chosen for this study. The composition of carbon steel ASTM A106 is carbon 0.3%; phosphorus 0.035%; sulphur 0.035% and manganese 0.26% (commercial grade).

The carbon steel ASTM A106 with surface dimensions 1.0 X 1.0 mm was mirror polished, degreased with ethanol.

### 3.3 Sample Preparation

The samples were prepared to produce a mirror like surface to analyze the materials microstructures. The sample preparation consists of sectioning, soldering, mounting, grinding and polishing processes.

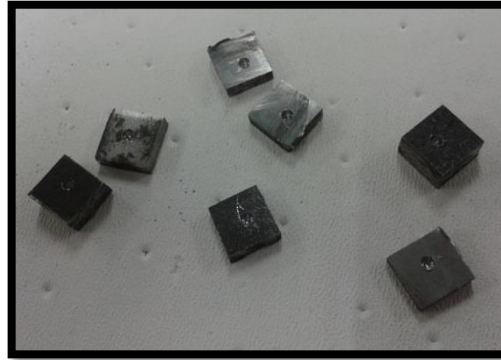
#### 3.3.1 Sectioning

Sectioning is the removal of a representative sample from the parent piece by removing a suitably sized specimen at desired location and orientation. The sectioning plane should be as close as to the desired location as possible. Figure 3.2 shows Precision Saw machine used for sectioning the samples. Precision saw machine was used for precise sectioning, so that the microstructure will not be altered in the process.



Figure 3.2: Precision saw machine for sectioning purpose

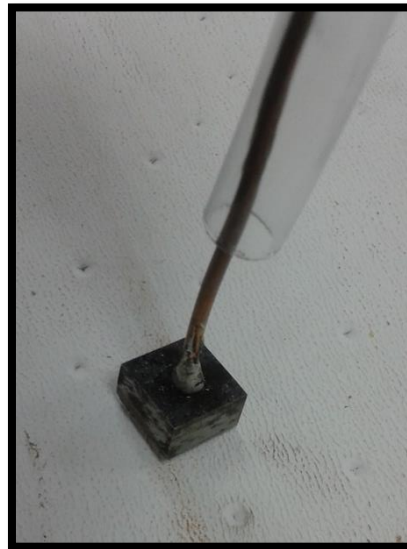
In this project, all of the samples obtained have been sectioned in the longitudinal plane of the parent sample. The average dimension of each sectioned sample was 1cm (length), 1cm (width) and 0.5cm (thickness). Figure 3.3 shows sectioned samples by using Precision Saw machine.



**Figure 3.3:** Sectioned samples with average dimension of 1cm (length), 1cm (width) and 0.5cm (thickness)

### **3.3.2 Soldering**

Soldering is a 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 3.4 shows a sample which was soldered to the copper wire.



**Figure 3.4:** Sample has been soldered to the copper wire

After soldering, the current flow connectivity must be tested by using multi-meter. The sample cannot be used if there is no current flow detected by multi-meter.

### 3.3.3 Mounting

The main purpose of mounting metallographic specimens is for convenience in handling specimens of difficult shapes or sizes during the subsequent steps of metallographic preparation and examination. Besides, mounting process will protect and preserve extreme edges or surfaces defects during metallographic preparation. There are two types of mounting methods that could be applied which is cold and hot mounting. Cold mounting is performed with a mixture of resin and hardener; meanwhile, hot mounting uses a certain amount of pressure and heat to mount the samples.

In this project, cold mounting was applied and it requires very simple equipment consisting of a cylinder-shaped ring, which serves as a mould and flat piece of plastic that serves as the base. The samples were placed on the base within the cylinder and the mixture poured in and allowed to set about 40 minutes.



Figure 3.5: Moulded samples inside cylinder-shape rings

Figure 3.5 shows the moulded samples inside the moulds. Below are the listed cold mounting parameters:

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

### **3.3.4 Grinding and Polishing**

Grinding has 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. All of the grinding steps were performed with water as lubricant. Moreover, water also minimized specimen heating and prevented the abrasive from becoming loaded with metal removed from the specimen being prepared.

The final step in producing a deformation-free surface that is flat, scratch free and mirror-like in appearance is polishing. This step involves observation of the true microstructure for subsequent metallographic interpretation, both qualitative and quantitative. Polishing can be divided into two parts. Rough polishing is a further limitation of the deformation zone produced by fine grinding and final polishing is to remove the deformation zone produced during rough polishing.

The samples underwent grinding steps as shown in the Table 3.1. The polishing is done with 6 and 1 $\mu$ m diamond paste charged onto a low nap cloth. A control sample was also prepared from an as-cast tube made from the same alloy to compare the microstructures with the microstructures of the creep-tested and ex-service samples.

**Table 3.1: SiC grit size and proposed wheel speed for grinding**

<b>SiC Grit Size</b>	<b>Wheel Speed (RPM)</b>
120	100 - 250
320	100 - 250
400	100 - 250
600	100 - 250
800	100 - 250
1200	100 - 250

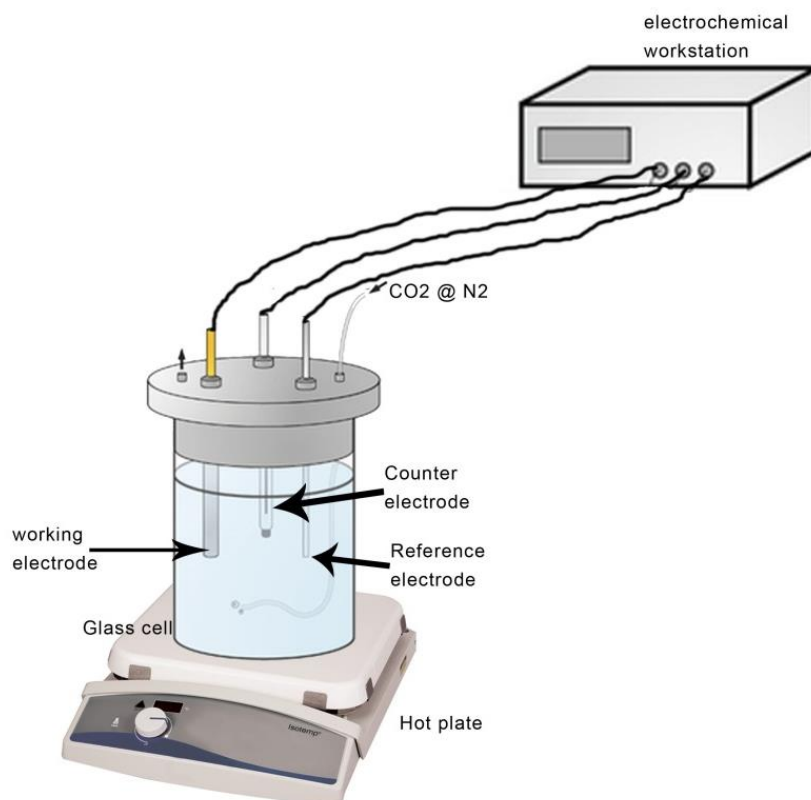
### **3.4 Experimental procedures**

The experiments were performed in a one-liter glass cell. A schematic representation of the experimental setup is shown in Figure 3.6. The glass cell was filled with one l liters of deionised (DI) water to which 3% by weight of NaCl salt was added. All experiments were conducted at a given pH, and a fixed temperature, 60° C. Three electrodes cell assembly are used. The working electrode is carbon steel ASTM A106 while Silver/Silver Chloride (Ag/AgCl) was used as the reference electrode and stainless steel electrode was used as counter (auxiliary) electrode. Three electrodes were connected to electrochemical workstation properly.

CO<sub>2</sub> or nitrogen gas has been used to deoxygenate the solution for at least an hour. It should be pointed out that the volume of the solution was maintained at desired value throughout the experiment by minute addition of a correct portion of DI water and NaCl salt. Before introduction, the specimens was polished successfully using various grit sand paper.

In order to establish baseline results, experiments were started without corrosion inhibitor and biocide at pH 4. The corrosion rate of this experiments are expected. These baseline results then served as a means of comparison with experiments in the presence of different dosage of corrosion inhibitor and biocide. Typical experiments were conducted over a period of one day in order to see

stabilized corrosion rate. Table 3.2 outlines the experimental test matrix. At the end of the test, the samples were removed from the cell and stored in a moisture free cabinet for SEM and XRD analysis.



**Figure 3.6: Typical glass cell set up used in the experiment**

### 3.5 Test Matrix

The test matrix for this study is shown in Table 3.2; there are eight systems to be tested within the project timeline. Test 1, 2, 3, 4A, 5A, 5B and 5C were simulated under carbon dioxide environment at 1 Bar and 60°C while test 4B was simulated under nitrogen condition at 25°C.

Table 3.2: Test Matrix

TEST	CONDITION	CORROSION INHIBITOR	BIOCIDE	CHARACTERIZATION
1	CO <sub>2</sub> Pressure -1 BAR Temperature- 60°C	-	-	SEM, XRD
2	CO <sub>2</sub> Pressure -1 BAR Temperature- 60°C	Optimum dosage	-	SEM, XRD
3	CO <sub>2</sub> Pressure -1 BAR Temperature- 60°C	Half dosage of test 2	-	SEM, XRD
4A	CO <sub>2</sub> Pressure -1 BAR Temperature- 60°C	-	500ppm	SEM, XRD
4B	Nitrogen Pressure -1 BAR Temperature- 25°C	-	500ppm	SEM, XRD
5A	CO <sub>2</sub> Pressure -1 BAR Temperature- 60°C	Dosage from test 2 + until get minimum corrosion rate	500ppm	SEM, XRD
		<b>INJECT BIOCIDES FIRST</b>		
5B	CO <sub>2</sub> Pressure -1 BAR Temperature- 60°C	Dosage from test 2 + until get minimum corrosion rate	500ppm	SEM, XRD
		<b>INJECT SIMULTANEOUSLY</b>		
5C	CO <sub>2</sub> Pressure -1 BAR Temperature- 60°C	Dosage from test 2 + until get minimum corrosion rate	500ppm	SEM, XRD
		<b>INJECT CORROSION INHIBITOR FIRST</b>		

### **3.5.1 Test 1 (Blank test without corrosion inhibitor)**

To find the baseline corrosion rate, no corrosion inhibitor and biocide being injected into the solution. The corrosion rate was measured by using linear polarization method (LPR).

### **3.5.2 Test 2 & 3 (inject corrosion inhibitor only)**

To compare the corrosion inhibitor efficiency, Imadizoline based type corrosion inhibitor was injected into the solution until the minimum corrosion rate is obtained. Test 2 was injected with the optimum dosage corrosion inhibitor while test 3 is injected half dosage corrosion inhibitor from test 2. The corrosion rate of each test was compared to each other in order to compare corrosion inhibition efficiency.

### **3.5.3 Test 4A & 4B (inject biocide only)**

Both tests, 4A & 4B were injected with fixed dosage of biocide which is 500ppm. The purpose of test 4A is to monitor the corrosion rate of carbon dioxide environment in the presence of biocide only. Test 4B was performed to monitor the corrosion rate of biocide itself under nitrogen environment.

### **3.5.4 Test 5A, 5B & 5C (Compatibility simulation: corrosion inhibitor + biocide)**

To study interference and compatibility between corrosion inhibitor and biocide, both chemical oilfields were injected in test 5A, 5B and 5C. Biocide was injected firstly in test 5A while biocide and corrosion inhibitor were injected simultaneously in test 5B. For test 5C, corrosion inhibitor was injected first. The initial dosage of corrosion inhibitor is based on test 2 meanwhile dosage of biocide is fixed at 500ppm. The additional injection of corrosion inhibitor is continued until achieves the lowest corrosion rate. However, the maximum dosage of corrosion inhibitor is limited to 500ppm.



### 3.6 Electrochemical studies - Linear Polarization Resistance

To get data from Linear Polarization Resistance method, Sequencer software was used. The steps are elaborated as per Figure 3.7, 3.8, 3.9 and 3.10.

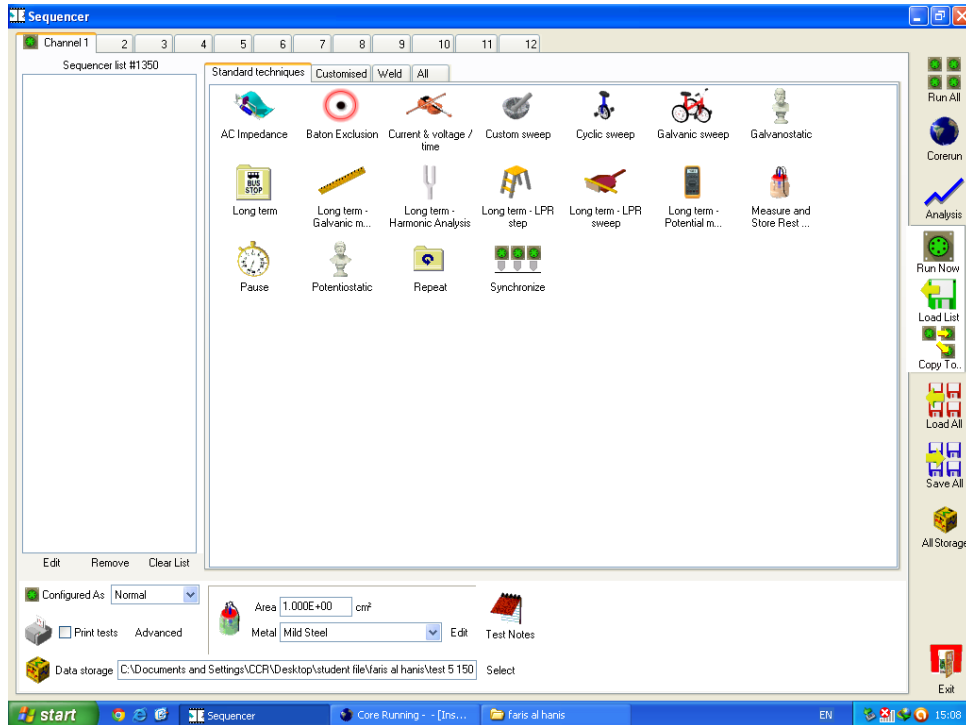


Figure 3.7: Step 1 - Open Sequencer software

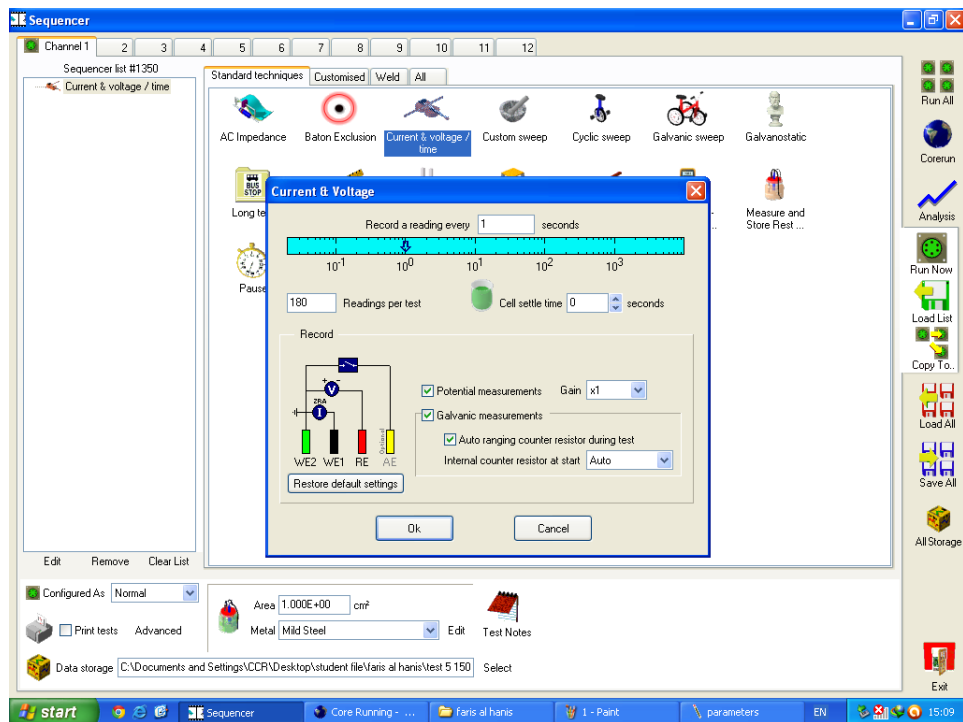


Figure 3.8: Step 2 - Click "Current & Voltage/ time" button & click "OK"

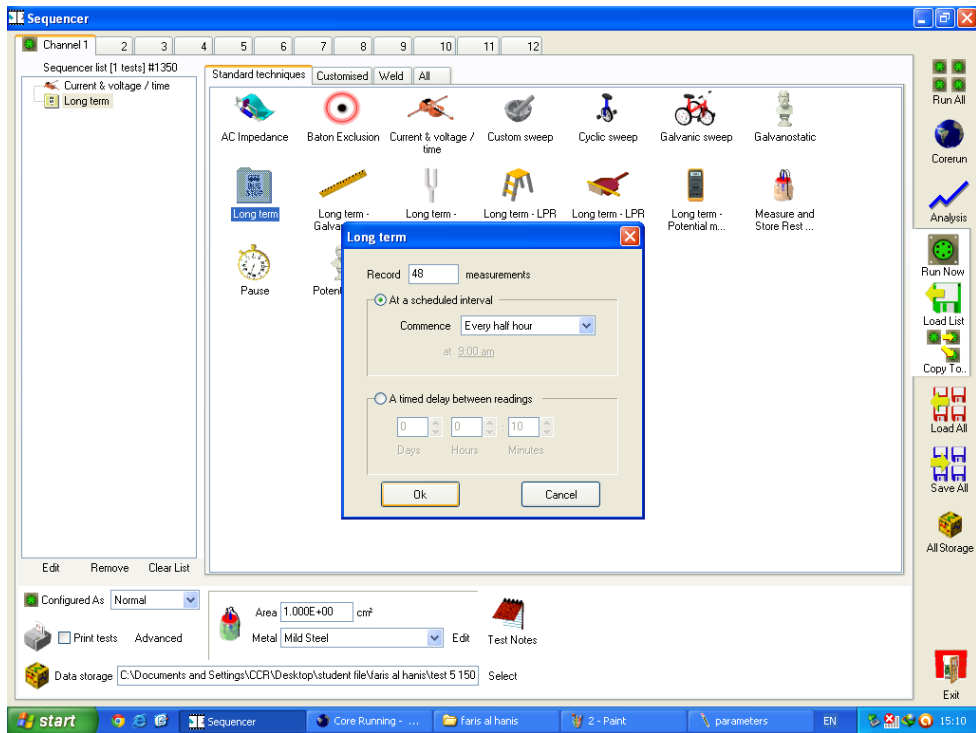


Figure 3.9: Step 3 - Click "Long Term" button and put desired amount of measurement

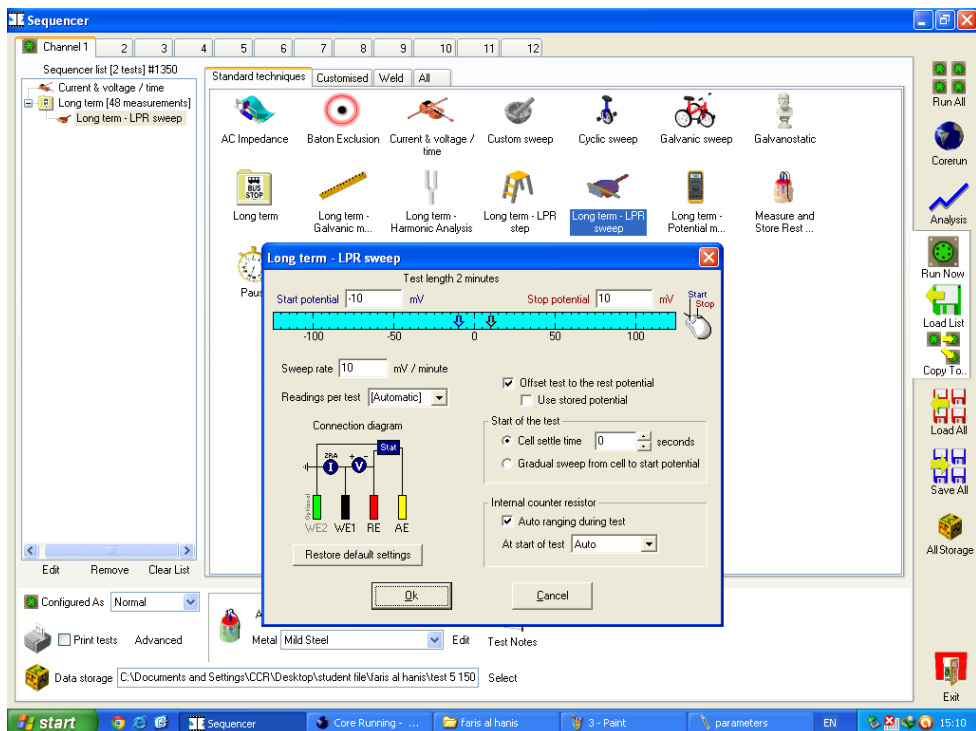


Figure 3.10: Step 4 - Click "Long term - LPR sweep" button and click "OK"

Next, Click button "Run Now" to run the experiment. Then, Potential (E) vs log current (i) plots are recorded at a sweep rate 10mV/min. Finally, data obtained is converted into excel to get the corrosion rate data.

### 3.7 Characterization methods

These carbon steel specimens were immersed in various test solutions for a period of 24 hours. After 24 hours, the specimens were taken out, sprayed with ethanol and dried. The nature of the film formed on the surface on the metal specimens were analyzed by the several surface analytical techniques. Microstructure observation and image capturing of the samples are to be performed using Scanning Electron Microscope (SEM). For identification of the compound, X-Ray Diffraction (XRD) is applied.



Figure 3.11: Scanning Electron Microscope (SEM)



Figure 3.12: X-Ray Diffraction (XRD)

## 4 RESULTS AND DISCUSSIONS

### 4.1 Baseline corrosion rate

The baseline corrosion rate data for individual effect of CO<sub>2</sub> environment, corrosion inhibitor and biocide is conducted as below:

- Test 1 (Blank test)
- Test 2 and 3 (corrosion inhibitor only)
- Test 4A and 4B (biocide only)

#### 4.1.1 Test 1 (Blank Test)

Baseline experiments were conducted without corrosion inhibitor and biocide at 60°C and 1 Bar CO<sub>2</sub>, to determine the corrosion rate in the absence of corrosion inhibitor and biocide. Figure 4.1 shows the average corrosion rate trend for experiments without corrosion inhibitor and biocide at 60°C and 1 bar CO<sub>2</sub>. An average corrosion rate of test 1 is 2.67 mm/yr.

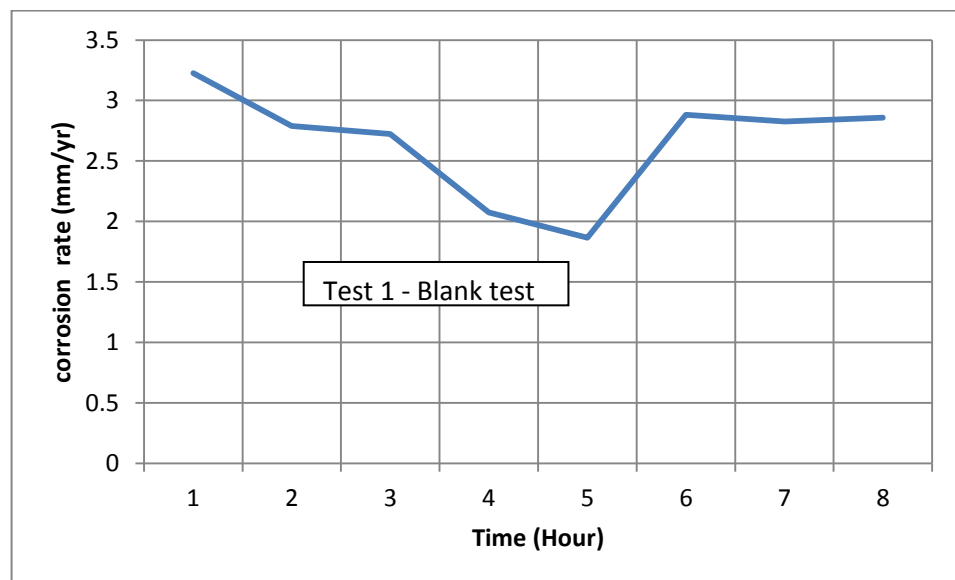


Figure 4.1: Average corrosion rate trend curve at 60°C and 1 bar CO<sub>2</sub>

#### 4.1.2 Test 2 (25 ppm Corrosion Inhibitor)

Figure 4.2 shows the effect of 25ppm CI injection on the corrosion rate at 60°C and 1 bar CO<sub>2</sub>. Corrosion rate reduced from 1.4mm/yr to 0.04mm/yr. An average of 0.06mm/yr obtained when injecting 25ppm CI. The efficiency of 97.1% corrosion inhibition was recorded.

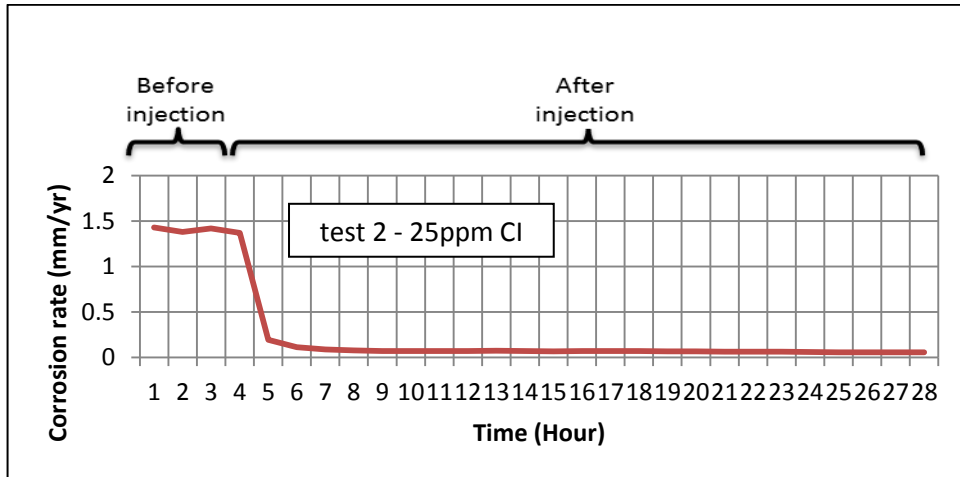


Figure 4.2: Effect of 25ppm CI injection at 60°C and 1 bar CO<sub>2</sub>

#### 4.1.3 Test 3 (12.5 ppm corrosion inhibitor)

Figure 4.3 shows the effect of 12.5ppm CI injection on the corrosion rate at 60°C and 1 bar CO<sub>2</sub>. Corrosion rate reduced from 2.0mm/yr to 0.08mm/yr. An average of 0.11mm/yr obtained when injecting 12.5ppm CI. The efficiency of 96% corrosion inhibition was recorded.

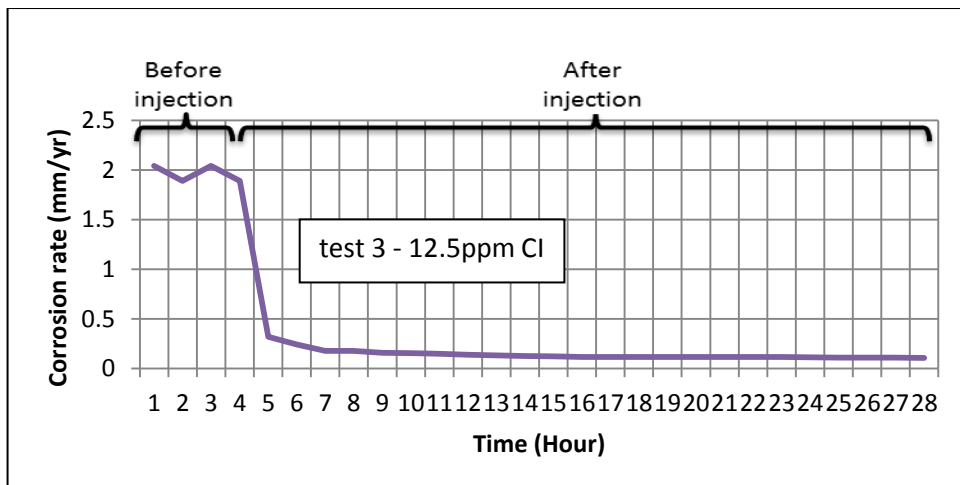


Figure 4.3: Effect of 12.5ppm CI injection at 60°C and 1 bar CO<sub>2</sub>

#### 4.1.4 Test 4A (500ppm biocide)

Figure 4.4 shows the effect of 500ppm biocide on the corrosion rate at 60°C and 1 bar CO<sub>2</sub>. An average of 5.6mm/yr obtained when injecting 500ppm biocide. 500ppm biocide increased corrosion rate from 2.5mm/yr to 5.67mm/yr.

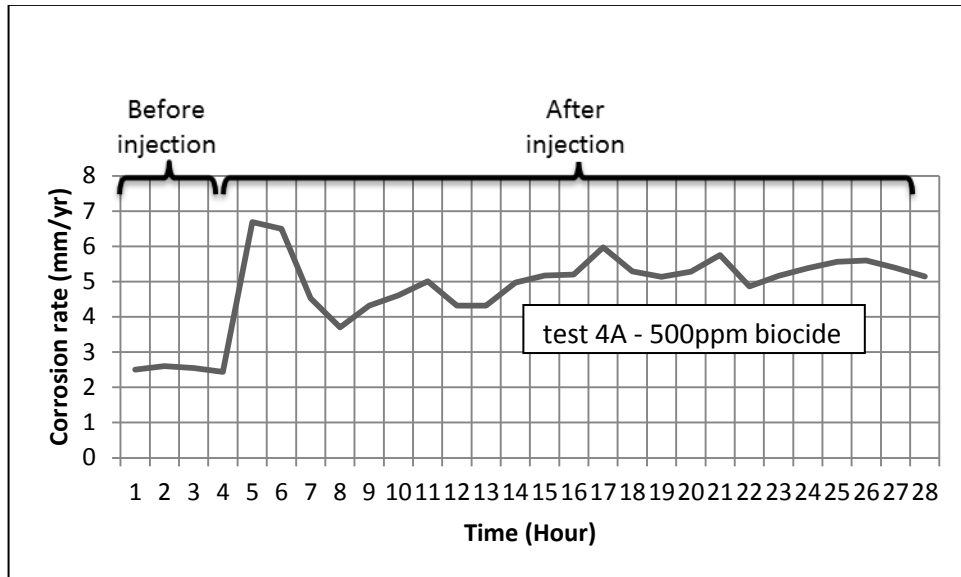


Figure 4.4: The effect of 500ppm biocide injection on corrosion rate at 60°C and 1 bar CO<sub>2</sub>

## 4.2 Compatibility mode

The effect of possible reactions of biocide and CI was studied based on injection sequence as below:

- Test 5A (Inject biocide first)
- Test 5B (Inject simultaneously)
- Test 5C (Inject CI first)

### 4.2.1 Test 5A (Inject biocide first)

Figure 4.5 shows the effect of injection method of injecting biocide first on the corrosion rate. Test 5A is a sequential dosing experiment and performed within 10 days period. 500ppm biocide was injected first in the solution. An amount of corrosion inhibitor or biocide or both was injected sequentially into the solution as per table 4.1. corrosion rate increased with the injection of 500ppm biocide from 2.95mm/yr to 6.85mm/yr. The subsequent injection of CI reduced the corrosion rate less efficiently at 25% efficiency. With 500ppm CI, the corrosion rate reduced to 0.86mm/yr, representing efficiency of 71%.

Table 4.1: Corrosion rate for Test 5A

Day	Corrosion Inhibitor (ppm)	Biocide (ppm)	Average corrosion rate (mm/yr)
1	Blank		2.95
2	-	500	6.85
3	25	500	2.20
4	125	500	1.88
5	225	500	1.18
6	275	500	0.98
7	300	500	0.90
8	350	500	0.81
9	450	500	0.87
10	500	500	0.86

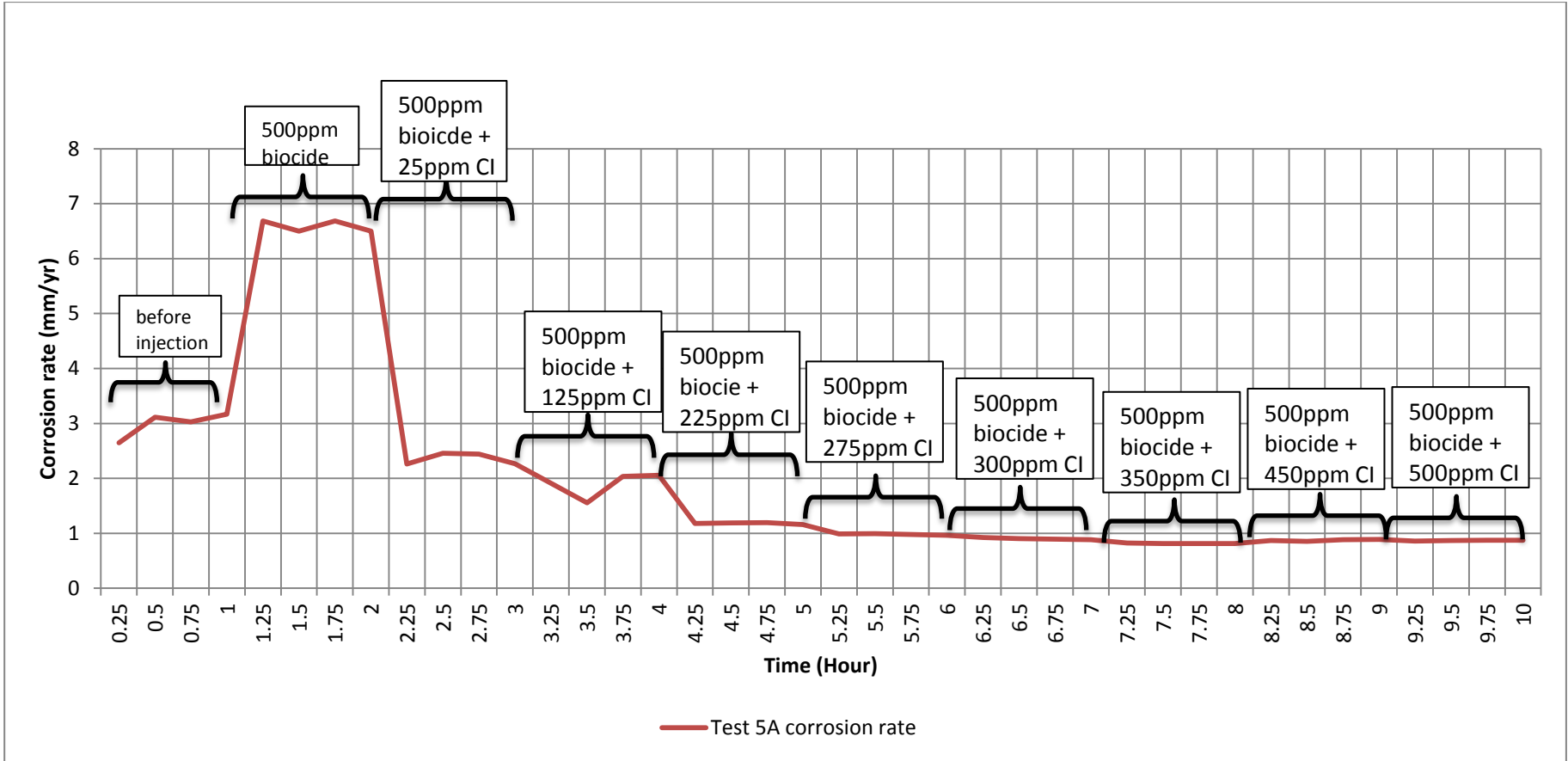


Figure 4.5: Effect of injection method of injecting biocide first on the corrosion rate.



#### 4.2.2 Test 5B (inject simultaneously)

Figure 4.6 shows the effect of injection method of injecting biocide and CI simultaneously on the corrosion rate. Test 5B is a sequential dosing experiment and performed within 10 days period. For test 5B, biocide and corrosion inhibitor were injected simultaneously in the solution. An amount of corrosion inhibitor or biocide or both was injected sequentially into the solution as per table 4.2. with 25ppm CI and 500ppm biocide, the corrosion rate reduced from 1.94mm/yr to 1.89mm/yr, representing efficiency of 2.5%. The sequential injections of CI (75-500ppm) reduced corrosion rate to 0.43mm/yr with 78% efficiency.

Table 4.2: Corrosion rate for test 5B

Day	Corrosion Inhibitor (ppm)	Biocide (ppm)	Average corrosion rate (mm/yr)
1	Blank		1.94
2	25	500	1.89
3	75	500	1.05
4	125	500	0.97
5	175	500	0.73
6	225	500	0.93
7	275	500	0.71
8	375	500	0.68
9	475	500	0.60
10	500	500	0.43

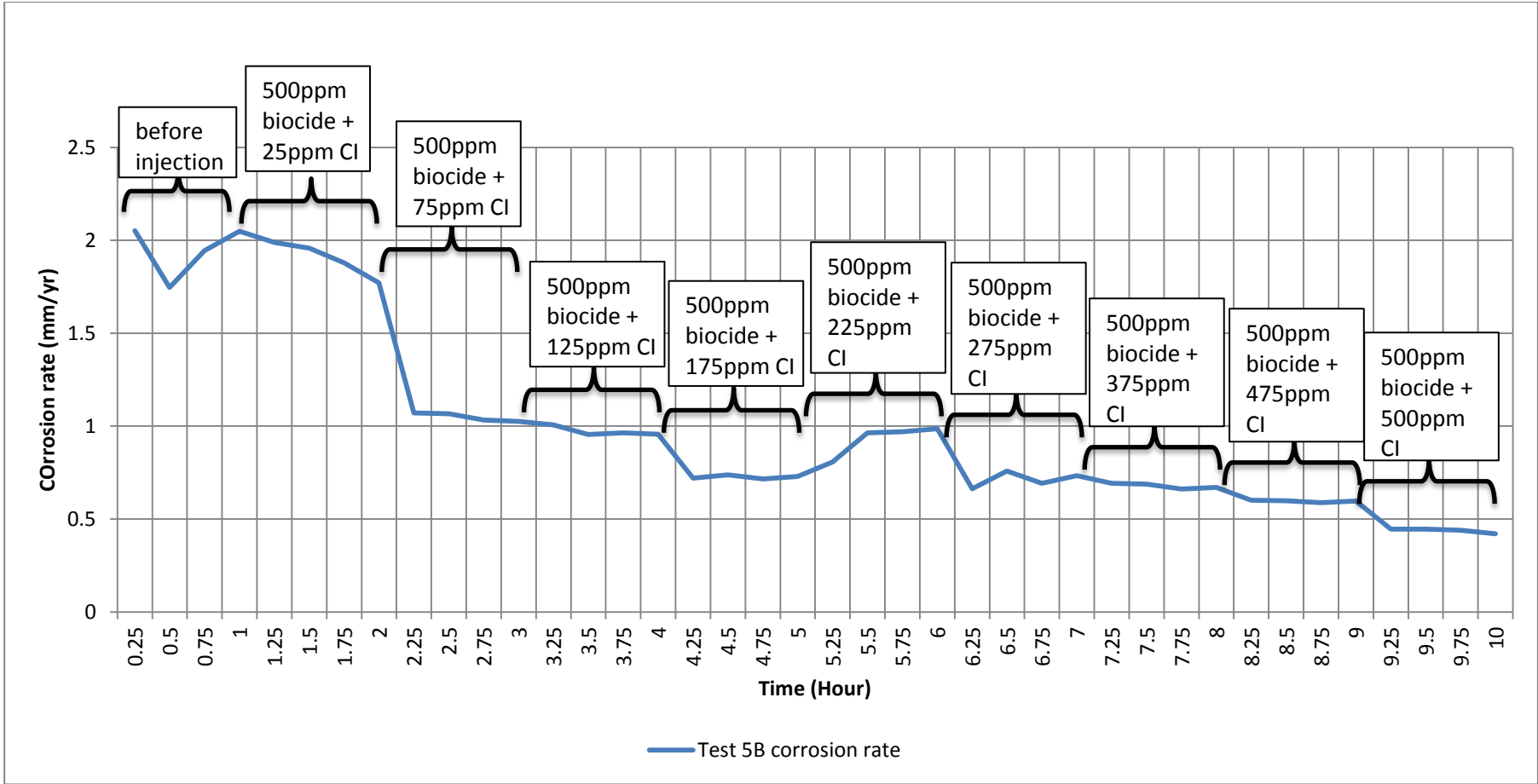


Figure 4.6: Effect of injection method of injecting biocide and CI simultaneously on the corrosion rate

### 4.2.3 Test 5C (inject corrosion inhibitor first)

Figure 4.7 shows the effect of injection method of injecting CI first on the corrosion rate. Test 5C is a sequential dosing experiment and performed within 10 days period. For test 5C, corrosion inhibitor was injected first in the solution. An amount of corrosion inhibitor or biocide or both was added into the solution as per table 4.3. With 25ppm CI, corrosion rate reduced from 4.17mm/yr to 0.18mm/yr. However, with the presence of 500ppm biocide, corrosion rate increased to 4.74mm/yr, higher than the biocide corrosion rate. The corrosion rate only reduced to 1.41mm/yr only with the injection of total 500ppm CI, representing of 66% corrosion efficiency.

Table 4.3: Corrosion rate for test 5C

Day	Corrosion Inhibitor (ppm)	Biocide (ppm)	Average corrosion rate (mm/yr)
1	Blank		4.17
2	25	-	0.18
3	25	500	4.74
4	75	500	4.29
5	125	500	3.12
6	175	500	2.56
7	275	500	2.03
8	375	500	1.71
9	475	500	1.51
10	500	500	1.41

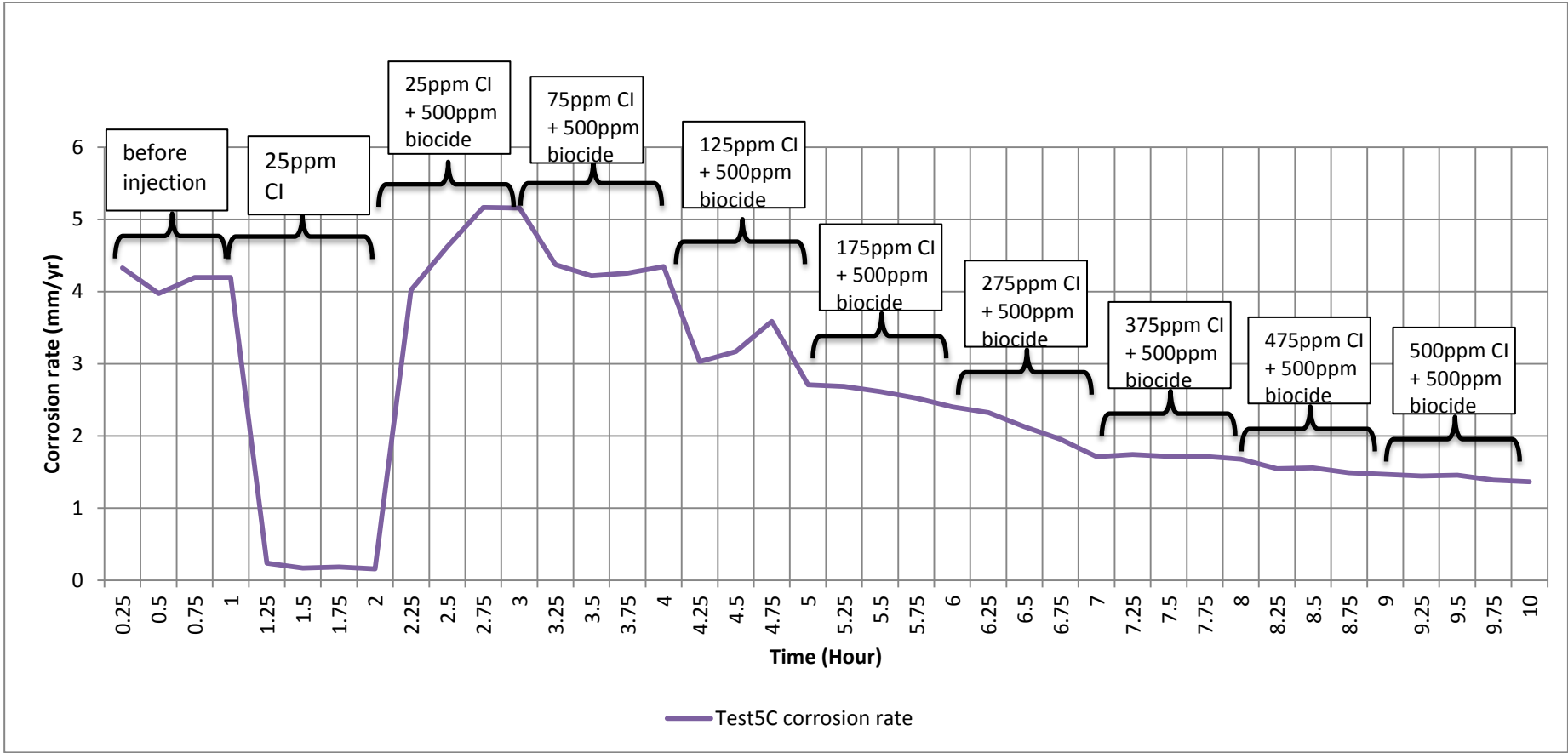


Figure 4.7: Effect of injection method of injecting CI first on the corrosion rate.

### 4.3 Corrosion rate comparison

#### 4.3.1 Individual effect

Figure 4.8 shows the comparison of corrosion rate trends of test 1, 2, 3 and 4A over a day. We see a variation in the corrosion rate and there is a direct relation between dosage of oil chemical (CI and biocide) and corrosion rate. Test 2 (25ppm CI) with the lowest corrosion rate has the highest corrosion efficiency of 97%. Test 4 (500ppm biocide) has the highest corrosion rate compare to others.

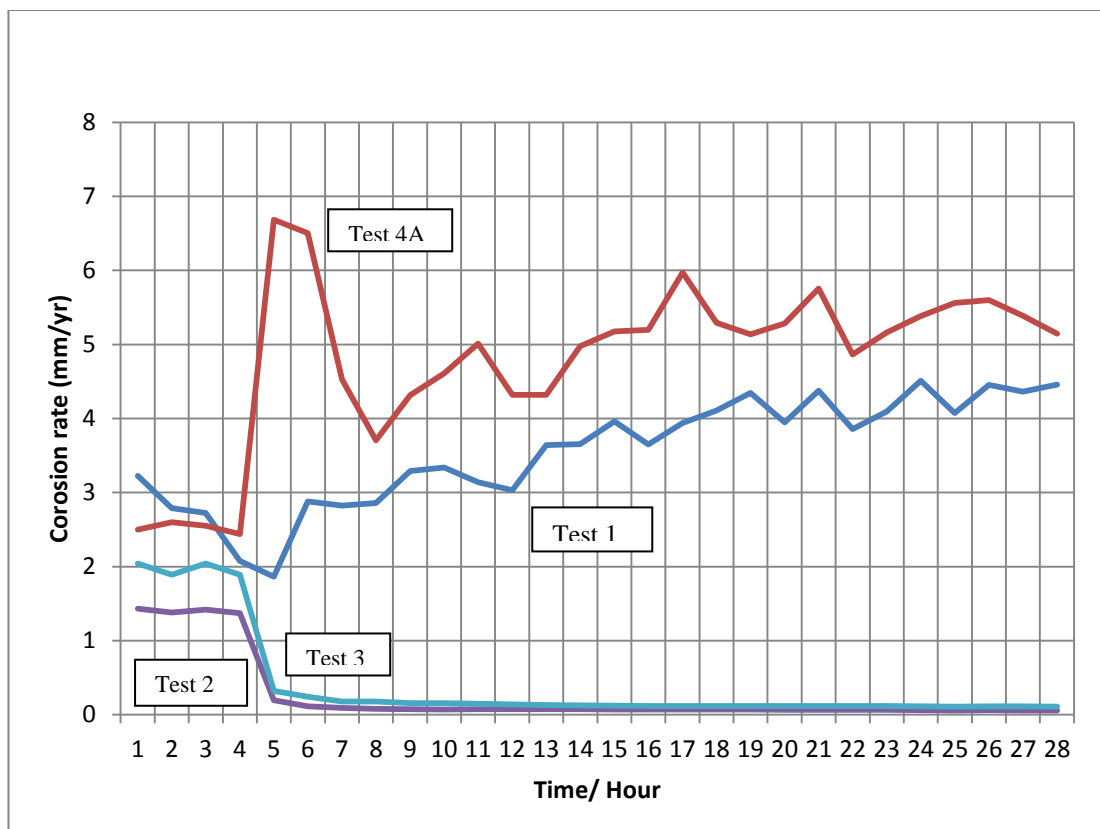


Figure 4.8: Comparison of corrosion rate trends of test 1, 2, 3 and 4A

### 4.3.2 Compatibility effect on corrosion rate

Figure 4.9 shows the comparison of corrosion rate trends of test 5A, 5B and 5C over 10 days. We see variation in injection methods and corrosion rate. There is a direct relation between injection method and final corrosion rate.

From figure 4.9, the final corrosion rate achieved by test 5A was 0.8mm/yr while 5B achieved final corrosion rate of 0.45mm/yr. Test 5C achieved final corrosion rate of about 1.3mm/yr. The lowest final corrosion rate was achieved by test 5B by means injecting corrosion inhibitor and biocide simultaneously at the beginning of the experiment.

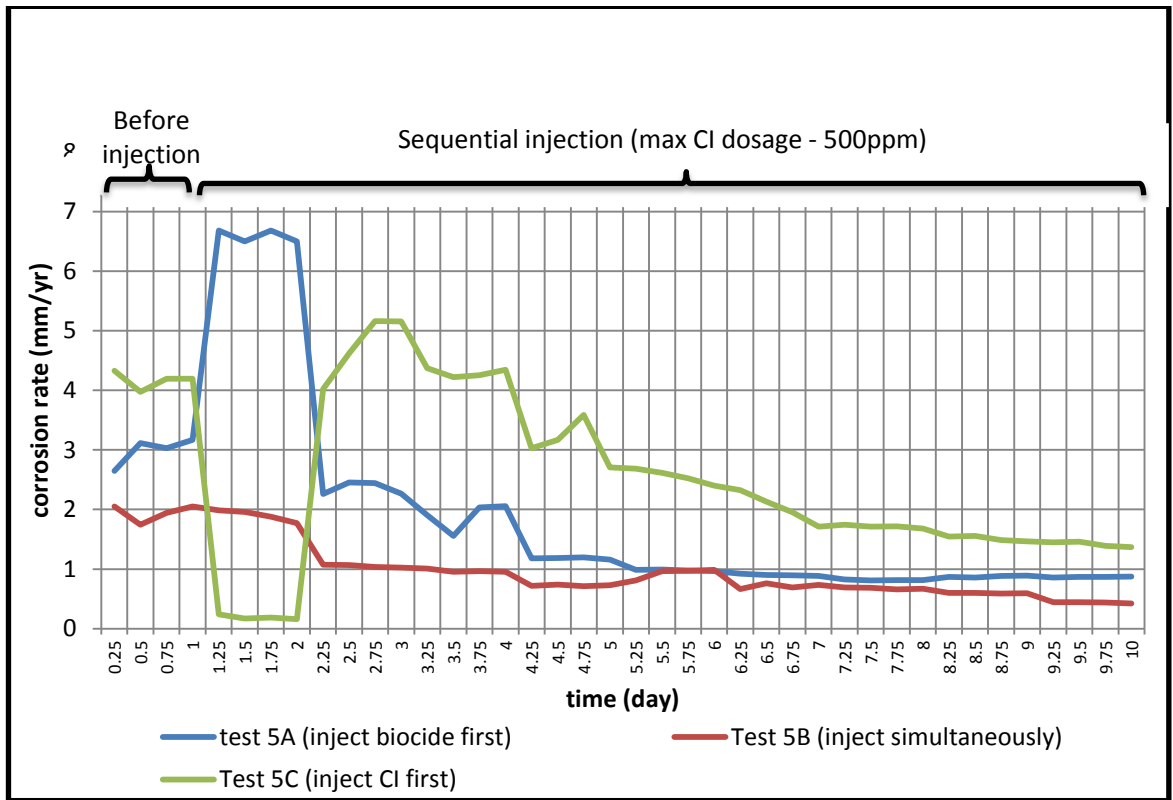


Figure 4.9: Comparison of corrosion rate change curves of test 5A, 5B and 5C over 10 days

## 4.4 Physical interaction of CI and biocide

### 4.4.1 Test 1 (Blank Test)

Figure 4.10 shows the general view of the surface at 500X magnification while Figure 4.11 shows the localized corrosion on the surface at 2000X magnification. Evidence of general corrosion was observed by existence of pitting corrosion as in figure 4.11. The surface was also covered partially with  $\text{FeCO}_3$  film.

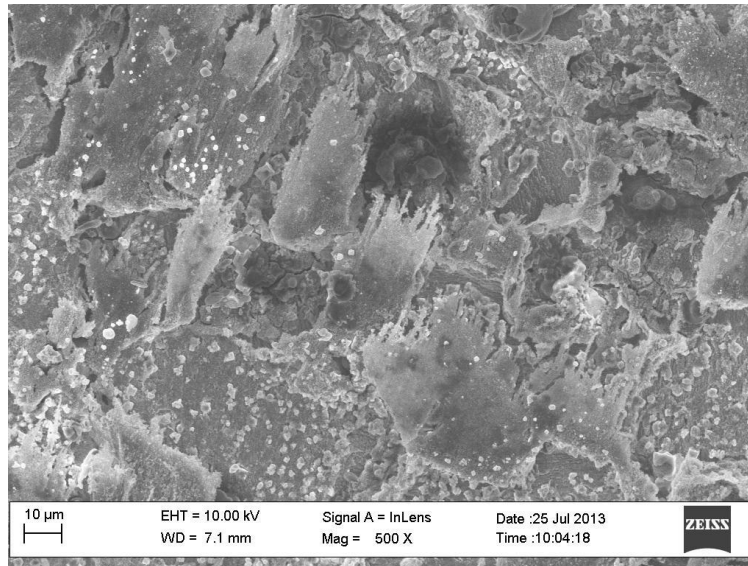


Figure 4.10: General corrosion SEM pictures (front view) of the test 1 specimen at 500 X, blank test, 60°C, 1 bar  $\text{CO}_2$

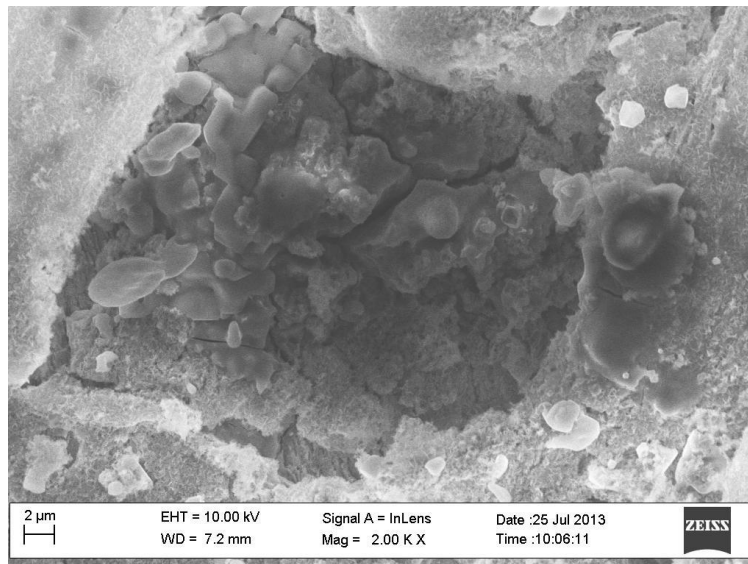


Figure 4.11: Pitting corrosion SEM pictures (front view) of the test 1 specimen at 2000 X, blank test, 60°C, 1 bar  $\text{CO}_2$

#### 4.4.2 Test 2 (25ppm corrosion inhibitor)

Figure 4.12 shows the general view of the surface at 500X magnification. No general corrosion was observed due to existence of CI film on the surface.

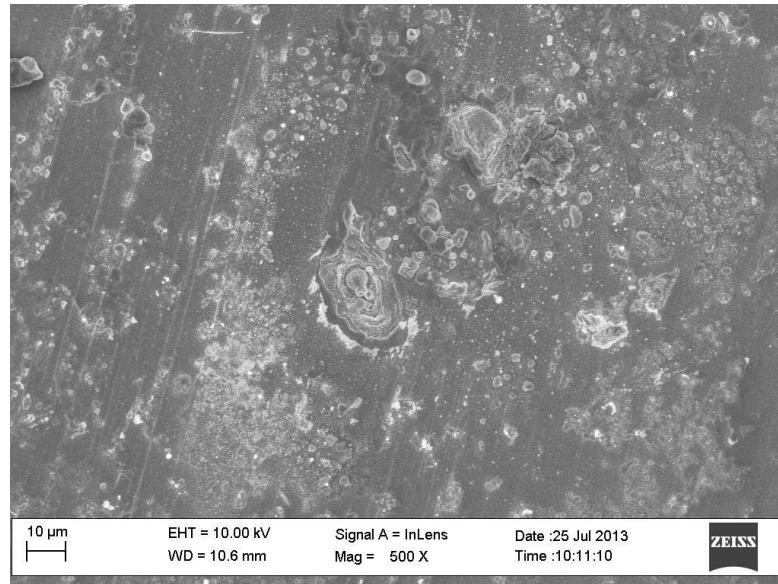


Figure 4.12: General SEM pictures (front view) of the test 2 specimen at 500 X, 60°C, 1 bar CO<sub>2</sub>

#### 4.4.3 Test 5B (corrosion inhibitor + biocide)

Figure 4.10 shows the general view of the surface at 500X magnification while Figure 4.11 shows the big crack on the surface at 2000X.

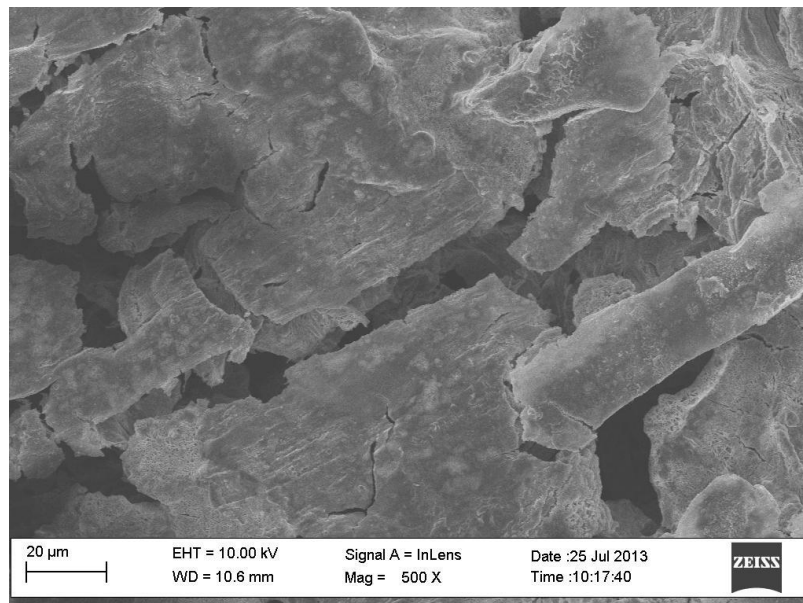


Figure 4.13: General SEM pictures (front view) of the test 5B specimen at 500 X, 60°C, 1 bar CO<sub>2</sub>



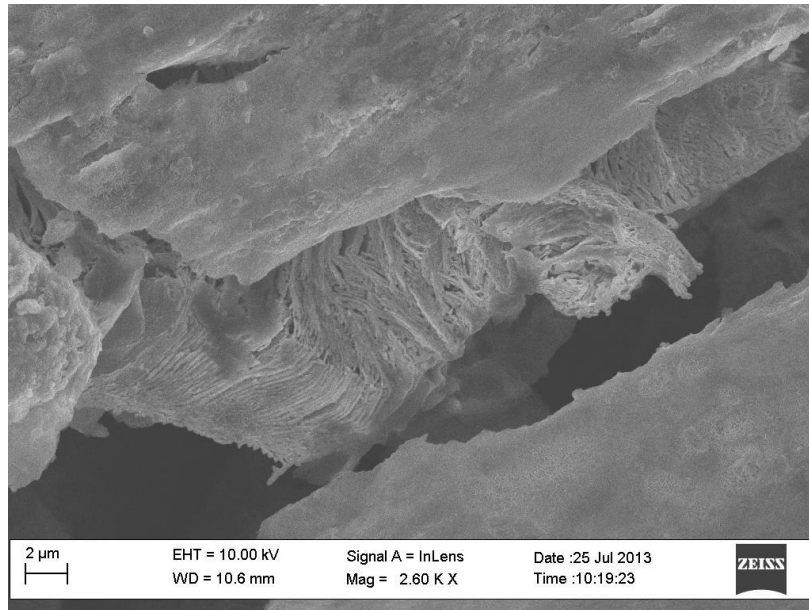


Figure 4.14: Crack SEM pictures (front view) of the test 5B specimen at 2000 X, 60°C, 1 bar CO<sub>2</sub>

#### 4.5 Chemical interaction between CI and biocide

The X-Ray diffraction patterns of the surface of the carbon steel ASTM A106 specimens in various test solution were given in figure 4.15. Peaks at  $2\theta = 13^\circ$ ,  $36.5^\circ$ , and  $51.5^\circ$  can be assigned to oxides of iron. The peaks due to iron appear at  $2\theta = 44.8^\circ$  and  $65.5^\circ$ . Thus, it was observed that in absence of corrosion inhibitor (Figure 4.15- label test 1), the surface of metal contains iron oxides of  $\text{Fe}_3\text{O}_4$ ,  $\text{FeOOH}$  and  $\text{FeCO}_3$ . The XRD patterns of inhibited surface (Figure 4.15 – label Test 2) shows the presence of iron peaks only, the peaks due to oxide of iron were found to be absent. For test 4 and 5 (Figure 4.15), it was observed that in presence of both corrosion inhibitor and biocide, the surface of metal contains iron oxides of  $\text{Fe}_3\text{O}_4$ ,  $\text{FeOOH}$  and  $\text{FeCO}_3$ .

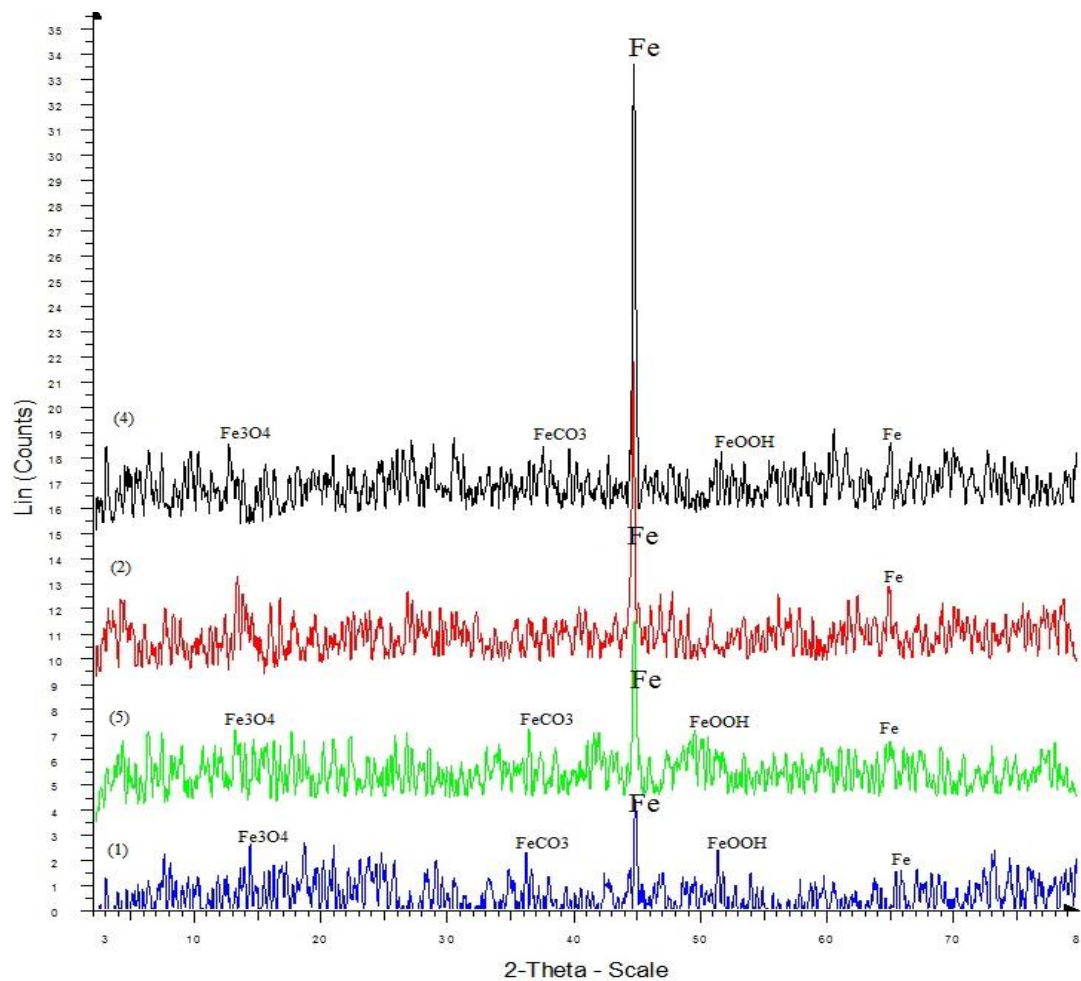


Figure 4.15: XRD superimpose results

## **5 CONCLUSION AND RECOMMENDATION**

As a conclusion, 25ppm CI reduced corrosion rate from 1.4mm/yr to 0.04mm/yr with 97% efficiency. The presence of biocide reduced the performance of CI. Thus, more dosage of CI required to increase inhibition efficiency. By using Scanning Electron Microscope (SEM), the existence of CI layer has been proved by no detection of general corrosion on the surface. The X-ray diffraction (XRD) patterns of inhibited surface shows the presence of iron peaks only, the peaks due to oxide of iron were found to be absent.

For future work recommendations, this project should be focused more on the effects of injection type onto corrosion rate. Possible mechanism can studied through X-ray photoelectron spectroscopy (XPS), Energy disruptive X-ray (EDX) and hardness test.

## 6 REFERENCES

- A. Rajasekar, N. Muthukumar. (2005). Role of corrosion inhibitor on bacterial corrosion in petroleum product pipelines. *Indian journal of chemical technology*, 567-575.
- E.J Akpabio, E.J Ekott and M.E Akpan. (2011). Inhibition and Control of Microbiologically Influenced Corrosion in Oilfields Materials. *Medwell Journal*, 59-65.
- Effects of Inhibitors on Corrosion Processes*. (n.d.). Retrieved from corrosion doctors: <http://corrosion-doctors.org/Inhibitors/Processes.htm>
- Gunasekaran, G. (2001). *Corrosion Science*. 1615-1626.
- Ibrahim, S. (2011). Corrosion Inhibitor in the Oilfield.
- Jordan, S. (1996). *Inactivation of Glutaraldehyde by Reaction with Sodium Bisulfite*. J. Tox. Envir. Health.
- Klechka, E. W. (january 2001). Use of Corrosion Inhibitor on the Trans Alaska Pipeline. *Supplement to Materials Performance*.
- Maruthamutu, S. (1996). Interference between biocides and inhibitor for cooling water system. *1st conference on water treatment chemicals*. Mumbai, India: NACE.
- Mathiyarasu, J. (1997). *Bull. Electrochem*. 161.
- Mohanan, S. (2002). *Role of Quaternary Ammonium Compounds & ATMP on Biocidal Effect & Corrosion Inhibition of Mild Steel & Copper*. Karaikudi, India: Central Electrochemical Research Institute.
- Mr. Nalli, K. (2010). *Corrosion and its Mitigation in the Oil and Gas Industry*. Petromin pipeliner.
- Rajendiran, S. (1998). *Anticorrosion Meth. Mater*. 338.
- Ramesh, S. (2003). Effect of inhibitors and biocide on corrosion control of mild steel in natural aqueous environment. *ScienceDirect*, 4547-4554.

- Randy K. Kent, M. P. (n.d.). *Frequently Asked Question about Microbiologically Influenced Corrosion (MIC)*. Retrieved 2013, from MDE Inc: [www.mde.com/publications/MIC\\_QA.pdf](http://www.mde.com/publications/MIC_QA.pdf)
- S. Rajendiran. (1999). Anticorrosion. *Meth. Mater.* 338.
- Schwanck, D. (1990). *App. Environ. Microbial.*
- Schweitzer, P. A. (2006). *Corrosion of Linings and Coating Cathodics and Inhibitor Protection & Corrosion Monitoring*. CRC Press.
- Shanthy, P. (2009). Corrosion inhibition and biocidal activity of a cationic surfactant. *Indian journal of chemical technology*, 328-333.
- Veres, A. (1992). *Brit. Corr. Journal*, 147.