

**Pipeline Corrosion in CO₂ Environment with the Presence of High Amount
Organic Acid**

by

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Supervised by

Associate Professor Ir. Dr. Mokhtar Che Ismail

Dissertation submitted in partial fulfillment of
the requirement for the
Bachelor of Engineering (Hons)
(Petroleum Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

Associate Professor Ir. Dr. Mokhtar Che Ismail

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

MOHAMAD IZZUDDIN BIN ISMAIL

ABSTRACT

The threat to the integrity of pipeline is not only from CO₂ corrosion but also due to the presence of organic acid which originates from reservoir and injection of acid during Enhanced Oil Recovery (EOR). Corrosion on pipelines is identified as the most common problem caused by the presence of acetic acid (HAc). However, the extent of corrosion problem due to the presence of high amount of HAc is not clear and not really documented. The objective of the project is to study the mechanism of CO₂ corrosion in presence of high amount of acetic acid and also determine the effects of CO₂ corrosion and high amount of organic acid on the integrity of pipelines. The role of high concentration of acetic acid on a carbon steel pipelines in CO₂ corrosion is investigated using Linear Polarization Resistance (LPR) techniques. A series of experiments are conducted to investigate the effect of various concentration of acetic acid on mild steel. A typical brines from North Sea oilfield is synthesized in laboratory to stimulate the field conditions. The oil field production parameters used in this project are typical of a North Sea oil field due to the presence of high concentration of acetic acid found in produced water. A brine similar to the composition of produced water is synthesized in laboratory to stimulate an oilfield brine. All experiments are conducted at fixed temperature, pressure and partial pressure. At the end of the experiments, the corrosion rate of each sample will be calculated using a series of equations. It was observed that general corrosion rate for all concentrations of acetic acid increased slightly with time and then decreased to a stable value. The corrosion rate also increased as the temperature increased. As a conclusion, the presence of dissociated for acetic acid is volatile and can significantly increase the corrosion rate on the mild steel.

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Nomenclatures

Abbreviation

| | |
|--|--------------|
| Centre of Corrosion Research | - CRR |
| Enhanced Oil Recovery | - EOR |
| Linear Polarization Technique | - LPR |
| Universiti Teknologi Petronas | - UTP |
| Electrochemical Impedance Spectroscopy | - EIS |
| Corrosion current density | - i_{corr} |

Symbols

| | |
|---|-------------|
| Acetic Acid | - HAc |
| Carbon Dioxide | - CO_2 |
| Hydrogen Sulfide | - H_2S |
| Iron | - Fe |
| Acetate | - Ac^- |
| Equilibrium constant for HAc dissociation | - K_{HAc} |
| Bicarbonate | - HCO_3^- |
| Silver/Silver Chloride | - Ag/AgCl |
| Iron (II) carbonate | - $FeCO_3$ |

CHAPTER 1

INTRODUCTION

1.1 Background Study

Downhole tubing, surface facilities, pressure vessels, and storage tanks in oil and gas production are subject to internal corrosion due to the presence of carbon dioxide (CO₂) and hydrogen sulfide (H₂S) in the gas phase. Organic acid that is found in formation water greatly contributes to the corrosion of reservoir. The most common organic acid found in reservoir is acetic acid (HAc).

Organic acid is not only found in reservoir, but often used during Enhanced Oil Recovery (EOR). When reservoir pressure decreases, production of hydrocarbon also reduces. To solve this problem, organic acids such as acetic acid and formic acid are pumped into the wells to stimulate production by increasing formation permeability in the near wellbore region.

There is a great concern among oil companies about the usage of organic acid during EOR on well integrity. A number of studies has been conducted to investigate this problem. According to Harris and Aime (1961), acetic acid can be effectively inhibited against almost all types of steel at elevated temperatures for extended periods of time. Organic acids are often used at high temperature when there is a need for a longer contact times between acid and pipe. Integrity of pipelines and tubing materials also can be seriously affected by CO₂ gases that already in reservoir or applied during CO₂ gas injection. Carbon steel, commonly used and most preferred material of pipelines, has a tendency to corrode in the presence of CO₂. Therefore, a research need to be conducted to fully understand this problem and selection of material is justified.

Thus, it is important to know that organic acid is not only present in formation water, but also widely used during EOR phase. There is a possibility of presence of high amount organic acid in process fluid. Therefore, in this study, the corrosion behavior of carbon steel in CO₂ environment with high amount of organic acid will be investigated. The effects are to be incorporated in laboratory study using a real pipeline material under reservoir conditions so that a reliable results can be achieved.

1.2 Problem Statement

The presence of high amount of acetic acid in formation water can cause severe corrosion to mild steel material. The material also can be seriously affected by acidization treatment during EOR employment.

1.3 Objectives

The objective of this research is to investigate the effects of high amount organic acid on mild steel.

As a whole, the project's objectives are as follow:

1. To study the mechanism of carbon dioxide (CO₂) corrosion in presence of high amount acetic acid.
2. To investigate the effects of CO₂ corrosion and high amount of organic acid on well integrity.

1.4 Scope of Study

The scope of the study is basically divided into two phases. The first phase of the study is working on literature review in order to gather information regarding selected project. During experimental phases, most of the study will be carried on laboratory. The experiment will be based on varying the concentrations of organic acid and figuring its effects on carbon steel pipelines. The main technique used in the study to measure the corrosion rate is Linear Polarization Resistance (LPR). All experiments will be conducted in standard glass cell setup.

1.5 Relevancy of the Research

Water and carbon dioxide – produced or injected for secondary recovery can cause severe corrosion to completion strings. Acid that is used to reduce formation damage around the well or to remove scale is known to cause a harm on metal. Corrosion caused by organic acid in oil and gas industry has caused numerous problems to oil companies. The question is how significant the effects of high concentration of organic acid on the reservoir pipelines. This research is basically to observe the problem caused by the presence of acetic acid in CO₂ environment and at the end of the study, come up with

recommendations to mitigate the problem. This study seems to be fit as a platform for the author to apply his knowledge and skills in solving industry problem. The outcome of this research is deemed crucial in providing better information regarding behavior of corrosion with high amount of acetic acid.

1.6 Feasibility of the Research

This research is feasible to complete within the timeframe which in 2 semesters. This project requires execution a number of laboratory tests that could be done at Universiti Teknologi PETRONAS (UTP) laboratories or at any corrosion monitoring laboratory outside the university. The proposed methods and equipment are feasible and available and objectives of the project can be achieved within the timeframe given.

CHAPTER 2

LITERATURE REVIEW

2.1 Presence of Organic Acid in Formation Water

Formation water is water that formed naturally within the pores of rock and important medium for hydrocarbon generation and migration. The long term contact of formation waters with oil and gas must leave some organic components in the formation waters and the chemical composition of formation water is closely related to the formation of oil and reservoirs. The water may contain dissolved gases, such as carbon dioxide (CO₂) and hydrogen sulfide (H₂S), nitrogen, organic acids, sulfur-reducing bacteria, dissolved and suspended solids and traces of hydrocarbon compounds (Abdou et al., 2011). The most common organic acid found in reservoir is acetic acid (HAc).

In article published by Xianqing and Dujie (2003), they explored the characteristics of organic components in formation water using water samples taken from Ordovician Majiagou Formation in the central gas field of the Ordos Basin. The samples contain formic acid, acetic acid, propanoic acid and butonic acid acid. Generally, carboxylic acid is predominated by acetic acid (mainly 40% to 90%) and contains minor formic acid.

2.2 Roles of Acetic Acid in Well Stimulation and Completion

During drilling or completion operations, there is a high possibility of formation damage occurring due to pore throats blockage by solid and mud filtrate invasion. Both factors cause a reduction in reservoir permeability and lead to a decrease in oil production.

Acetic acid has been used in many years to solve the problem. It has many uses in well stimulation and mostly utilized as a perforating fluid. Acetic acid is adaptable as a perforating fluid in the completion of wells. According to Harris (1961), it can be assumed that acid enters each perforation as penetration into the formation is made. The acid will react with cement fines and hydrated clay such that those found in drilling mud thus regaining normal formation permeability.

In well stimulation, acetic acid is often utilized in limestone formation. Because of the different reaction rates between hydrochloric acid and acetic acid on limestone under

identical conditions, an attempt was made to utilize this difference in obtaining a significant retardation by blending the acids (Harris, 1961). Laboratory studies of a 50-50 blend revealed the reaction rate as shown in Figure 1. The acetic acid is pumped as a first-stage treatment followed immediately by a conventional hydrochloric acid treatment in which the theory is that the leading edge of the treatment will be considerably retarded, thus lessening the possibility of pumping spent acid.

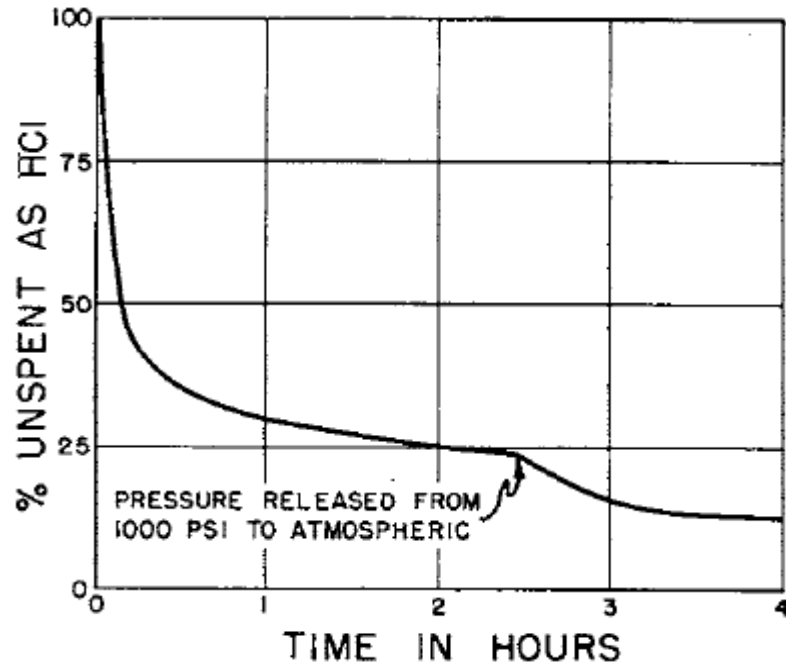
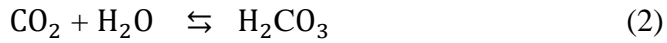


FIGURE 1 REACTION TIMES OF 50-50 ACETIC ACID-HYDROCHLORIC ACID MIXTURES WITH 0.1 INCH FRACTURE, 80°F, AND 1000 PSI

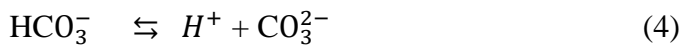
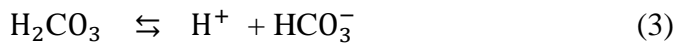
2.3 CO₂ Corrosion

Carbon dioxide (CO₂) corrosion is one of the most studied form of corrosion in petroleum industry and due to the fact that the crude oil and natural gas from the oil reservoir usually contain certain amount of CO₂. CO₂ corrosion on steel has been the subject of various interest in many years with reference to issues of pipeline failures in the oil and gas industry and transportation industry. De Waard and Milliams (1991) came up with a theory to explain the mechanism of CO₂ corrosion was the direct reduction of carbonic acid. Nescic et. al (1996) also have proposed a mechanistic models to predict CO₂ corrosion a few years later.

The following is a summary of reactions which define CO₂ corrosion. CO₂ dissolves in water to form carbonic acid through the hydration of water.

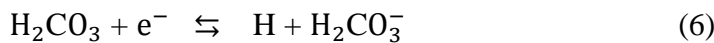


The carbonic acid then dissociates into bicarbonate and carbonate in two steps as in equations (3) and (4),

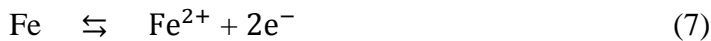


In their theory, De Waard and Milliams (1991) explained that the reduction of the undissociated acid molecule (H₂CO₃) occurs after it is absorbed onto the metal surface. As this is the rate determining step of process, the corrosion rate of the surface of metal is directly related to the concentration of the undissociated acid in solution.

The corrosion of carbon steel in CO₂ media has been investigated by many researchers and several mechanisms for CO₂ corrosion have been proposed. There are two possible cathodic reactions occur in the corrosion mechanism:

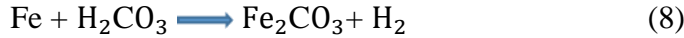


At anode, single anodic reaction occurs



Whether or not the direct reduction of carbonic acid (6) actually occurs on the metal surface is debated since it could be argued that carbonic acid would dissociate into a hydrogen ion faster than it could diffuse to the surface of the steel (George, 2003). If the reaction takes place in the boundary layer, it would only serve as an additional source of hydrogen ions and the hydrogen reduction (5) shall be the only cathodic reaction in the corrosion process.

The overall CO₂ corrosion reaction for Fe in an aqueous medium is



George (2003) also states that the solubility of iron carbonate in salt water decreases with an increase in system temperature. The protective film made up from the iron carbonate precipitate might occur depending on the solution composition, pressure, and temperature of the system.

2.4 Acetic Acid Corrosion

Acetic acid has influenced the rate of corrosion of carbon steel in oilfield brines containing CO_2 and has been the subject of numerous studies since the 1980's. In the case of carbon steel in brine, the dominating factors influencing the corrosion rate are the presence of acetate (Ac^-) and dissolved CO_2 gas.

Acetic acid dissociates into hydrogen and acetate ions according to equation 9: \rightleftharpoons



The equilibrium constant for HAc dissociation, K_{HAc} is:

$$K_{\text{HAc}} = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} \quad (10)$$

And depends on temperature according to Kharaka (1989):

$$K_{\text{HAc}} = 10^{-(6.66104 - 0.0134916 * T_k + 2.37856 * 10^{-5} * T_k^2)} \quad (11)$$

Hedges and McVeigh (1999) confirmed that the presence of Ac^- can significantly increase the rate of corrosion of carbon steel. They proposed that the corrosion rate can increase even if the pH increases. This observation does not match with most of the corrosion prediction models at that time as they successfully proved that Ac^- increases the corrosion rate more than bicarbonate (HCO_3^-) reduces it. The presence of Ac^- only affects the corrosion rate and not the corrosion mechanism. The mechanism in which HAc increases the corrosion rate may be explained by its ability to reduce the pH and solubilize Fe^{2+} , thus decreasing the iron carbonate film thickness. In summary they found the following:

- a. Bicarbonate ions decreased the corrosion rate (CR)
- b. Acetic acid decreases the pH and increases the corrosion rate.
- c. Sodium acetate ions increases the pH and increases the corrosion rate.

George (2003) investigated the effects of HAc on the cathodic and anodic reactions of CO_2 corrosion using linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and potentiodynamic sweeps. In his theory, he stated that HAc did not affect the charge of transfer mechanism of the cathodic reaction but did affect the limiting currents. When the temperature is set at 22°C, the HAc serves as a source of hydrogen ions and the HAc needs an 'activation time' for its effect to be measured.

CHAPTER 3

METHODOLOGY

3.1 Flow Chart

The project is mainly divided into two phases which are FYP 1 and FYP 2. Research on project is conducted during FYP 1 to further enhance understanding towards project title. During FYP 2, experimental works will be conducted and results will be collected and interpreted. Finally, all findings will be documented and submitted to supervisor for review.

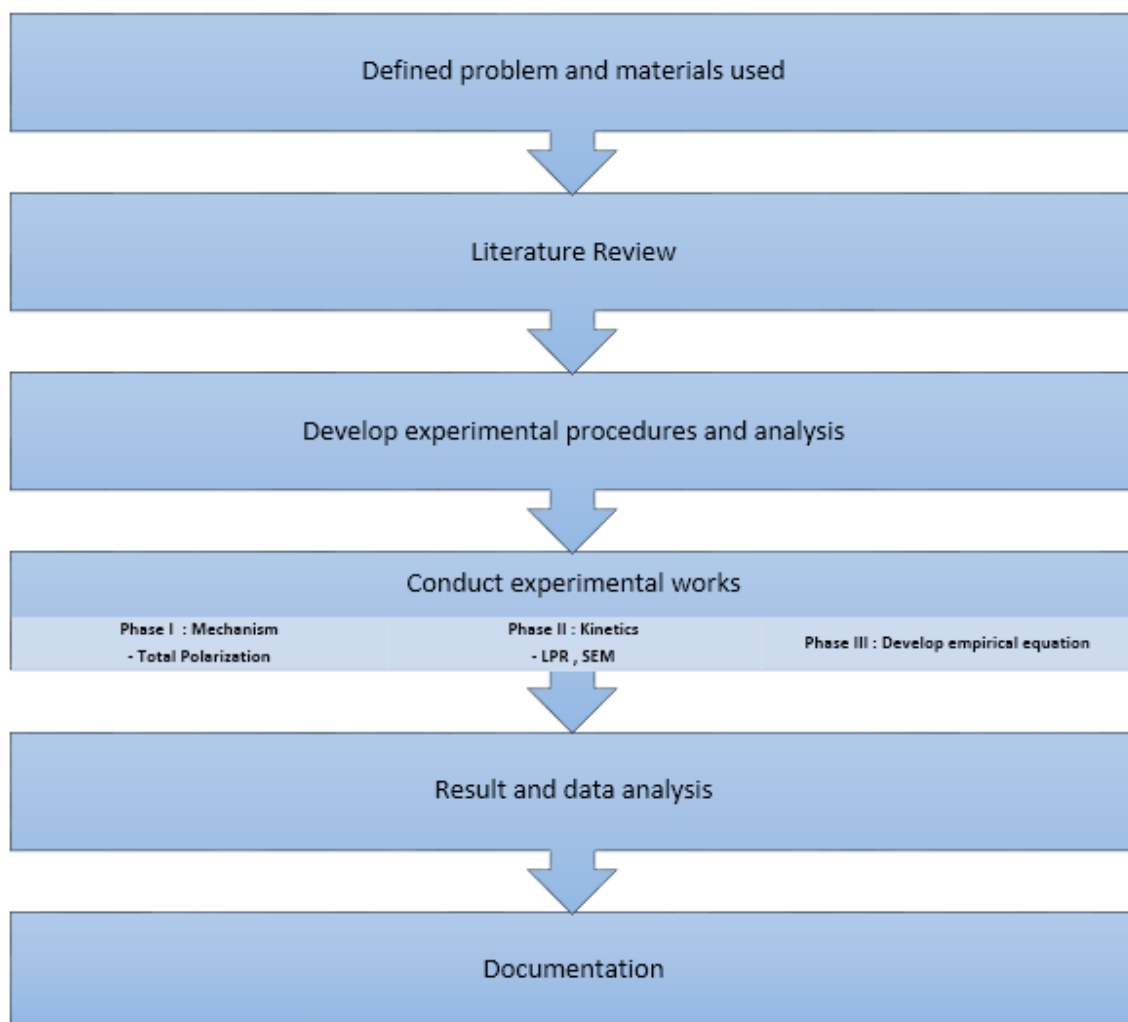


FIGURE 2 GENERAL METHODS INVOLVED IN THE PROJECT

3.2 Gantt Chart

TABLE 1 GANTT CHART FOR FYP 1

| Project Activities | Week | | | | | | | | | | | | | |
|----------------------------------|------|---|---|---|---|---|---|---|---|----|----|----|----|----|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| Project draft | | | | | | | | | | | | | | |
| Literature review | | | | | | | | | | | | | | |
| Preparation of extended proposal | | | | | | | | | | | | | | |
| Extended proposal submission | | | | | | | | | | | | | | |
| Experiment procedure development | | | | | | | | | | | | | | |
| Receiving Procument | | | | | | | | | | | | | | |
| Sample preparation | | | | | | | | | | | | | | |
| Proposal defense | | | | | | | | | | | | | | |
| Preparation of interim report | | | | | | | | | | | | | | |
| Interim report submission | | | | | | | | | | | | | | |

3.3 Key Milestones

TABLE 2 KEY MILESTONES

| FYP 1 | No. | Milestone | Date |
|-------|-----|--|------------------------|
| | 1 | Submission of Extended Proposal | 10 July 2013 (Week 8) |
| | 2 | Proposal Defense | 24 July 2013 (Week 10) |
| | 3 | Laboratory Equipment Familiarization | August 2013 |
| | 4 | Submission of Progress Report | August 2013 (Week 13) |
| FYP 2 | No. | Milestone | Date |
| | 1 | Completion of Phase I | Week 3 |
| | 2 | Completion of Phase II | Week 6 |
| | 3 | Completion of Phase III | Week 8 |
| | 4 | FYP Presentation | Week 10 |
| | 5 | Documentation and Submission of FYP Hardcopy | Week 13 |

3.4 Corrosion Monitoring Techniques

The main objective of corrosion monitoring is to ensure the design life is not being adversely affected or compromised by the threat of corrosion. It also is conducted to maximize the safety and economic operational life of a facility.

When conducting corrosion test, it is important not to rely on just one method. By using range of techniques, the best results will be obtained. Some corrosion measurement techniques can be used on-line, constantly exposed to the process stream, and a number of techniques provide off-line measurement, as determined in a laboratory analysis. Some techniques offer a direct measure of corrosion rate, such as metal loss of coupon by calculating its weight loss after exposure.

3.4.1 Linear Polarisation Resistance Technique (LPR)

The electrochemical technique, usually referred as Linear Polarization Resistance in industry, is the only corrosion monitoring method that allows the corrosion rate to be measured directly in real time.

The main principles of this method were first introduced by Stern and Geary in 1957. The measurement involves polarizing the metal of interest and measuring the resulting current. At small voltage perturbations (between 5mV and ± 30 mV), the current is linearly related to the voltage giving a constant called the polarization resistance (R_p).

$$R_p = \Delta E / \Delta i$$

Where: R_p – polarization resistance (ohms)

ΔE – potential difference (V)

Δi – change in current (A)

The polarization resistance can be converted into a corrosion rate using the Stern-Geary equation.

$$i_{\text{corr}} = B / R_p.A$$

Where: i_{corr} – corrosion current density ($A \text{ cm}^{-2}$)

B – Stern-Geary constant

A – Electrode area (cm²)

The corrosion current (I_{CORR}), generated by the flow of electrons from anodic to cathodic sites, could be used to compute the corrosion rate by the application of a modified version of Faraday's Law:

$$CR = 3.27 \times 10^{-3} \text{ icorr EW} / d$$

Where: CR – Corrosion rate in mm/year

icorr – Corrosion current density (A cm⁻²)

EW - Equivalent weight of the corroding metal (g)

d – Density of corroding metal (g/cm³)

3.4.2 The Electrochemical Cell

The cell have a number of purposes. It provides a mean to establish the environmental conditions under which the measurement is to be performed. Variables that can be manipulated throughout the experiment include the solution chemistry, temperature, and the surface condition. A stable reference electrode with known potential is used to measure and control the surface potential throughout the polarization studies.

There are three primary parts to the typical electrochemical cell. It includes the cell body, the electrodes, and the variables used to monitor and control the environment.

i) Cell Body

The body of the cell is important to contain the test environment, which could be aggressive or non-aggressive. Before selecting the material for the cell body, a consideration must be put into an account on the requirements of the experiment such as the operating temperature, pH, or dissolved oxygen content. Glass is normally used because it can handle most of the temperature, resistant to environments and high pH solution.

ii) Electrodes

Three electrodes are used in electrochemical cell – the working electrode, the counter electrode, and the reference electrode. The working electrode is the sample being used for the experiment in which for this case is the mild steel. The reference electrode provides a stable reference against which the applied potential may be accurately measured. The counter electrode or auxiliary electrode, is used to provide the applied current, and must be composed of highly corrosion resistant material. Stainless steel is used for this experiment.

iii) Environmental Control

Variables that can be controlled throughout the experiment include the temperature, the dissolved oxygen concentration, the solution chemistry, and the pH. Temperature control is achieved using an external heater or internal heating coil. Inert gases such as nitrogen and argon are typically used to reduce the dissolved oxygen concentration, while air is often bubbled through to maintain a high concentration. For this experiment, the solution chemistry is vary by changing the acetic acid concentration.

3.5 Experimental Set Up

In order to polarization scan on aqueous solution, a few components must be assembled and appropriately prepared. The first part is an electrochemical cell which contains both the metal to be investigated and the environment in which the polarization studies is to be performed. Before the experiment is started, the metal surface must be prepared such that the initial condition of the measurement is well defined and does not vary from test to test. The final part of the experiment is to identify the equipment capable of performing the measurement and acquiring data.

3.5.1 Specimen preparation before exposure

- a) The specimen is cut into rectangular shapes with dimension 1.0 cm and 1.0 cm (Refer Figure 4).
- b) Before specimen is ready for experiment, the metal must be coated with resin. Copper wire is used as conductor and is attached at the top of the specimen. Epoxy resins and hardeners are mixed together with ratio 5:1 and then poured into the specimen. The specimen is left to dry for about 24 hours before further use (Refer Figure 5).
- c) The specimen is grinded with emery papers of different grades starting with 240 grits follow by 400 grits and 600 grits (Refer Figure 6). For further guidelines, ASTM G1 is referred for experimental procedures on grinding process.
- d) The specimen is rinsed with acetone and deionized water. Then, it is left to dry in a desiccator.

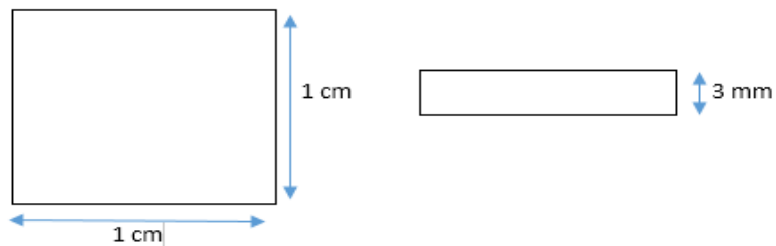


FIGURE 3 SPECIMEN DIMENSION



FIGURE 4 SPECIMEN AFTER MOUNTED IN EPOXY



FIGURE 5 GRINDING MACHINE

3.5.2 Test procedures

- a) All experiments are conducted in a standard glass cell. The basic solution inside the glass cell contained 1 liter of synthetic brine (formulate to match the formation water).
- b) The solution is purged with carbon dioxide (CO_2) for at least one hour. The temperature of the solution is set at 60°C and heated using hot plate stirrer. The temperature is continuously monitored during early part of experiment until the reading is stable.
- c) Three electrodes cell assembly are used. All electrodes are immersed into the test solution. The working electrode is mild steel while Silver/ Silver Chloride (Ag/AgCl) is used to as the reference electrode and stainless steel electrode as auxiliary electrode (Refer Figure 7).
- d) Reference electrode is connected with the test solution. Polarization studies is carried out using an Electrochemical Work Station Autolab Potentiostat. Potential (E) vs current (i) plots are recorded at a sweep rate ± 10 mV/min.
- e) Corrosion rate reading is set at 15 minutes interval. 4 readings are taken for each hour. Each test will last for 24 hours and 96 readings will be taken during that period.
- f) All readings are recorded and corrosion rate graph will be plotted at the end of the experiment.

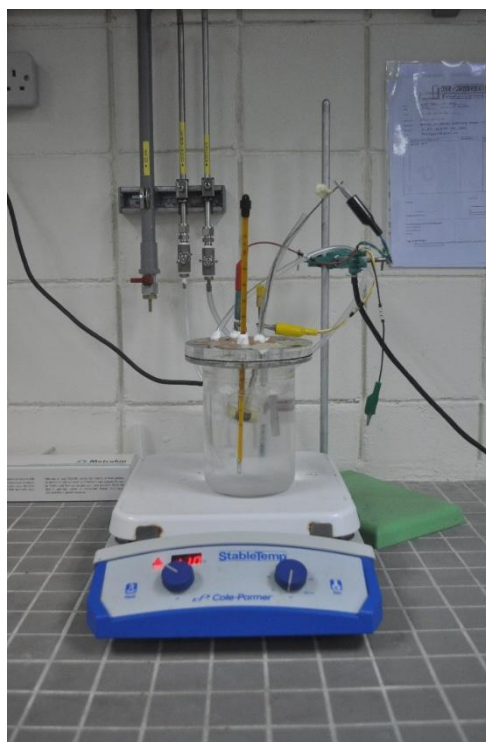


FIGURE 6 GLASS CELL SET-UP

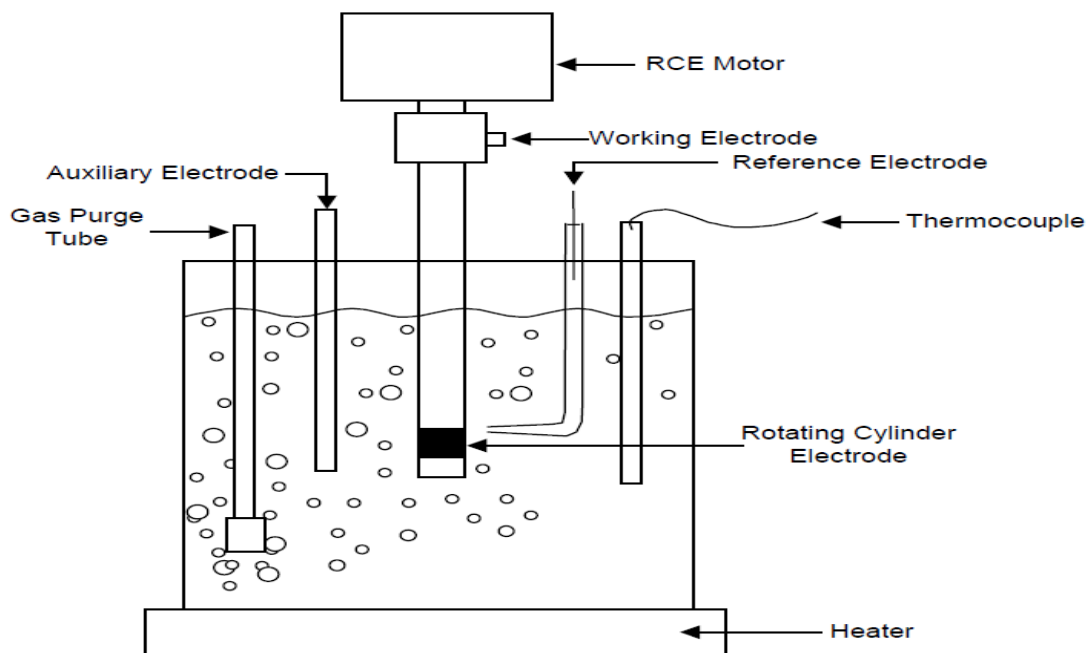


FIGURE 7 SCHEMATIC DIAGRAM FOR GLASS CELL SET-UP

3.6 Test Parameters and Matrices

The oil field production parameter used in this project will be based on typical of a North Sea oil field. The production contains 0.47 mol% CO_2 and no H_2S . Other parameters include:

- ❖ $P_{res} = 20$ MPa
- ❖ $T_{res} = 90^\circ C$
- ❖ Acetate concentration = 455 ppm

By referring the above data, a series of experiments will be conducted to evaluate the effect of high concentrations of acetic acid on the pipelines. The baseline data for the experiments are listed below:

- a. CO_2 corrosion
- b. CO_2 partial pressure = 1 bar
- c. Temperature = $60^\circ C$
- d. Material = Mild Steel A106 Grade B
- e. Software = ACM Sequencer V. 5.1.4
- f. Duration = 96 measurements (24 hours) for each solution

Formation water composition is as shown in Table 1. The brine used for this experiment will be formulated based on the composition in Table 1. Test matrix for corrosion test is listed below:

- i) Baseline. Only formation water with no acetic acid concentration.
- ii) Test Matrix A - Formation water + 250 ppm Acetic Acid.
- iii) Test Matrix B - Formation water + 500 ppm Acetic Acid.
- iv) Test Matrix C - Formation water + 1000 ppm Acetic Acid.
- v) Test Matrix D - Formation water + 1000 ppm Acetic Acid ($80^\circ C$)

TABLE 3 FORMATION WATER COMPOSITION

| Formation Water Composition (North Sea Oil Field) | | |
|--|------|------------------------------|
| Dissolved Solids | | Concentrations (mg/l) |
| Cations | | |
| Sodium | Na | 29910 |
| Potassium | K | 325 |
| Calcium | Ca | 2120 |
| Magnesium | Mg | 540 |
| Barium | Ba | 270 |
| Strontium | Sr | 600 |
| Iron(total) | Fe | 2.5 |
| Dissolved Iron | Fe | <0.05 |
| Anions | | |
| Chloride | Cl | 52110 |
| Sulphate | SO4 | 10 |
| Carbonate | CO3 | 0 |
| Bicarbonate | HCO3 | 570 |
| Hydroxide | OH | 0 |
| Additional Elements | | |
| Lithium | Li | 4 |
| Silicon | Si | 21 |
| Phosphorus | P | <0.15 |
| Boron | B | 71 |
| Aluminium | Al | <0.5 |
| Volatile Fatty Acids | | |
| Acetate | | 455 |
| Propionate | | 47 |
| Butyrate | | <10 |

TABLE 4 TEST MATRICES

| | | | | | |
|-----------------------------|------------------------------|------------|------------|-------------|--------------------|
| Temperature | 60°C | | | | |
| Pressure | 1 bar | | | | |
| Concentrations (ppm) | Baseline (none added) | 250 | 500 | 1000 | 1000 (80°C) |

CHAPTER 4

RESULT & DISCUSSION

4.1 Experimental Results

A series of standard glass cell tests were conducted in produced fluids with acetic acid concentration range from 250-1000 ppm. The test fluids were synthetic produced water and formulated to match a real produced water from North Sea oil field. Working electrode from mild steel was used to electrochemically measure corrosion rates.

A. Baseline

No acetic acid was added into the solution. The test solution was entirely composed of synthetic formation water. The temperature was set at 60°C and CO₂ partial pressure is at 1 bar. Corrosion rate reading was taken every 15 minutes and duration of each test set at 24 hours. Overall 96 readings were taken.

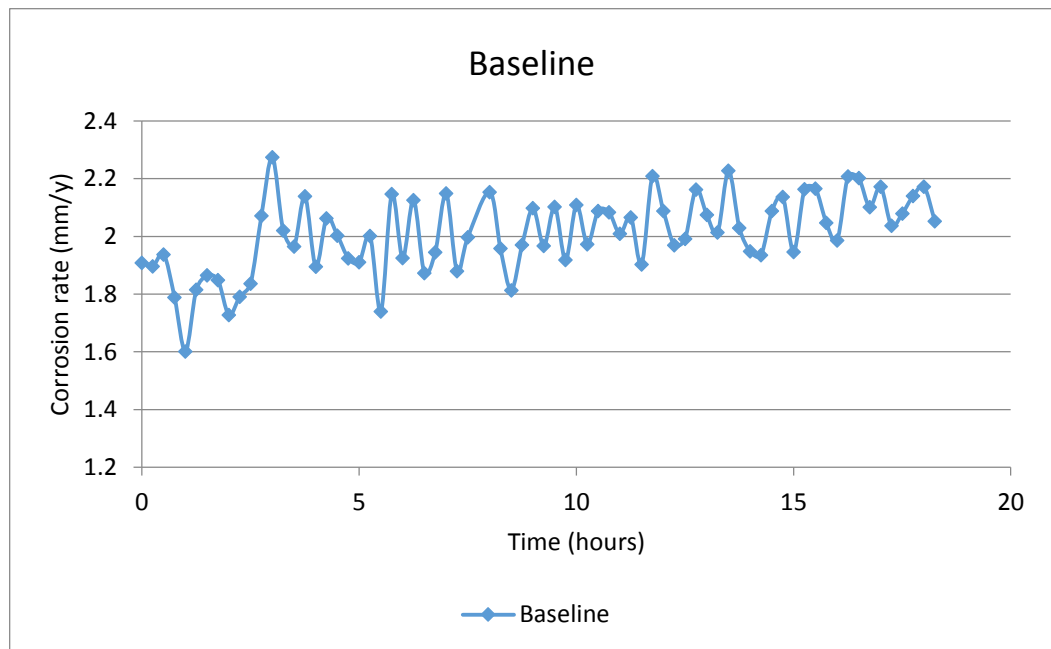


FIGURE 8 CORROSION RATE OF BASELINE SOLUTION

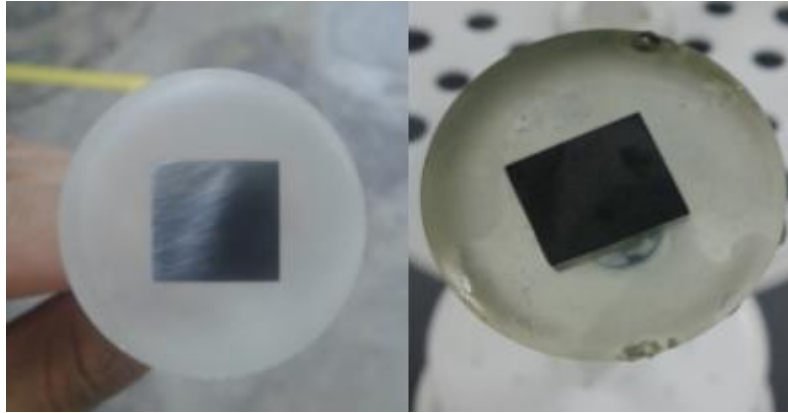


FIGURE 9 SAMPLE BEFORE AND AFTER POLARIZATION

Figure 9 shows the effect of formation water on the corrosion rate of mild steel. The measure corrosion rates were ranging from 1.8 to 2.2 millimeter per year. The trend line of the graph is increasing for the first 5 hours and stable after that.

B. Test Matrix A - Formation water + 250 ppm Acetic Acid

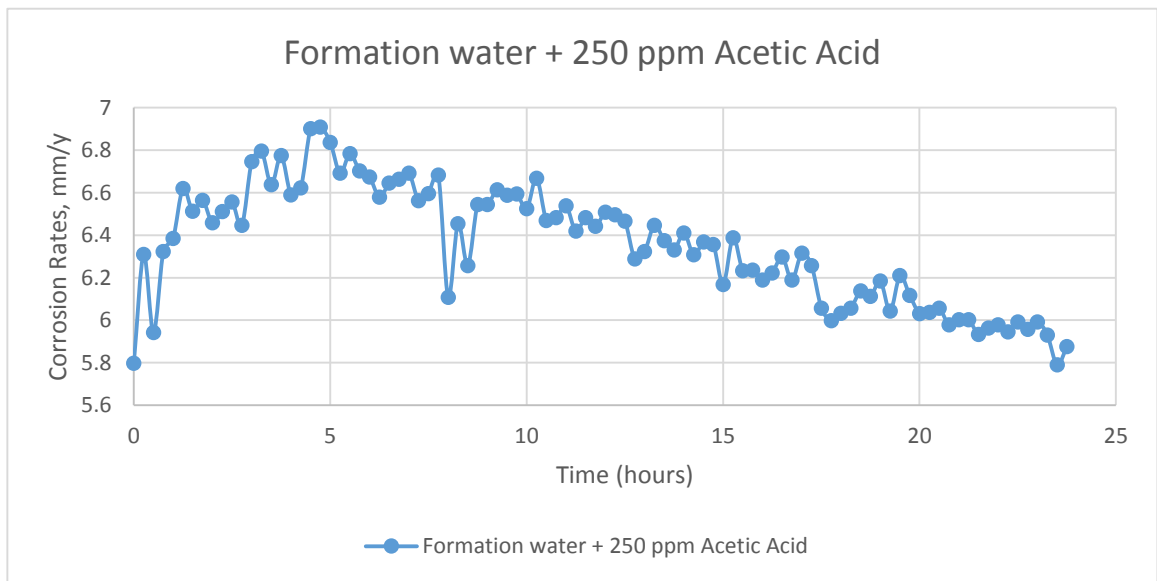


FIGURE 10 CORROSION RATE OF TEST MATRIX A

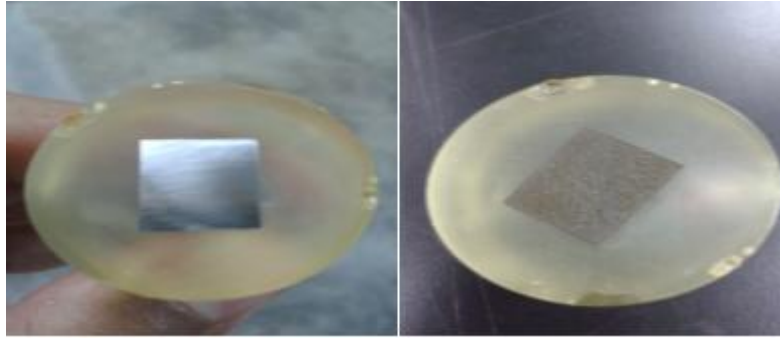


FIGURE 11 SAMPLE BEFORE AND AFTER POLARIZATION



FIGURE 12 SAMPLE BEFORE AND AFTER POLARIZATION

Figure 11 shows the effect of Test Matrix A on the corrosion rate of mild steel. The graph shows a high reading of corrosion rate which is around 5.8 to 6.8 mm/y. There is a high increment of corrosion rate compared to previous test (baseline solution).

C. Test Matrix B – Formation Water + 500 ppm Acetic Acid

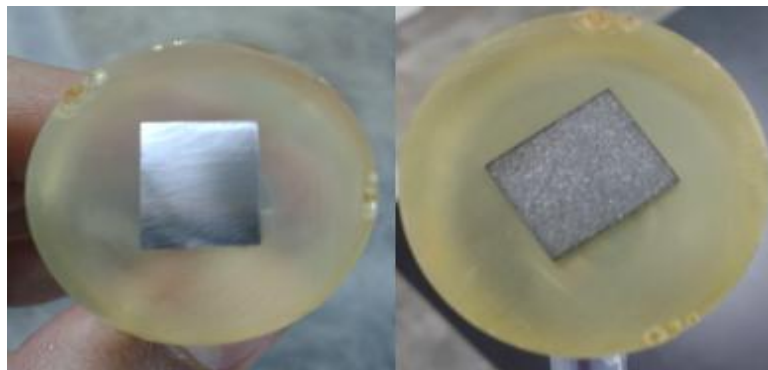


FIGURE 13 SAMPLE BEFORE AND AFTER POLARIZATION

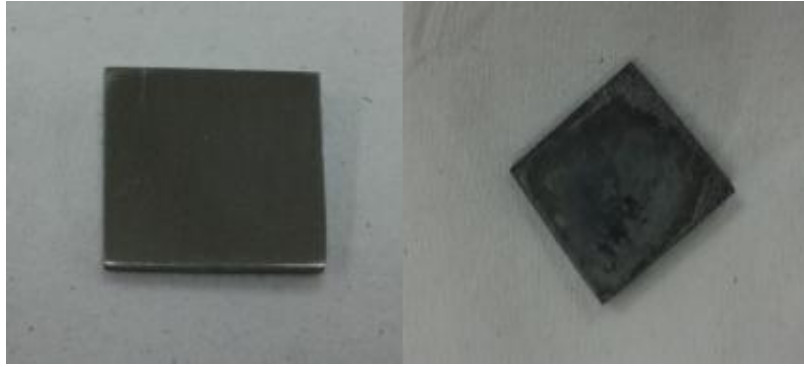


FIGURE 14 SAMPLE BEFORE AND AFTER POLARIZATION

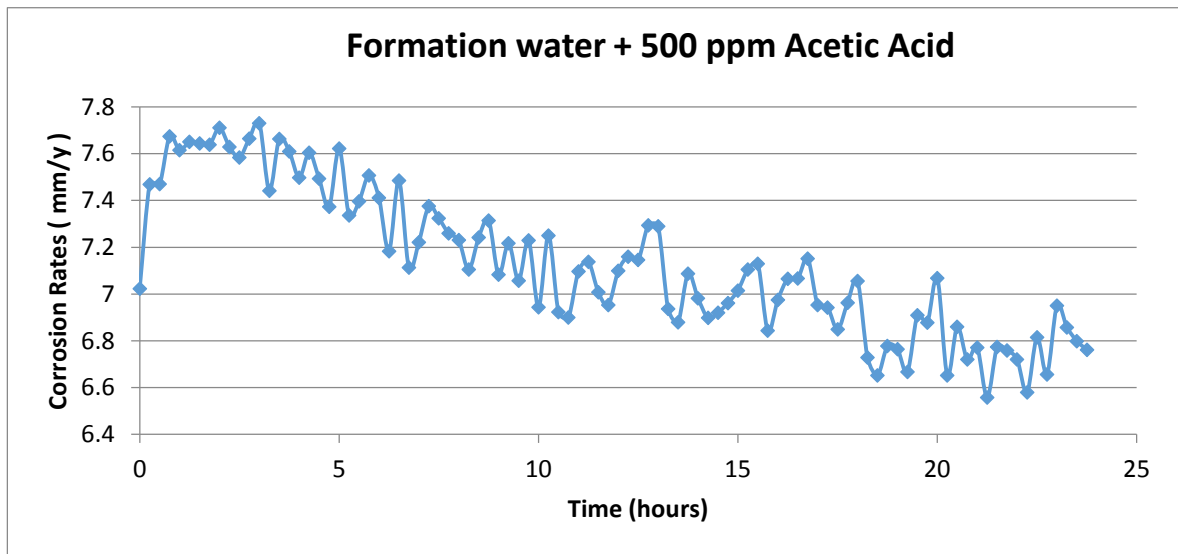


FIGURE 15 CORROSION RATE OF TEST MATRIX B

Figure 16 shows the effect of Test Matrix B on the corrosion rate of mild steel. The corrosion rate reading, as expected, gives a much higher reading than previous solution which is around 6.6 to 7.7 mm/y. The corrosion rate hits the peak for the first 5 hours of experiment and continue to decline for the remaining hours.

D. Test Matrix C – Formation Water + 1000 ppm Acetic Acid

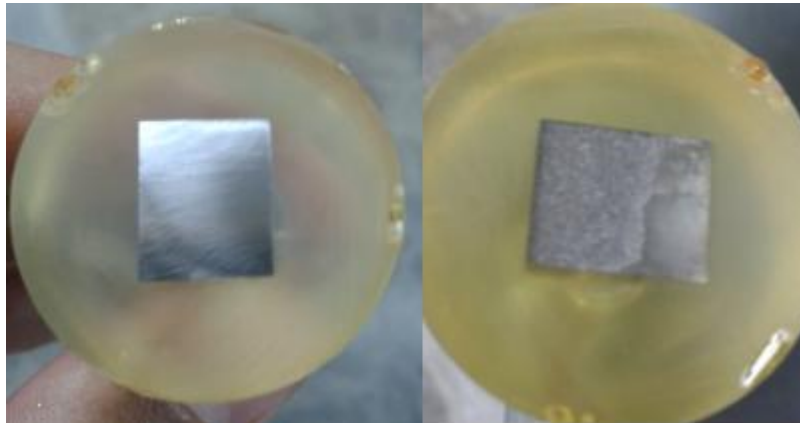


FIGURE 16 SAMPLE BEFORE AND AFTER POLARIZATION

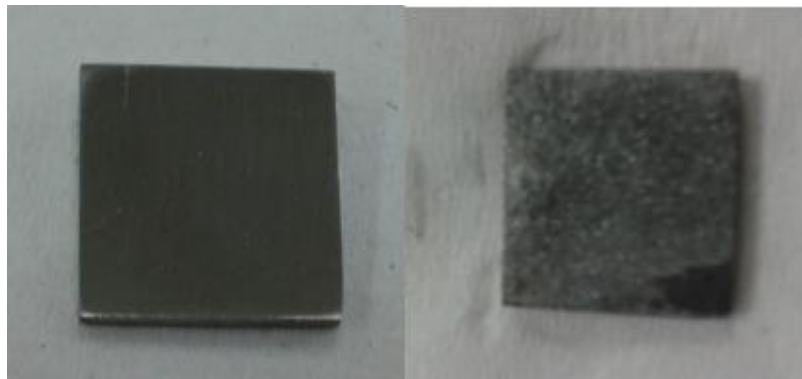


FIGURE 17 SAMPLE BEFORE AND AFTER POLARIZATION

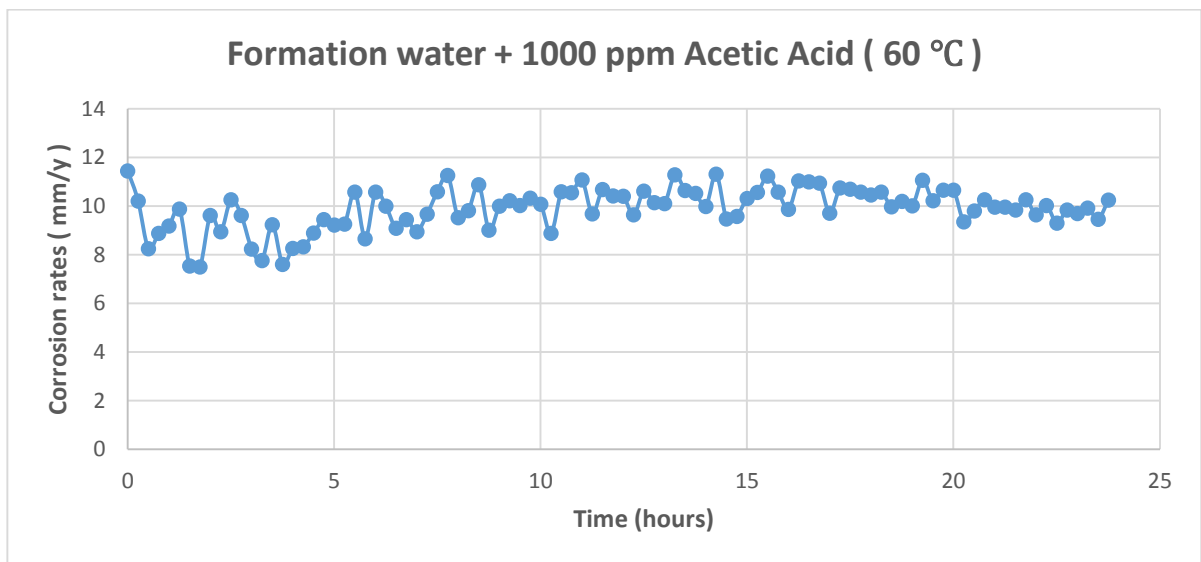


FIGURE 18 CORROSION RATE OF TEST MATRIX C

The highest concentration tested in the experiment is 1000 ppm of acetic acid as formulated in Test Matrix C. The corrosion rate rises higher as the concentration increased which is around 8.0 to 11.5 mm/y. The rate is much more stable throughout the duration of the test compared to previous solutions and shown no sign of decreasing.

E. Test Matrix D - Formation Water + 1000 ppm Acetic Acid (80°C)



FIGURE 19 SAMPLE BEFORE AND AFTER POLARIZATION

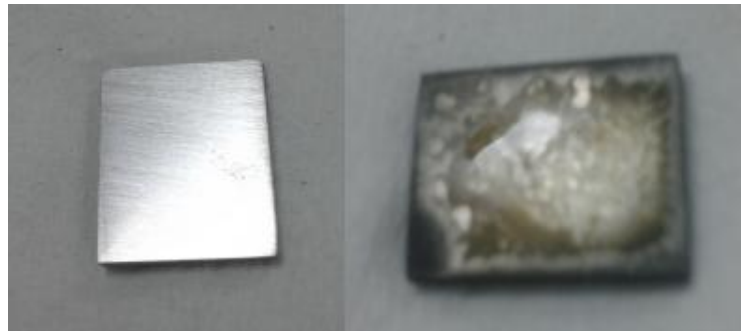


FIGURE 20 SAMPLE BEFORE AND AFTER POLARIZATION

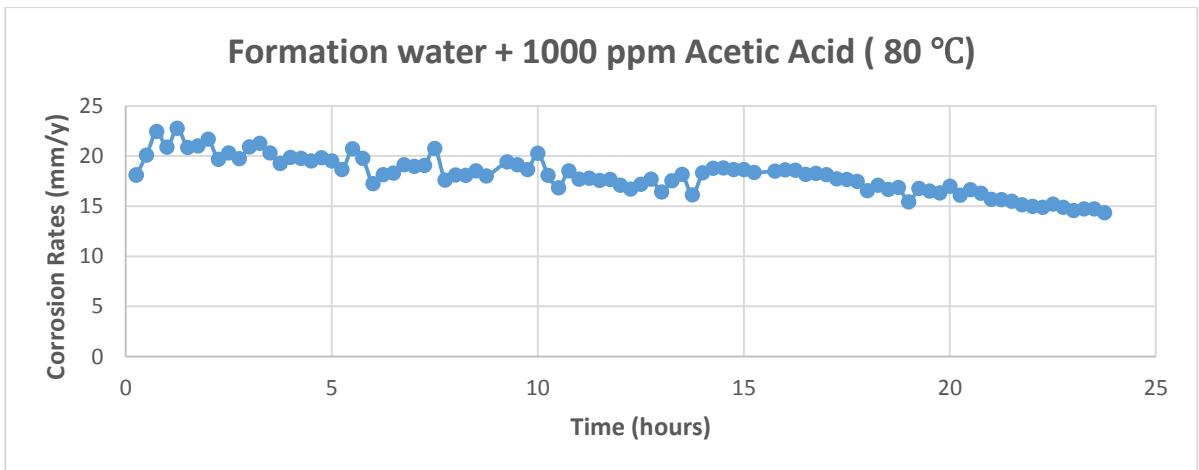


FIGURE 21 CORROSION RATE OF TEST MATRIX D

For the final solution, the temperature is increased from 60°C to 80°C. The concentration of acetic acid in the solution is 1000 ppm same as the previous solution. As the temperature increases, the corrosion rate shows a significant increase compared to Test Matrix C which is around 15.0 to 23.0 mm/y. However, the corrosion rate seems to decline after 10 hours of polarization.

4.2 Corrosivity Analysis

4.2.1 General Corrosion

The general corrosion rate of the system under study was monitored using Linear Polarization Technique (LPR) monitoring techniques and the results obtained are shown in figures below.

It was observed that general corrosion rate for all concentrations of acetic acid increased slightly with time and then decreased to a stable value. The slight initial increase is assumed to be due to imperfection on the surface of the metal due to corrosion reaction. Thick attack changes the surface area of the exposed area of the exposed metal and most likely leads to increase in the electrochemical process.

The observed decrease in corrosion rate with time is due to the formation of corrosion product on the surface of the metal. The driving force for precipitation is the supersaturation of iron carbonate (FeCO_3). The precipitation rate is generally slow, and a high degree of supersaturation of FeCO_3 in the water is necessary in order to get sufficient amounts of FeCO_3 deposits on the metal surface. To confirm this, the working electrode was removed at the end of each experiment. By visual observations, it can be observed that the surface of the electrode was covered with dark gray and almost black corrosion product.

4.2.2 Effect of Acetic Acid

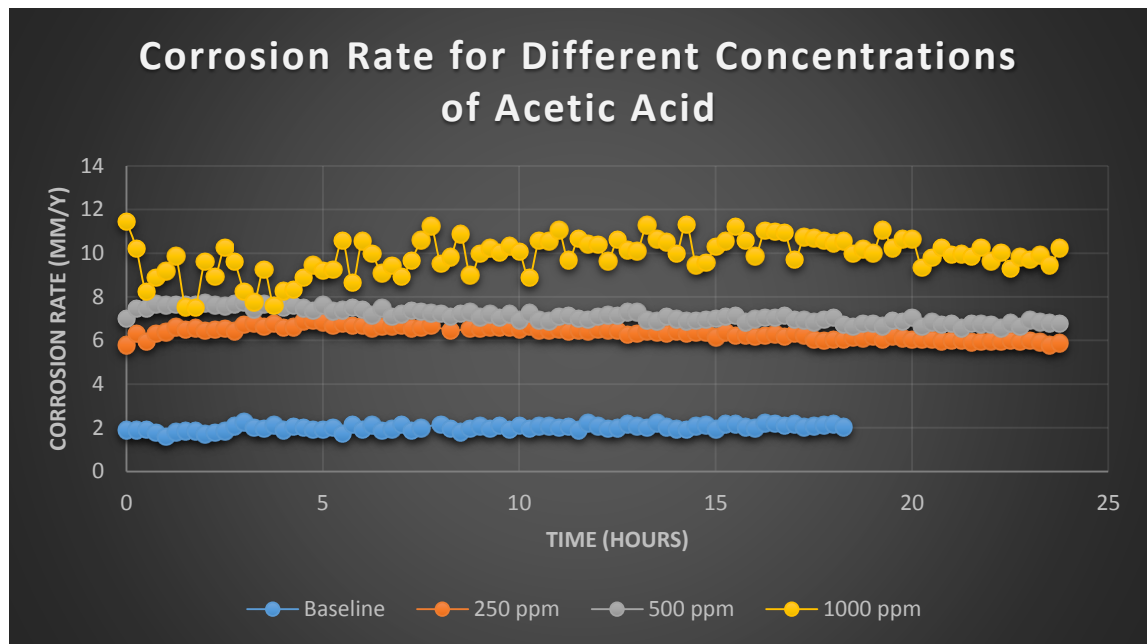


FIGURE 22 CORROSION RATE FOR DIFFERENT CONCENTRATIONS OF ACETIC ACID

In refineries, higher molecules weight of organic acids are insoluble in water but soluble in oil phase and pose a corrosion threat when the temperature is high. However, low molecular weight of organic acid mostly are soluble in water and known to cause corrosion problems to mild steel. Acetic acid (HAc) is the most common low molecular weight organic acid found in produced water.

As shown in figure above, the presence of acetic acid was observed to increase the rate of general corrosion. It is due to the abundance of undissociated HAc and its effects on the cathodic reactions of the corrosion process. Increase in undissociated HAc increase the corrosion rate due to the increase in the contribution of acetic acid to the hydrogen reduction process of cathodic reaction.

4.2.3 Effects of Temperature

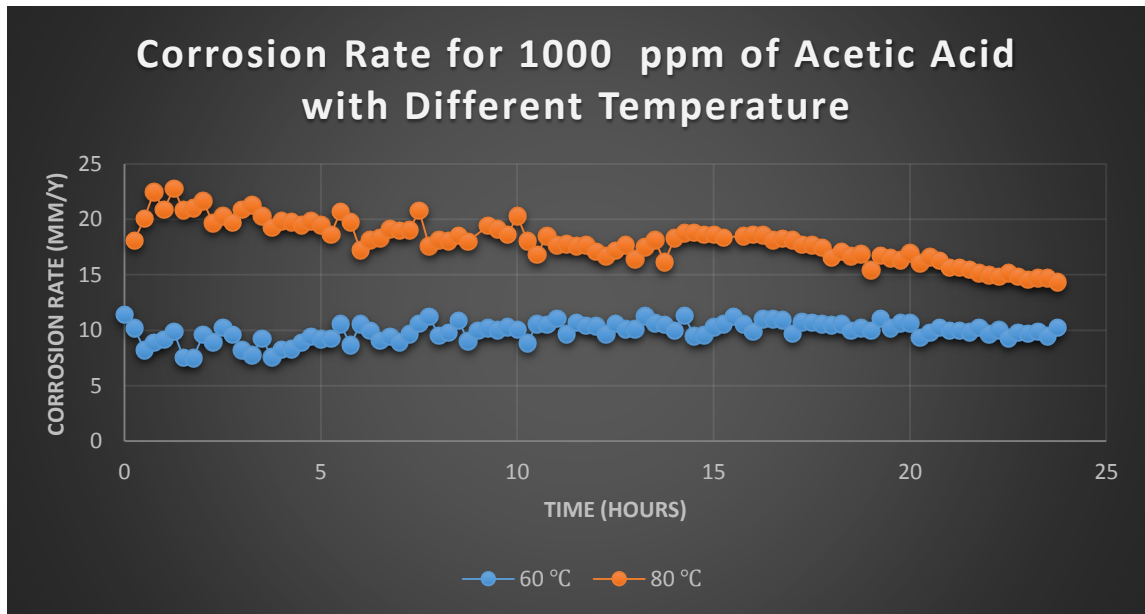


FIGURE 23 CORROSION RATE FOR DIFFERENT TEMPERATURES

Temperature accelerates all the mechanisms involved in corrosion such as electrochemical, chemical and transport. Early assumptions made before the experiment is conducted is the corrosion rate would steadily increase as the temperature increases. This situation is only applicable when the solution has a low pH and precipitation of corrosion product (normally FeCO_3) or other protective layers does not occur. From many studies, the peak in the corrosion rate is usually seen between 60°C and 80°C. As shown in figure above, the corrosion rate increases as the temperature rises. As the temperature increases, there is a clear acceleration of both anodic and cathodic reaction rates.

CHAPTER 4

CONCLUSION AND RECOMMENDATION

4.1 Conclusion

A detail methodology has been developed to investigate the effect of high amount high amount of acetic acid concentration on mild steel pipelines in CO₂ environment. With the addition of 250 ppm of acetic acid into the formation water, the corrosion rate increases by 250-270 % in comparison to baseline solution. The concentration of acetic acid then is doubled to 500 ppm and the corrosion rate increases by 8-9 % compared to previous solution (250 ppm). Finally, 1000 ppm of acetic acid is added into solution and the corrosion rate increases by 17-19 % compared to previous solution (500 ppm). Hence, it can be concluded that the presence of dissociated form of acetic acid is volatile and can significantly increase the corrosion rate on mild steel. The presence of acetic acid increases the general CO₂ corrosion rate of mild steel as the concentration increases.

The effect of temperature on the potentiodynamic sweeps was also studied in formation water containing 1000 ppm HAc. When the temperature of solution is increased from 60°C to 80°C, the corrosion rate significantly increases by 90-100 %. In theory, there should a clear acceleration of both cathodic and anodic reaction rates with an increase in temperature and the theory is proved by the increased in corrosion rate in the system studied.

4.2 Recommendation

Implementation of corrosion inhibitor is highly recommended for a preventive action in reservoir with high amount of acetic acid. The lifetime of pipelines can be prolonged to extended period and eventually cutting some costs replacing it in the future. Selection of material also is important in minimizing corrosion problems. A systematic evaluation of different alternatives has to be performed to get the best material that gives the best performance under these conditions. Apart from carbon steel, corrosion resistant alloys (CRA) and Super 13 % Cr stainless steel can be considered as the best alternatives to mitigate the corrosion problem.

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Appendices

Corrosion rate for all solutions (96 measurements)

| Time (sec) | Time (hrs) | baseline | 250 ppm | 500 ppm | 1000 ppm | 1000 ppm (80 °C) |
|------------|------------|----------|---------|---------|----------|------------------|
| 0 | 0 | 1.9086 | 5.7981 | 7.0236 | 11.444 | 75.722 |
| 900.15 | 0.250042 | 1.8968 | 6.3088 | 7.4692 | 10.208 | 18.095 |
| 1800.4 | 0.500111 | 1.938 | 5.9416 | 7.4698 | 8.2432 | 20.078 |
| 2700.5 | 0.750139 | 1.7889 | 6.3221 | 7.6739 | 8.8822 | 22.437 |
| 3600.7 | 1.000194 | 1.6014 | 6.3842 | 7.6155 | 9.1856 | 20.875 |
| 4501 | 1.250278 | 1.8158 | 6.6198 | 7.6505 | 9.8759 | 22.763 |
| 5401.2 | 1.500333 | 1.8657 | 6.5118 | 7.6448 | 7.5321 | 20.832 |
| 6301.5 | 1.750417 | 1.8484 | 6.5639 | 7.6383 | 7.4997 | 20.996 |
| 7201.9 | 2.000528 | 1.7278 | 6.4583 | 7.7106 | 9.6108 | 21.669 |
| 8102 | 2.250556 | 1.7917 | 6.511 | 7.6295 | 8.9433 | 19.657 |
| 9002.4 | 2.500667 | 1.8371 | 6.5557 | 7.5844 | 10.255 | 20.313 |
| 9902.6 | 2.750722 | 2.0721 | 6.4469 | 7.665 | 9.6093 | 19.719 |
| 10802 | 3.000556 | 2.2749 | 6.7453 | 7.7305 | 8.24 | 20.893 |
| 11703 | 3.250833 | 2.021 | 6.7949 | 7.4423 | 7.7631 | 21.269 |
| 12603 | 3.500833 | 1.9653 | 6.6374 | 7.6638 | 9.2382 | 20.301 |
| 13503 | 3.750833 | 2.1391 | 6.7738 | 7.6099 | 7.6078 | 19.239 |
| 14403 | 4.000833 | 1.8957 | 6.5887 | 7.4981 | 8.2645 | 19.865 |
| 15304 | 4.251111 | 2.0633 | 6.6222 | 7.6045 | 8.3311 | 19.747 |
| 16204 | 4.501111 | 2.0027 | 6.9008 | 7.4932 | 8.8904 | 19.513 |
| 17104 | 4.751111 | 1.9246 | 6.9088 | 7.3727 | 9.4464 | 19.838 |
| 18005 | 5.001389 | 1.9112 | 6.8367 | 7.6229 | 9.2182 | 19.516 |
| 18905 | 5.251389 | 2.0016 | 6.6909 | 7.3365 | 9.2661 | 18.641 |
| 19805 | 5.501389 | 1.74 | 6.7828 | 7.3965 | 10.576 | 20.717 |
| 20705 | 5.751389 | 2.1475 | 6.7022 | 7.5078 | 8.6552 | 19.775 |
| 21606 | 6.001667 | 1.9249 | 6.6738 | 7.411 | 10.57 | 17.237 |
| 22506 | 6.251667 | 2.1266 | 6.5789 | 7.1835 | 9.9968 | 18.143 |
| 23406 | 6.501667 | 1.873 | 6.6445 | 7.4856 | 9.0856 | 18.296 |
| 24306 | 6.751667 | 1.9453 | 6.6622 | 7.1128 | 9.4383 | 19.124 |
| 25207 | 7.001944 | 2.1492 | 6.6922 | 7.2221 | 8.9419 | 18.976 |
| 26107 | 7.251944 | 1.8802 | 6.5621 | 7.3755 | 9.6686 | 19.059 |
| 27007 | 7.501944 | 1.997 | 6.5953 | 7.324 | 10.594 | 20.764 |
| 27908 | 7.752222 | 1.2571 | 6.6819 | 7.2592 | 11.252 | 17.596 |
| 28808 | 8.002222 | 2.1544 | 6.1077 | 7.2312 | 9.5183 | 18.115 |
| 29708 | 8.252222 | 1.9586 | 6.4537 | 7.1049 | 9.8163 | 18.058 |
| 30608 | 8.502222 | 1.8134 | 6.2572 | 7.2417 | 10.88 | 18.514 |
| 31508 | 8.752222 | 1.9704 | 6.5443 | 7.3143 | 9.0042 | 18.001 |
| 32409 | 9.0025 | 2.0979 | 6.5434 | 7.0826 | 9.9918 | 69.909 |

| | | | | | | |
|-------|----------|--------|--------|--------|--------|--------|
| 33309 | 9.2525 | 1.9672 | 6.6129 | 7.218 | 10.225 | 19.409 |
| 34209 | 9.5025 | 2.103 | 6.5874 | 7.0572 | 10.018 | 19.134 |
| 35109 | 9.7525 | 1.9183 | 6.5935 | 7.2295 | 10.323 | 18.639 |
| 36009 | 10.0025 | 2.1091 | 6.5237 | 6.9442 | 10.078 | 20.279 |
| 36910 | 10.25278 | 1.9736 | 6.6677 | 7.2499 | 8.8785 | 18.067 |
| 37810 | 10.50278 | 2.0887 | 6.4694 | 6.9231 | 10.582 | 16.826 |
| 38710 | 10.75278 | 2.0841 | 6.4818 | 6.8996 | 10.544 | 18.511 |
| 39610 | 11.00278 | 2.0092 | 6.5379 | 7.0975 | 11.069 | 17.681 |
| 40511 | 11.25306 | 2.0667 | 6.4189 | 7.1386 | 9.6842 | 17.783 |
| 41411 | 11.50306 | 1.9035 | 6.4819 | 7.0085 | 10.685 | 17.565 |
| 42311 | 11.75306 | 2.2096 | 6.442 | 6.9535 | 10.42 | 17.662 |
| 43211 | 12.00306 | 2.0889 | 6.5074 | 7.0997 | 10.398 | 17.082 |
| 44112 | 12.25333 | 1.9698 | 6.4953 | 7.16 | 9.6374 | 16.702 |
| 45012 | 12.50333 | 1.9919 | 6.4662 | 7.1456 | 10.619 | 17.161 |
| 45912 | 12.75333 | 2.1629 | 6.2879 | 7.2942 | 10.135 | 17.693 |
| 46812 | 13.00333 | 2.0747 | 6.3226 | 7.29 | 10.096 | 16.416 |
| 47713 | 13.25361 | 2.0142 | 6.4465 | 6.9368 | 11.286 | 17.532 |
| 48613 | 13.50361 | 2.228 | 6.3733 | 6.8799 | 10.643 | 18.158 |
| 49513 | 13.75361 | 2.0299 | 6.3299 | 7.0868 | 10.517 | 16.136 |
| 50413 | 14.00361 | 1.9486 | 6.4106 | 6.9821 | 9.9871 | 18.314 |
| 51313 | 14.25361 | 1.9354 | 6.3081 | 6.8985 | 11.316 | 18.761 |
| 52214 | 14.50389 | 2.0881 | 6.3673 | 6.9208 | 9.4707 | 18.802 |
| 53114 | 14.75389 | 2.137 | 6.3553 | 6.9621 | 9.5815 | 18.629 |
| 54014 | 15.00389 | 1.9465 | 6.1684 | 7.0153 | 10.316 | 18.654 |
| 54915 | 15.25417 | 2.1643 | 6.3879 | 7.1049 | 10.562 | 18.363 |
| 55815 | 15.50417 | 2.1666 | 6.2324 | 7.1302 | 11.228 | 69.176 |
| 56715 | 15.75417 | 2.0478 | 6.2358 | 6.8434 | 10.579 | 18.493 |
| 57615 | 16.00417 | 1.986 | 6.1881 | 6.9746 | 9.8691 | 18.62 |
| 58515 | 16.25417 | 2.2086 | 6.2225 | 7.0652 | 11.041 | 18.586 |
| 59415 | 16.50417 | 2.2022 | 6.2974 | 7.0665 | 10.99 | 18.164 |
| 60316 | 16.75444 | 2.1022 | 6.1889 | 7.1514 | 10.948 | 18.261 |
| 61216 | 17.00444 | 2.1724 | 6.3149 | 6.954 | 9.7126 | 18.125 |
| 62116 | 17.25444 | 2.0373 | 6.2568 | 6.9422 | 10.74 | 17.707 |
| 63016 | 17.50444 | 2.0795 | 6.0568 | 6.849 | 10.692 | 17.666 |
| 63917 | 17.75472 | 2.1405 | 5.998 | 6.9626 | 10.579 | 17.465 |
| 64817 | 18.00472 | 2.1723 | 6.0325 | 7.0556 | 10.462 | 16.524 |
| 65717 | 18.25472 | 2.0525 | 6.0565 | 6.7291 | 10.57 | 17.092 |
| 66618 | 18.505 | | 6.1376 | 6.6519 | 9.9742 | 16.678 |
| 67518 | 18.755 | | 6.112 | 6.7781 | 10.187 | 16.865 |
| 68418 | 19.005 | | 6.1842 | 6.7648 | 10.005 | 15.426 |
| 69318 | 19.255 | | 6.0428 | 6.6678 | 11.062 | 16.75 |

| | | | | | | |
|-------|----------|--|--------|--------|--------|--------|
| 70218 | 19.505 | | 6.2094 | 6.9094 | 10.226 | 16.497 |
| 71118 | 19.755 | | 6.1163 | 6.8782 | 10.659 | 16.324 |
| 72018 | 20.005 | | 6.0304 | 7.0679 | 10.65 | 16.979 |
| 72919 | 20.25528 | | 6.0372 | 6.6522 | 9.3482 | 16.081 |
| 73819 | 20.50528 | | 6.056 | 6.8601 | 9.7985 | 16.636 |
| 74719 | 20.75528 | | 5.9776 | 6.7208 | 10.258 | 16.277 |
| 75620 | 21.00556 | | 6.0015 | 6.7712 | 9.9548 | 15.685 |
| 76520 | 21.25556 | | 6.0024 | 6.5584 | 9.9624 | 15.633 |
| 77420 | 21.50556 | | 5.9334 | 6.7744 | 9.8421 | 15.469 |
| 78320 | 21.75556 | | 5.963 | 6.7595 | 10.255 | 15.14 |
| 79221 | 22.00583 | | 5.9783 | 6.721 | 9.6468 | 14.985 |
| 80121 | 22.25583 | | 5.9451 | 6.5794 | 10.017 | 14.862 |
| 81021 | 22.50583 | | 5.9918 | 6.8148 | 9.2982 | 15.181 |
| 81922 | 22.75611 | | 5.9564 | 6.657 | 9.8328 | 14.871 |
| 82822 | 23.00611 | | 5.9919 | 6.9506 | 9.6947 | 14.573 |
| 83722 | 23.25611 | | 5.9307 | 6.858 | 9.9125 | 14.713 |
| 84622 | 23.50611 | | 5.7896 | 6.7992 | 9.4623 | 14.702 |
| 85523 | 23.75639 | | 5.876 | 6.7616 | 10.243 | 14.337 |

Simulated Brine Construction Worksheet Water Analysis

Brine Volume (L) = 1

| | Concentration (mg/L) | | Concentration (mg/L) |
|-----------------------|----------------------|---------------------------|----------------------|
| Sodium (Na) | 29910 | Chloride (Cl) ** | 52110 |
| Calcium (Ca) | 2120 | Bicarbonate (HCO3) | 570 |
| Magnesium (Mg) | 540 | Sulphate (SO4) | 10 |
| Potassium (K) | 325 | Carbonate (CO3) | 0 |
| Barium (Ba) | 270 | | |
| Strontium (Sr) | 600 | | |
| Lithium (Li) | 4 | | |

| Compounds | Weigth Compounds (mg) | mg/L Chloride | mg/L Sodium |
|------------|-----------------------|---------------|-------------|
| CaCl2.2H2O | 6930.257678 | 3750.672389 | |
| MgCl2.6H2O | 4514.737708 | 1575.231434 | |
| KCl | 619.6739372 | 294.6739372 | |
| BaCl2.2H2O | 480.1771684 | 139.3972052 | |
| SrCl2.6H2O | 1825.062771 | 485.5055923 | |
| LiCl | 24.42933295 | 29.21252054 | |
| NaHCO3 | 784.8152459 | | 214.7311475 |
| Na2CO3 | 0 | | 0 |
| Na2SO4 | 14.78608457 | | 4.786084567 |
| NaCl | 75474.44963 | 45783.96686 | |

All Calcium should be combined as calcium chloride (CaCl2.2H2O)
 All Magnesium should be combined as magnesium chloride (MgCl2.6H2O)
 All Potassium should be combined as potassium chloride (KCl)
 All Barium should be combined as barium chloride (BaCl2.2H2O)
 All Strontium should be combined as strontium chloride (SrCl2.6H2O)
 All Lithium should be combined as lithium chloride (LiCl)
 All Bicarbonate should be combined as sodium bicarbonate (NaHCO3)
 All Sulphate should be combined as sodium sulphate (Na2SO4)
 All Carbonate should be combined as sodium carbonate (Na2CO3)
 All remaining sodium and chloride should be combined as sodium chloride (NaCl)

| Sum total of Sodium | Sum total of Chloride ** |
|---------------------|--------------------------|
| 219.5172321 | 52058.65994 |

** To compare if the concentration required of Cl is equivalent to the sum total of the contributions of every compound

| Measured Values | |
|------------------------|-------------------|
| Rw _____ | ohms-m @ _____ °F |
| Specific Gravity _____ | g/cc @ _____ °F |
| PPM _____ | mg/L _____ |

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