

**Study of Carbon Dioxide Corrosion on Carbon Steel  
at Different Salt Concentrations**

by

NAWAL BINTI SHAMSUDDIN

Dissertation submitted in partial fulfillment  
of the requirements for  
Bachelor of Engineering (Hons)  
(Mechanical Engineering)

UNIVERSITI TEKNOLOGI PETRONAS  
TRONOH, PERAK  
Sept 2011

**CERTIFICATION OF APPROVAL**

**Study of Carbon Dioxide Corrosion on Carbon Steel  
at Different Salt Concentrations**

by

**Nawal Binti Shamsuddin**

A project dissertation submitted to the

Mechanical Engineering Programme

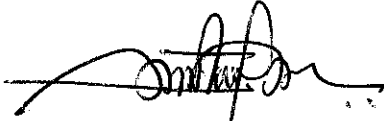
Universiti Teknologi PETRONAS

in partial fulfilment of the requirement for the

**BACHELOR OF ENGINEERING (Hons)**

**(MECHANICAL ENGINEERING)**

Approved by,



(Dr. Othman bin Mamat)

**UNIVERSITI TEKNOLOGI PETRONAS**

**TRONOH, PERAK**

Sept 2011

## **CERTIFICATION OF ORIGINALITY**

This is to certify that I am accountable 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.



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**NAWAL BINTI SHAMSUDDIN**

## ABSTRACT

CO<sub>2</sub> corrosion is a major threat in the oil and gas industry. Several possible mitigation methods have been developed to reduce the corrosion rate in these pipelines to acceptable levels. In order to reduce the corrosion of carbon steel pipelines in CO<sub>2</sub> environment, inhibitors are added to control corrosion rate to an acceptable level. The usage of the corrosion inhibitor is an economical and flexible method while being widely used in various applications. Corrosion inhibitor is a chemical compound which is added to the fluid phase and has an effect on the metal surface. The effectiveness of the corrosion inhibitor does not only depend on the inhibitor formulation but also on operational parameters such as temperature, pH and flow conditions. Pipelines in the oil and gas industry are located in seawater environment which is a natural corrosive environment. The objective of this project is to investigate the influence of salt concentration towards the corrosion rate of carbon steel in CO<sub>2</sub> environment that has been added with corrosion inhibitor. The temperature and pH used for this study is 60°C and 4.0pH. The NaCl solution concentration are varied to 1%, 3%, 5%, 10% and 20%. The test medium is saturated with carbon dioxide gas at 1bar. The concentration of the corrosion inhibitor is also applied to see the effect of corrosion inhibitor concentration to the corrosion rate. The inhibitor used is AMTECH and of dosages 25ppm and 50ppm. The material used for this study is carbon steel X52. Results of the inhibited corrosion tests reveals at 25ppm the corrosion rate of X52 is the lowest. Meanwhile the corrosion rate of X52 at 50ppm dosage yields an inverse result in comparison to the results of uninhibited and 25ppm CI corrosion test. It is concluded that the corrosion rate of X52 increases with NaCl concentration and 25ppm is the optimum working dosage of the corrosion inhibitor.

## **ACKNOWLEDGEMENT**

I am extending my warm appreciations to all of those who have contributed either directly or indirectly to the completion of this dissertation. My utmost gratitude goes to my project supervisor, Dr Othman Mamat for his supervision, commitment, professionalism, suggestion and encouragement helped me in all the time of study and writing of this thesis. Special thanks to my family, my colleagues and to those who helped me to complete this study. Thank you.

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# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Study

The term corrosion can be general or specific depending on the perspective from which is defined. For example, corrosion is defined as an electrochemical process in aqueous system meanwhile corrosion is defined as the degradation of a material caused by an environment in general perspectives. Water, air, carbon dioxide, organic liquids, molten salts, gaseous sulfur are examples of environments which can cause corrosion. Some less common environments are basically neutron beams, ultraviolet light, nuclear fission fragments and gamma rays.[1]

CO<sub>2</sub> corrosion has been one of the most common corrosion problems in oil and gas industry because of both a high general corrosion rate and severe localized corrosion. Carbon steel pipelines are commonly employed in the transport of oil and gas. Carbon steel piping and the process equipment are subject to corrosion caused by the presence of water and acidic gases such as carbon dioxide (CO<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S) and acetic acid (CH<sub>3</sub>COOH). CO<sub>2</sub> corrosion would give rise to the failure of pipelines and equipments and result in great economic loss and catastrophic accidents. Leakage of crude oil due to CO<sub>2</sub> corrosion would induce fire accident, water resource and environmental pollution.

Several possible mitigation methods have been developed to reduce the corrosion rate in such pipelines to acceptable levels. In order to reduce the corrosion of carbon steels in the oil and gas industry, inhibitors are frequently added to the produced fluid to control corrosion as an economical and flexible method. The use of corrosion inhibitor and the manipulation of surface deposits are two possible ways of lowering the corrosion rate.[2]

Corrosion inhibitor is one of the corrosion prevention methods and is widely used in various applications and many plant operations are dependent on their successful application. Any corrosion retardation process is corrosion inhibition. Corrosion inhibition means the reduction in the oxidation rate of the metal by the addition of a chemical compound which is added either in the form of a liquid or vapor or both. Specifically, a corrosion inhibitor is a chemical compound which is added to the fluid phase so that it has an effect on the metal surface.

The most widely used inhibitors in the petroleum industry are nitrogen containing compounds such as amines, amides, quaternary ammonium salts and specially imidazolines and their derivatives. Some of the CIs are hexamine, phenylenediamine, dimethylethanolamine, sodium nitride, cinnamaldehyde, condensation products of aldehydes and amides (imines), chromates, nitrides, phosphates, hydrazine, ascorbic acid and others. There are several classes of inhibitors conveniently designated as passivators, organic inhibitors, including slushing compounds and pickling inhibitors and vapor phase inhibitors.[3,4]

Two processes are involved in the action of the inhibitor on the metal surface. Firstly, the process starts with the transportation of the inhibitor to the metal surface and secondly the process of chemical interaction between the inhibitor and the metal surface. The action of a corrosion inhibitor is similar to the action of a drug molecule on human physiology in that both involve the transport of the active chemical species to the site to be acted upon. Which is followed by an interaction of the active ingredients at the site.[1]

## **1.2 Problem statement**

Corrosion is costly and poses severe materials science problem. For economic considerations, taking United States as an example, the cost of corrosion in 1986 amounted to US\$160 billion out of which US\$24 billion could have been saved by adopting corrosion control methods. It is imperative that economical measures are taken to minimize corrosion thus cutting down unnecessary losses. Selection of corrosion inhibitor in earlier times were on trial and error basis. The most significant criteria involved in the selection of the inhibitors are hydrophobicity, molecular structure and electron density at the donor atom of the inhibitor and solubility of the inhibitor.[1]

For the purpose of this study, the idea is to know the efficiency of the selected corrosion inhibitor by measuring the corrosion rate for inhibited corrosion rate and uninhibited corrosion rate. The efficiency of the corrosion inhibitor may be reduced in the presence of corrosion product film. The effectiveness of a corrosion inhibitor is a function of multiple factors such as fluid composition, quantity of water and flow regime. Some of the mechanism of its effect is the formation of a passivation layer. The layer is a thin film on the surface of the material that prevents attacks of the corrosive substance to the metal, inhibiting either the oxidation or reduction part of the redox corrosion (anodic and cathodic inhibitors) or scavenging the dissolved oxygen.[2,4]

### **1.3 Objective**

The objective of this study is to investigate the effect of corrosion inhibitor to the corrosion rate of the carbon steel (X52) at different salt concentrations.

### **1.4 Scope of study**

The test variables that were kept constant throughout the study were the temperature value and pH level which was 60°C and 4.0pH. Different concentrations of the corrosion inhibitor were used to see the effect of different CI concentration to the corrosion rate of the carbon steel (X52). The CI concentration used is 25ppm and 50ppm. NaCl concentrations used for the test medium were 1%, 3%, 5%, 10% and 20%. The solution was saturated with carbon dioxide gas by purging the solution continuously with carbon dioxide gas at pressure of 1bar. The material used for this study is carbon steel X52. This study also focuses on the working mechanism of the inhibitor to reduce the corrosion rate based on the experimental works and previous work regarding corrosion inhibitors carried out by other researchers.

## CHAPTER 2

### LITERATURE REVIEW

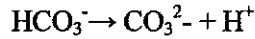
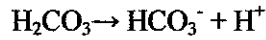
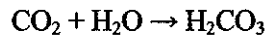
#### 2.1 Carbon Dioxide Corrosion in Oil and Gas Production

Corrosion of carbon steel is a significant problem in the oil and gas production and transportation systems and causes significant losses. The majority of oil and gas pipelines failures result from CO<sub>2</sub> corrosion of carbon and low alloy steel and occurs at all stages of production from downhole to surface equipment and processing facilities. The impact of corrosion in oil and gas industry will impact the capital expenditure, operational expenditure, health, safety and environment. The cost of corrosion is 30 cents (USD) for the production of each barrel of oil production. CO<sub>2</sub> corrosion had caused increases in cost and safety issues. According to him also, the mechanism of carbon dioxide corrosion is a complicated process that is influenced by many factors and conditions.[1]

Carbon steels and low alloy steels in the aqueous CO<sub>2</sub> environment could be susceptible to general corrosion and localized attack. When carbon dioxide dissolves in the presence of a water phase, carbonic acid forms, which is very corrosive to carbon steel. Numerous studies have been carried out to investigate the corrosion mechanism of carbon steel immersed in de-ionized water and brine solutions saturated with carbon dioxide. Most of the experiments in stirred beakers and small diameter flow loops. CO<sub>2</sub> dissolves in water to give carbonic acid, a weak acid compared to mineral acids since it does not fully dissociate. Concentration of dissolved CO<sub>2</sub> species in solution and mass transport of dissolved CO<sub>2</sub> to the steel surface have a critical influence on the reaction and corrosion rate and that every species present in the media can contribute to the cathodic reaction.

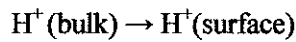
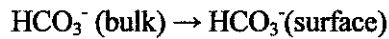
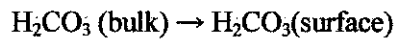
The overall corrosion process could be divided into four steps. The first step is the dissolution of carbon dioxide in the aqueous solution to form the various reactive species, which takes part in the corrosion reaction. The second step is the transportation of these reactants to the metal surface. The third step involves the electrochemical reactions (anodic and cathodic) taking place at the metal surface. The fourth step is the transportation of the corrosion products to the bulk of the solution. These can be shown as:-

1) Formation of reactive species in the bulk

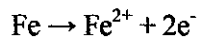
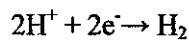
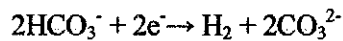
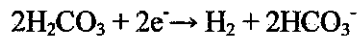


These 2 dissociation steps above are very fast compared to all other processes occurring simultaneously in corrosion of mild steel, thus preserving chemical equilibrium.

2) Transportation of reactants (bulk to surface)



3) Electrochemical reactions at the surface



4) Transportation of products (surface to bulk)

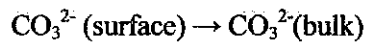
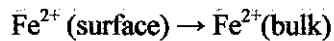


Figure below is a simplified model for carbon steel corrosion under multiphase flow conditions. The protons have to diffuse from the bulk region through the boundary layer to the metal surface, while the transport flux of carbonic acid needs to reflect both diffusion of  $\text{H}_2\text{CO}_3$  and hydration of  $\text{CO}_2$  in the boundary layer. He also suggested that the diffusion of hydrogen ions and carbonic acid is the rate-determining step.

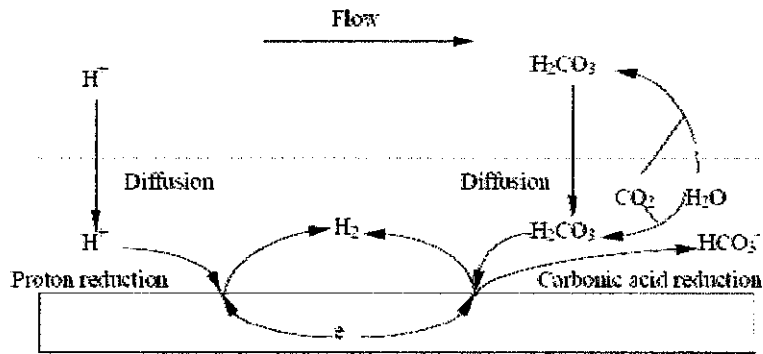
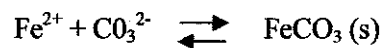


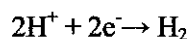
Figure 2.1: Simple model for CO<sub>2</sub> corrosion [5]

In CO<sub>2</sub> corrosion when the concentrations of Fe<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> ions exceed the solubility limit, they combine to form solid iron carbonate layers according to:

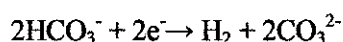
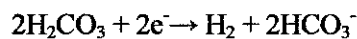


The protectiveness of solid iron carbonate will depend on the rate of precipitation (which is a strong function of temperature and supersaturation) and on the underlying corrosion rate. For high precipitation rates, and low corrosion rates, the protective iron carbonate is obtained and vice versa, low precipitation rates and high corrosion rates lead to formation of unprotective iron carbonate layers.

As a conclusion, when CO<sub>2</sub> dissolves into water, carbonic acid will form, which is more corrosive to carbon steel than a completely dissociated acid (such as HCl) at the same pH value. Several mechanisms have been proposed for the dissolution of carbon steel in CO<sub>2</sub> containing aqueous solution. The main cathodic process can be summarized by four reactions. At a lower pH, H<sup>+</sup> reduction is the dominant cathodic process because of the high concentration of H<sup>+</sup>.



When pH increase to 4-6, the direct reduction of HCO<sub>3</sub><sup>-</sup> and H<sub>2</sub>CO<sub>3</sub> become important.



At a high overpotential, the dominant cathodic reaction changes to direct reduction water



The anodic reaction is mainly the dissolution of iron. During these corrosion processes, a corrosion scale ( $\text{FeCO}_3$ ) would form on the surface of the carbon steels. The properties and morphology of the scales would influence the corrosion rate significantly.

Selection of Corrosion inhibitor in the earlier time was based on a trial and error basis. The most significant criteria involved in the selection of the inhibitors are hydrophobicity, molecular structure, and electron density at the donor atom of the inhibitor and solubility or dispersibility of the inhibitor. BP Corrosion inhibitor selection study is as follows: solubility /dispersibility screening, bubble test screening, rotating screening if there are still a large number of candidates for corrosion inhibitor and flow loop screening. [6]

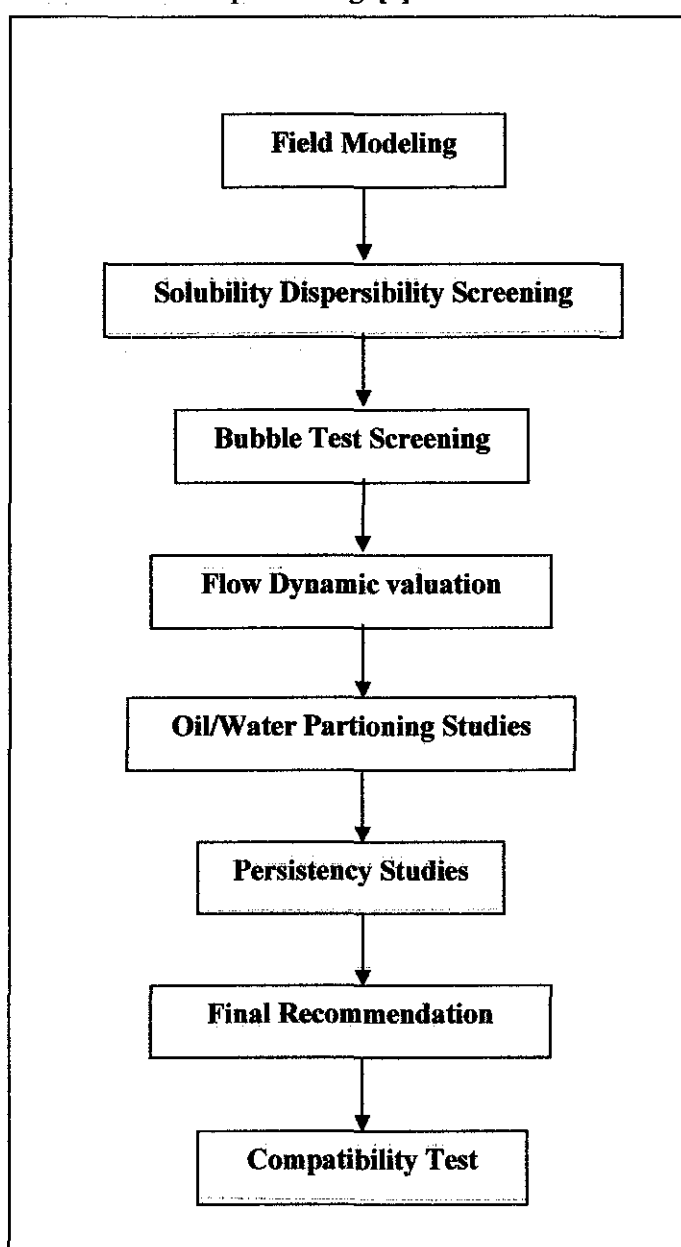


Figure 2.2: Flow chart of corrosion inhibitor selection process

Types of CO<sub>2</sub> corrosion damage are pitting, mesa attack and flow induced localized corrosion. Pitting occurs at low velocities and around the dew point temperature in gas producing wells. Pitting damage increases with temperature and CO<sub>2</sub> partial pressure. Study show that Pb addition inhibited localized corrosion through deposition at local anodes, and study also shows that pitting at the carbon steel in CO<sub>2</sub> containing environment was almost independent of chloride content. Mesa attack is a type of localized corrosion occurs in low to medium flow condition where the protective iron carbonate film forms but unstable to withstand the operating regime. Flow induced localized corrosion start from the pits and sites of mesa attack above the critical flow intensities.[5]

CO<sub>2</sub> corrosion is influenced by a number of parameters including environmental, physical and metallurgical variables. Notable parameters affecting CO<sub>2</sub> corrosion include:

- Fluid makeup as affected by water chemistry, pH, water wetting, hydrocarbon characteristic and phase ratios
- CO<sub>2</sub> and H<sub>2</sub>S content
- Temperature
- Steel surface, including corrosion film morphology, presence of wax, and asphaltene
- Fluid dynamic
- Steel chemistry

Environmental factors that affect the corrosivity of the aqueous phase therefore will affect CO<sub>2</sub> corrosion. Environmental parameters included solution chemistry, CO<sub>2</sub> partial pressure, temperature, the in-situ pH, H<sub>2</sub>S, and the effect of the organic acids. Physical parameters influence hydrodynamics of the system and the interface between the environment and the steel substrate. Physical parameters included water wetting, wax effect, surface films, crude oil and fluid dynamics. Their interactive and complementary influences affect the onset of film formation and removal. Metallurgical parameters included chemical composition, heat treatment and microstructure of the carbon steels in CO<sub>2</sub> environments. Overall, CO<sub>2</sub> corrosion of mild steel is not very sensitive to flow, at least not so when compared to mild steel in strong acids or even in organic acids. This is due to the fact that the main corrosive species in CO<sub>2</sub> corrosion is H<sub>2</sub>CO<sub>3</sub>, which can easily be depleted to a slow chemical step. Therefore the limiting rate of CO<sub>2</sub> corrosion is primarily affected by the rate of this chemical reaction which is a function of temperature and CO<sub>2</sub> partial pressure and not very sensitive to the flow.



## **2.2 Corrosion Inhibitor**

In the oil and gas exploration or production and also processing industries, low-grade carbon steel represents that most commonly used construction material for pipelines. However, they are very susceptible to corrosion in environments containing CO<sub>2</sub>. The resistance of materials is affected of CO<sub>2</sub> injection for enhanced oil recovery and the active exploration of deep natural reservoir containing CO<sub>2</sub>. In order to improve their performance, Corrosion Inhibitors are frequently used. The corrosion inhibitor treatment program is often the most cost-effective option to ensure the integrity of the system over the lifetime of the asset. Amine and its salts have been used successfully in the oil and gas field application. [3]

The most widely used inhibitors in the petroleum industry are nitrogen containing compounds such as amines, amides, quaternary ammonium salts and specially imidazolines and their derivatives. Corrosion inhibitor falls below three categories which are anodic inhibitor, cathodic inhibitor and mixed inhibitor. Chromate, anodic inhibitor which forms a passivation layer on aluminium and steel surfaces which prevents the oxidation of the metals. Nitrite is another anodic inhibitor which used at low concentration can actually aggravate pitting corrosion as they form a nonuniform layer with local anodes. Example of cathodic inhibitors is Zinc Chloride, which retards the corrosion by inhibiting the reduction of water to hydrogen gas and if oxidants such as oxygen are excluded, the rate of the corrosion can be controlled by the rate of water reduction. Mixed inhibitors are the inhibitors act in a combination of anodic inhibitors and cathodic inhibitors manner. The imidazoline derivative acts as a mixed-type inhibitor from the indication of decreasing in corrosion rate associating with a shift of both cathodic and anodic branches of polarization curves towards lower current densities, together with a slight positive shift in corrosion potential.[4]

## **2.3 Laboratory works related to Corrosion Inhibitors**

Extensive basic studies on corrosion inhibitor and the factors governing their effectiveness have only been in progress for the last fifty years. The effectiveness of an inhibitor is determined not only by the properties of the gas and liquids contents of the pipeline and by the properties of the inhibitor itself, but also the way it is added to the pipeline and the operating conditions of the system such as temperature, flow rate and pressure.[7]

Modern instrumental techniques [such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and secondary ion mass spectroscopy (SIMS) coupled with electrochemical techniques which measure the polarization curves, polarization resistance,

electrochemical noise and electrochemical impedance have been proven to be of dominant importance in the explanation of corrosion inhibition mechanisms.

EIS, Electrochemical Impedance Spectroscopy, is a powerful technique to study about the corrosion processes and inhibitor performance in different environments. EIS also is a powerful technique for the corrosion study in various corrosion and protection fields such as organic coatings, passive films and corrosion scales analysis. It can provide the information on corrosion and protection mechanism, especially when an adsorbed film or an applied organic coating is present. EIS had been widely applied in the monitoring of inhibitor film persistency and in the study of inhibitive mechanisms of inhibitors. [8]

In the present work, both EIS and some standard direct current measurements which are LRP and  $E_{\text{corr}}$  were employed to study the corrosion process in carbon steel with two different microstructures such as annealed and quenched and tempered, also known as Q&T, as well as the effect of the heat treatment on the efficiency of benzimidazole as a corrosion inhibitor in CO<sub>2</sub> saturated brine media.

Corrosion tests should be reproducible and reliable. Corrosion tests may be classified as the simulated laboratory tests and field/plant tests. Laboratory tests may be either long-term or accelerated short-term tests. Long-term laboratory tests involve typical model apparatus using simulated field or plant conditions. These tests are usually use for the selection of materials. In accelerated short-term tests, one or several factors affecting the corrosion rate are made severe to speed up the corrosion process. This type of test is done in controlled conditions and is useful in quality control of materials or protective coatings.

In earlier studies, inhibitors were tested by agitation of the samples in inhibitor containing solutions and the effectiveness of the inhibitors was determined by the loss in weight of the samples. A paper referenced in *Chemical Abstracts* in 1909 states that the inhibitive power of some pigments on iron and steel were tested by agitating in water with a current of air and the loss in weight due to the rusting was determined. [8]

Most of the studies on the inhibition mechanism of imidazoline based inhibitors have been conducted in laboratory scale systems, such as rotating cylinder electrode cell or the laboratory scale flow loop, under a water or a water-oil phase. Under stagnant conditions, copper wire was attached to the back of the specimen, which was mounted in an epoxy resin leaving an area of 1cm<sup>2</sup> exposed to the solution. The five holes distributed at the cover of the container for CO<sub>2</sub> gas

entry, working electrode, reference electrode (saturated Ag/AgCl), counter electrode (graphite) and condenser. All experiments under flowing condensation were conducted in the modified rotating disc electrode system. It is well known that the corrosion rate in pipelines is strongly related to flow condition.[9]

Based on the data presented in the paper, the better methodologies are high pressure (500psi) linear polarization, flow loop test and rotating electrode for higher speeds. In these tests, only a few inhibitors resulted in more than 90% efficiency, and many inhibitors resulted in less than 60% inhibition. Three criteria by which a laboratory methodology can be judged relative to the information that it provides[8]:

- **Uniqueness** (Corrosion rate must be obtained and interpreted in terms of corrosion kinetics).
- **Relevancy** to the field for which the inhibitor is being evaluated; and
- **Predictive** capability of failure mechanism

The other experimental work regarding the corrosion inhibitor is the inhibition and adsorption of 2-undecyl-ethylamino imidazoline (2UEI) in CO<sub>2</sub> saturated 3% NaCl solution was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) as well as SEM observation. From the result and discussion, for the *potentiodynamic polarization measurements*, 2-Undecyl-1-ethylamino imidazoline (2UEI) inhibits the corrosion of N80 mild steel in CO<sub>2</sub>-saturated 3% NaCl solution and the extent inhibition is dependent on 2UEI concentration, temperature and exposure time. 2UEI mode of inhibition is due to the active sites blocking effect in the absence of corrosion products and geometric blocking effect in the presence of corrosion products.[10]

Factors that make the laboratory evaluation of Corrosion Inhibitor for application in oil and fields difficult, include the large number of laboratory methodologies that are available, the several correlations that can be used to convert corrosion rate and hence the inhibitor efficiency from one geometry to another, the vast variation of field operating conditions and the impossibility of reproducing in the laboratory all field operating conditions. Therefore, Uniform International standards should be developed by organizations such as NACE, ASTM and ISO in tandem. The development and usage of such standards will benefit all those involved as a result of increased effectiveness of CI, lower cost, fewer field failures and also increased safety.[11]

## **2.4 Protocol to test corrosion inhibitor in laboratory**

A set of standard operating procedures for corrosion test are important to establish confidence in the repeatability and reproducibility of test methods. The standard procedures should cover all aspects of the corrosion test from steel quality, specimen preparation, solution preparation, environmental conditions, flow regimes, through to corrosion monitoring method.

### **“Round Robin” Validation of test methods**

BP Round Robin protocol consists of uninhibited and inhibited test under the stimulation condition. Equivalent of the hydrodynamic conditions are used in each type of apparatus. In order to produce the solution, the quantities of salt cannot be added straight into the distilled water of 1 liter because it will lead greater volume of water more than 1 liter. To prevent scaling and precipitation, chloride have to dissolve first and follow by dissolution of the carbon dioxide and finally bicarbonate.

Standard steel is important because high sulfur content of carbon steel thus S element will act as corrosion inhibitor and affects corrosion rate. The active surface preparation as stated in this protocol. Cleanliness of the equipment also is important to obtain reliable data. The recommended cleaning after inhibitor are deionised water rinse, toluene rinse, petroleum ether rinse, acetone rinse and deionised water rinse at least 5 times.

Corrosion measurement in the testing of corrosion inhibitor can use weight loss measurements and Linear Polarization Resistance (LPR) to monitor the corrosion rates. In LPR, the working electrode in three electrode system is wept from 0-10mV at 300 MV/min. The polarization resistance is converted to the corrosion rate using Stern-Geary constant of 27.3mV.

### **Bubble Test Protocol**

“Bubble test” is a simple test which can be set up reasonably quickly and is ideal for rapidly carrying out a large number of tests. This test is also conducted in the first stage of corrosion inhibitor selection, or for screening a wide range of field conditions. The main limitation of the bubble test is shear stresses in the stirred solution are significantly lower than experienced in the pipeline. The operating procedure for bubble test is very crucial during the cleaning of the cell or called vessel.

## Standard Test method for conducting Potentiodynamic Polarization Resistance Measurement

Polarization resistance measurement is used to determine the corrosion rate of metal in a specific environment. The test method can be utilized to verify the performance of polarization measurements equipments. Polarization resistance can be related to the rate of general corrosion for metals at or near their corrosion potential, it is an accurate and rapid way to measure the general corrosion rate. This method also can be used as a way to rank inhibitor in the order of resistance to general corrosion.

The test procedures standard included are:-

- Test solution should be prepared and the standard test cell requires 900ml of test solution where the temperature must be maintained at 30<sup>0</sup>C within 1 celcius.
- Test cell must purge at 150cm<sup>3</sup>/min with an oxygen free gas. The purge is started at least 30 minutes before the specimen immersion and continue throughout the test.
- Working electrode is prepared, and experiment must be conducted within 1 hour of the preparing electrode. Preparation including sequential wet polishing with 240 grit and 600 grit SiC paper. Surface area of the specimen is determined to the nearest of 0.01 cm<sup>2</sup> and subtract the area under the gasket.
- Prior to the immersion of the specimen, it is degreased with a solvent such as acetone and rinsed with distilled water. The time delay between rinsing and immersion should minimal.
- The test specimen is transferred into the test cell and position the Luggin probe tip to 2 to 3 mm from the test electrode surface. The diameter of the tip must be not more than 1 mm.

## CHAPTER 3

### METHODOLOGY

#### 3.1 Laboratory Simulation Test

Laboratory simulation test is conducted to determine the effect of corrosion inhibitor to the corrosion rate of carbon steel at different salt concentration. The working electrode used is carbon steel (X52) and the NaCl solution concentration used is 1%, 3%, 5%, 10% and 20%. CI of dosages 25ppm and 50ppm is injected to the solution. Meanwhile temperature of 60°C and pH 4.0 is kept constant throughout the study.

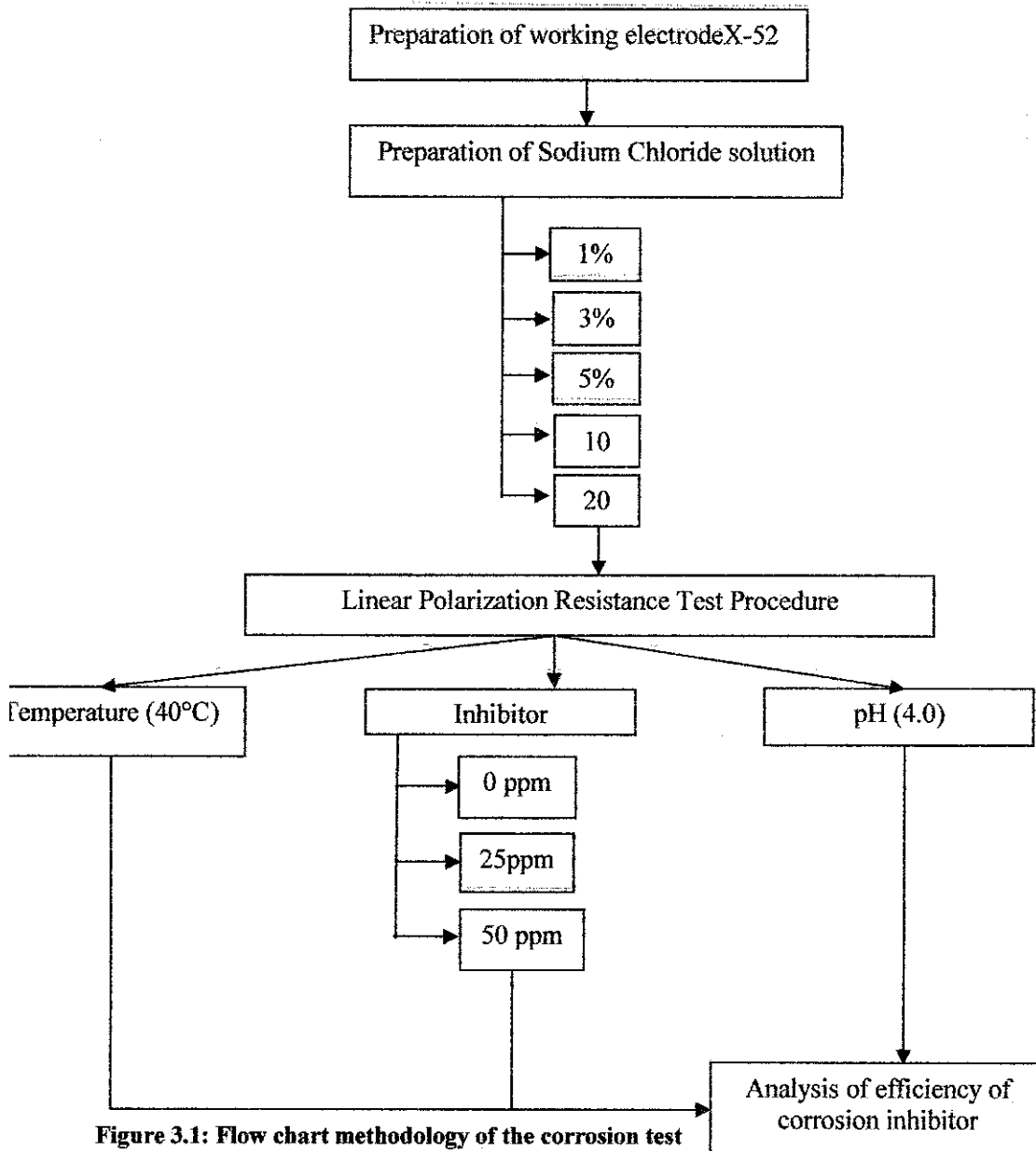


Figure 3.1: Flow chart methodology of the corrosion test

### 3.1.1 Test matrix

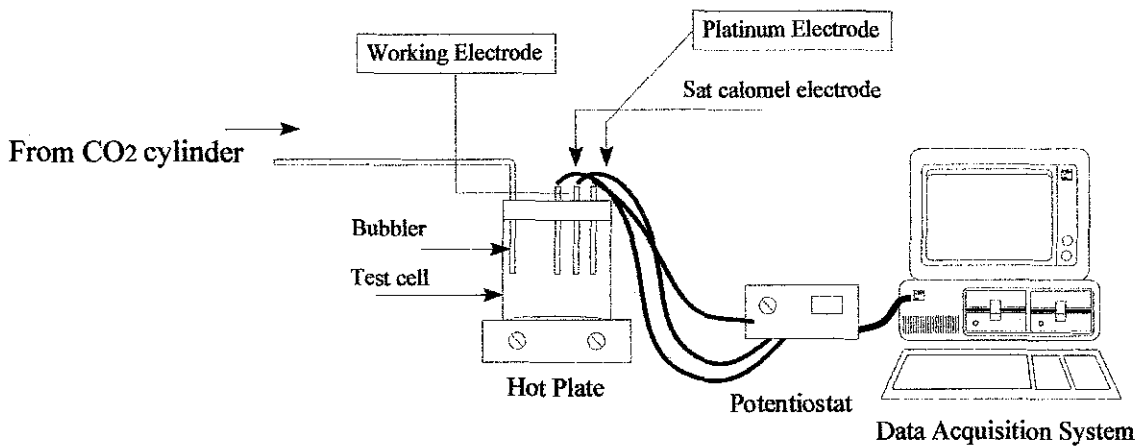
Table 3.1 indicates that fifteen tests are carried out. The operational parameters such as temperature and pH is kept constant at 60°C and 4.0 pH. Meanwhile NaCl concentration is varied to 1%, 3%, 5%, 10% and 20%. For each NaCl percentage concentration, corrosion inhibitor of dosages 0ppm, 25ppm and 50ppm is injected to the solution.

**Table 3.1: Test matrix for the laboratory works for Corrosion Inhibitor study**

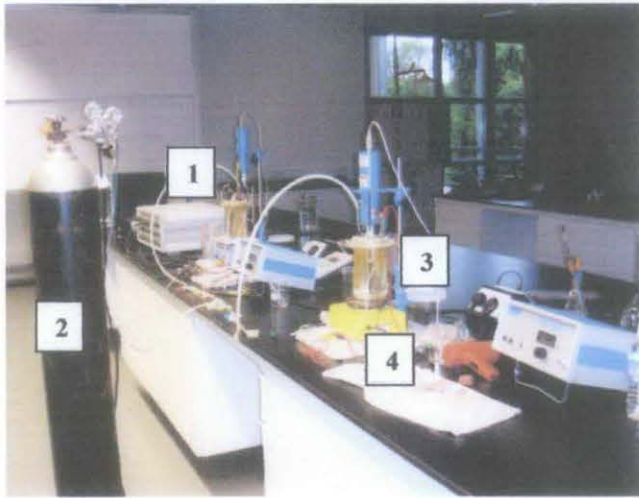
Cl (ppm)	NaCl concentration (%)					Temp (°C)	pH
	1	3	5	10	20		
0	Test 1	Test 2	Test 3	Test 4	Test 5	60	4.0
25	Test 6	Test 7	Test 8	Test 9	Test 10		
50	Test 11	Test 12	Test 13	Test 14	Test 15		

### 3.1.2 Laboratory Set-up

The set-up for the laboratory test using electrochemical measurement method of Linear Polarization Resistance experiments is showed in Figure 3.2 and Figure 3.3. The test assembly consists of one-liter glass cell bubbled with CO<sub>2</sub> gas. The required test temperature is set through the hot plate. The electrochemical measurements are based on a three-electrode system, using a commercially available potentiostat with a computer control system. The reference electrode used is a saturated calomel electrode (SCE) and the auxiliary electrode is a platinum electrode.



**Figure 3.2: Schematic diagram for static experimental set-up**



1. Data Acquisition System
2. CO<sub>2</sub> Cylinder
3. Test Cell
4. Hot Plate

**Figure 3.3: Real experiment set up in the laboratory**

Corrosion rate is measured by linear polarization resistance method following ASTM G59-97 Standard Method for conducting potentiodynamic polarization resistance measurement.[12]

### 3.2 Material

The working electrode or sample in this experiment is mild steel (X-52). Table 3.1 shows the composition of X-52

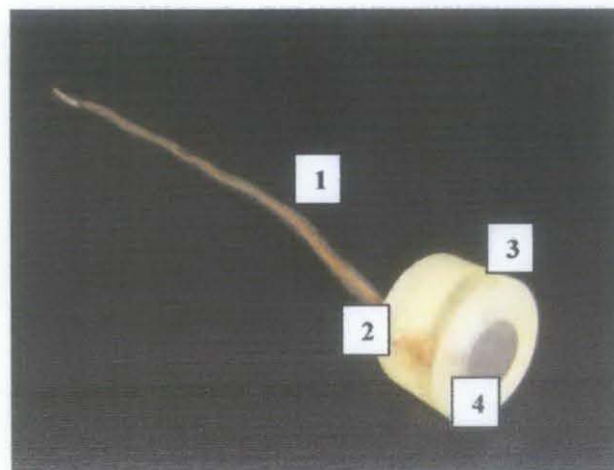
**Table 3.2: API 5L X52 chemical composition**

Carbon	Manganese	Phosphorus	Sulfur	Others
0.2	1.4	0.025	0.015	C,d

<sup>c</sup>Columbium (niobium), vanadium, titanium or combinations thereof may be used at the discretion of the manufacturer

<sup>d</sup>The sum of the columbium (niobium), vanadium and titanium contents shall not exceed 0.15%

Figure 3.4 shows the finished prepared of X-52 working electrode



1. Copper wire
2. Welded joint between copper wire and X52
3. Cold mounted
4. Carbon steel X52

**Figure 3.4: Photo of X52 working electrode**



The preparation of the working electrode is as follow:

1. The sample was spot welded with a copper wire
2. Next, it was mounted with epoxy by cold mounting and then polished to 800-grade finishing using silicon carbide paper
3. Lastly, it was degreased and rinsed with distilled water and ethanol

### **3.3 Preparation of Solutions**

The NaCl solution of concentration 1%, 3%, 5%, 10% and 20% is prepared by dissolving NaCl in distilled water. Next, the solution is saturated with CO<sub>2</sub> by purging the solution for one hour prior to the exposure of the electrode. The pH of the solution is adjusted by adding 1M NaHCO<sub>3</sub> until the desired pH level is obtained. The pH value is measured by using the microcomputer pH-meter METTLER TOLEDO Model 230 that has been calibrated using standard buffer solutions.

### **3.4 Experiment Environment**

The environment for the laboratory test is set according to the determined operational parameters. The test solution used is NaCl solution of concentration 1%, 3%, 5%, 10% and 20%. The pH value is adjusted to 4.0 and the temperature of the solution is heated to 60°C and kept constant. For the first of readings, corrosion inhibitor is not injected to the solution. Then, the tests are repeated for dosages of CI of 25ppm and 50ppm. The solution is purged with CO<sub>2</sub> at 1 bar to provide the environment of CO<sub>2</sub> corrosion.

### **3.5 Addition of Corrosion Inhibitor**

The Corrosion inhibitor used in this study is AMTECH. It is used in wet gas production and transportation, for gas lift systems to combat against corrosion associated with acid gasses and inorganic salts. It is comprised of ethoxylatedimidazolines which allows the CI to be stable in high temperature and pressure system. [13]

Corrosion inhibitor dosage of 25ppm and 50ppm is injected into the solution. Micropipette is used to measure the accurate volume of the corrosion inhibitor into the solution. The volume of corrosion inhibitor added into the solution is base on parts per million (ppm) according to the volume of solution used in the experiment. Figure 3.5 shows the corrosion inhibitor used.



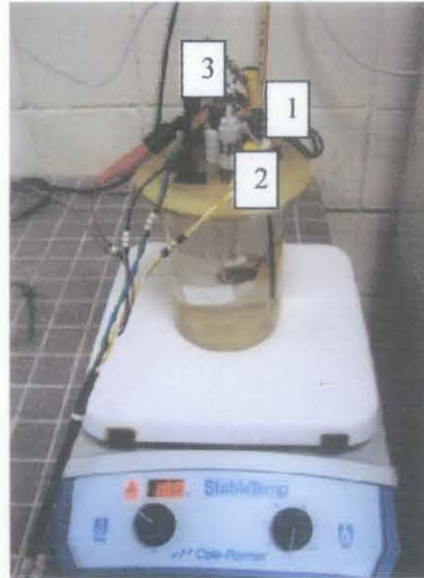
**Figure 3.5: Corrosion Inhibitor provided by AMTECH**

### **3.6 Experiment Procedures**

For this study, several laboratory tests is conducted by varying the concentration if the NaCl solution. Experiments procedures are as per described below:

1. Solution medium of sodium chloride 1% is prepared, 10g of sodium chloride is mixed into distilled water of 1 liter.
2. Working electrode is prepared as per describe in the section 3.2. And Setting up of the equipment for the laboratory test is as per described in section 3.1.
3. Purging of the carbon dioxide gas is started and the solution is left for continuous purging for one until the carbon dioxide is saturated in the solution. The pH meter is used to determine whether the solution is saturated with carbon dioxide or not.
4. The pH of the solution is added with 1M NaHCO<sub>3</sub> to attain a pH level of 4.0.
5. The solution is heated using a hotplate to attain a temperature of 60°C, the temperature is measured using a thermometer that is also set up in the beaker.
6. For the first set of readings, no Corrosion Inhibitor is injected into the solution.
7. Once the chemicals and electrodes are added into the solution, the data acquisition system is accessed, the computer is connected to the ACM Instruments Version 5, run Gill 12 Weld Tester Serial No. 1350 –Sequencer and the Core Running software.
8. Parameters of the test are keyed into the Sequencer software.
9. The ACM Instruments is run and data is gathered automatically into the ACM Analysis Version 4, where they record down the Linear Polarization Resistances and calculate the corrosion rate using the formula that will be discussed in the Section 3.2.7.
10. The test is repeated NaCl 3%, 5%, 10% , 20% and the CI of 25 ppm and 50 ppm is injected into the solution.

Figure 3.6 shows the set up of the test cell. All three electrodes; auxiliary electrode, working electrode and reference electrode has been set up and connected to the data acquisition system.



- |    |                     |
|----|---------------------|
| 1. | Auxiliary Electrode |
| 2. | Reference electrode |
| 3. | Working electrode   |

**Figure 3.6: Static bubble test using Linear Polarization Resistance method set up in the laboratory**

### 3.7 Theory behind calculation

From the linear polarization resistance test, we can determine the corrosion rate of the sample. The theory of the calculation for linear polarization is as shown below:

The corrosion current density is related to polarization resistance by Stern\_Geary coefficient, B. The Stern-Geary Constant, B, is approximated as 25 mV for all pH.[14]

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

**Equation 3.1**

The dimension of  $R_p$  is ohm-cm<sup>2</sup>,  $i_{\text{corr}}$  is mA/cm<sup>2</sup>, and B is in V. B also can be written as:

$$B = \frac{b_a b_c}{2.303(b_a + b_c)}$$

**Equation 3.2**

Where  $b_a$ ,  $b_c$  is the Tafel slope for cathodic and anodic reaction. According to the soft ware that we are using in the lab to do the calculation, Tafel Slope, **B** used in the calculation is 26.

The corrosion rate, CR in mm/year can be determined from the formula shown below:

$$CR = 3.27 \times i_{\text{corr}} \text{ EW} / \text{density of the corroding material}$$

**Equation 3.3**

Where, **EW** is the equivalent weight of the corroding species in grams and the density of the corroding material is in  $\text{g/cm}^3$ . In this case equivalent weight of iron is **27.92 g** and density of the corroding material is iron, thus, iron density is **7.8  $\text{g/cm}^3$** .

## CHAPTER 4

### RESULT AND DISCUSSION

#### 4.1 Laboratory Simulation Test Result

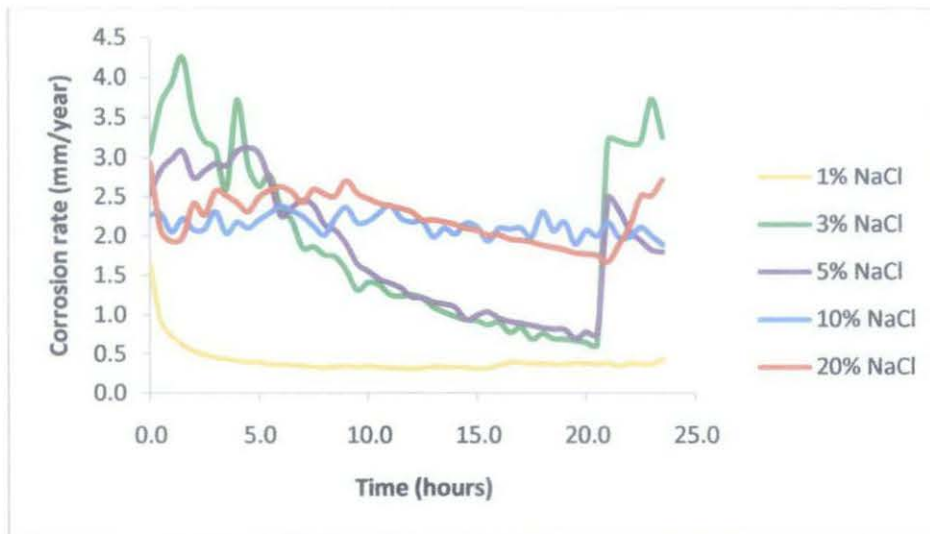
Laboratory simulation test results are divided according to different variables which are NaCl concentration and corrosion inhibitor dosage. For this study there are fifteen laboratory tests that are carried out in order to study the effect of the corrosion inhibitor to the corrosion rate of X 52. The laboratory tests are:

**Table 4.1: Laboratory tests for the corrosion inhibitor study**

pH 4.0 , 60°C		
• 1% NaCl , 0ppm CI	• 1% NaCl, 25ppm CI	• 1% NaCl, 50ppm CI
• 3% NaCl, 0ppm CI	• 3% NaCl, 25ppm CI	• 3% NaCl, 50ppm CI
• 5% NaCl, 0ppm CI	• 5% NaCl, 25ppm CI	• 5% NaCl, 50ppm CI
• 10% NaCl, 0ppm CI	• 10% NaCl, 25ppm CI	• 10% NaCl, 50ppm CI
• 20% NaCl, 0ppm CI	• 20% NaCl, 25ppm CI	• 20% NaCl, 50ppm CI

##### 4.1.1 Laboratory Tests 1

Figure 4.1 shows the corrosion rate for 1%, 3%, 5%, 10% and 20% NaCl concentration with no corrosion inhibitor added to the test solution.



**Figure 4.1: Corrosion rate versus Time for 0ppm CI**



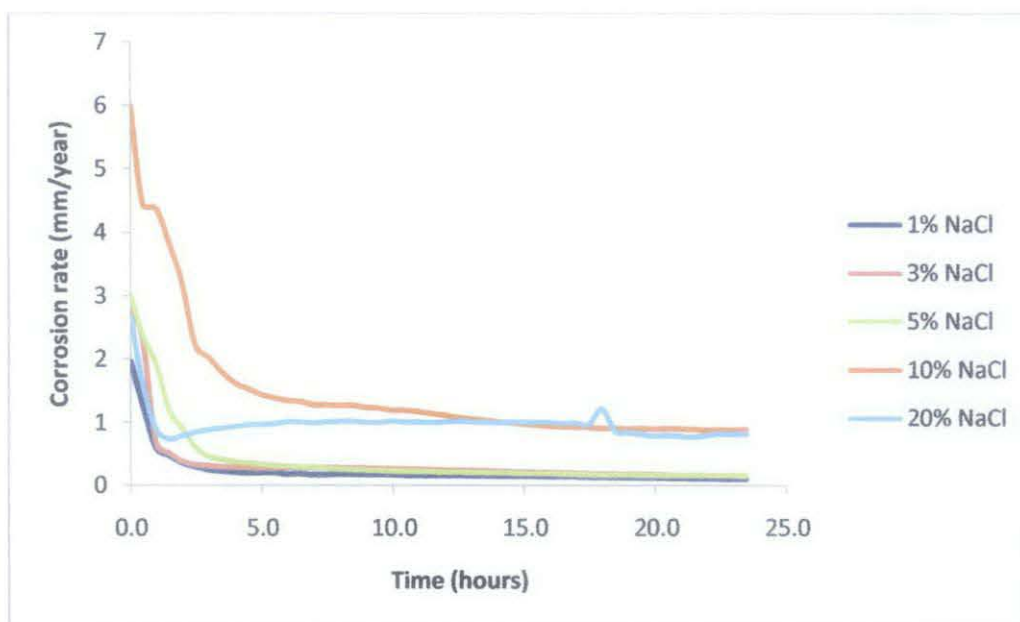
The bubble static testing is done using linear polarization resistance method to measure the corrosion rate of the mild steel using different conditions with different variables. For the first laboratory tests, no corrosion inhibitor is added to the solution as this set of readings serves as a reference basis for uninhibited corrosion rate. From Figure 4.1, it is observed that with the increase of the NaCl concentration, the corrosion rate of the mild steel also increases. For the 1% NaCl test solution, the highest reading for the corrosion rate is 1.5mm/year at the start of the test. The corrosion rate decreases until it reaches a reading of about 0.5mm/year until the end of the test.

For 3% NaCl test solution, the highest reading for the corrosion rate is 4.0mm/year during the first hour of the test. After the fifth hour, the corrosion rate decreases but at the twentieth hour an anomaly occurred where the corrosion rate had a sudden and sharp increase. The reading of 0.5mm/year increased sharply to 3.0mm/year and then increasing further to 3.5mm/year. That trend could also be seen for test solutions 5% NaCl and 20% NaCl. A plausible explanation for that trend could be caused by the sensitivity of the data acquisition system. As the reading shows a contradicting trend of increasing corrosion rate for three tests, there could have been disturbance or system error of the data acquisition system.

The most unstable reading for tests 1 runs is for the solution of 10% NaCl. The corrosion rate is a scattered reading with the range of the corrosion rate between 2.0 and 2.5. It is suspected that this test solution had been contaminated and compromised in terms of its chemical composition thus effecting the readings for this run. Overall it can be concluded that the corrosion rate increases with the concentration of NaCl to the solution.

#### 4.1.2 Laboratory Tests 2

Figure 4.1 shows the corrosion rate for 1%, 3%, 5%, 10% and 20% NaCl concentration with 25ppm corrosion inhibitor injected to the test solution.



**Figure 4.2: Corrosion rate versus time for 25ppm CI**

From Figure 4.2 it is observed that the readings for the different NaCl solution test solution are more stable and follow the trend of decreasing corrosion rate. For 1% NaCl, 3% NaCl and 5% NaCl test solution, the readings and trend are almost the same with corrosion rate at the beginning of the test ranging from 2-3mm/year. All three corrosion rate readings decreases with time with a corrosion rate of 0.5mm/year. Thus it can be summarized that for 1%, 3% and 5% NaCl concentration, the corrosion rate is lower compared to the 10% and 20% NaCl concentration test run. It is also observed that the corrosion inhibitor has reduced the corrosion rate to an acceptable level. It is interesting to note that, even though the NaCl concentration is increased the corrosion inhibitor is still able to reduce the corrosion rate, indicating that its mechanism is not affected by the NaCl concentration of the test solution.

Meanwhile for the 10% and 20% NaCl test solution, a higher corrosion rate is observed with the increase of the salt concentration level. In comparison, the 10%NaCl solution yields a higher corrosion rate compared to 20%NaCl, this could be due to the sensitivity of the data acquisition system. Nevertheless, the corrosion rate of both test solution decreases to 1mm/year, a fifty percent increase in the corrosion rate compared to the earlier test runs. It can be seen that with

the increase of NaCl concentration, the corrosion rate increases but the corrosion inhibitor is still able to reduce the corrosion rate to an acceptable level.

### 4.1.3 Laboratory Tests 3

Figure 4.1 shows the corrosion rate for 1%, 3%, 5%, 10% and 20% NaCl concentration with 50ppm corrosion inhibitor injected to the test solution.

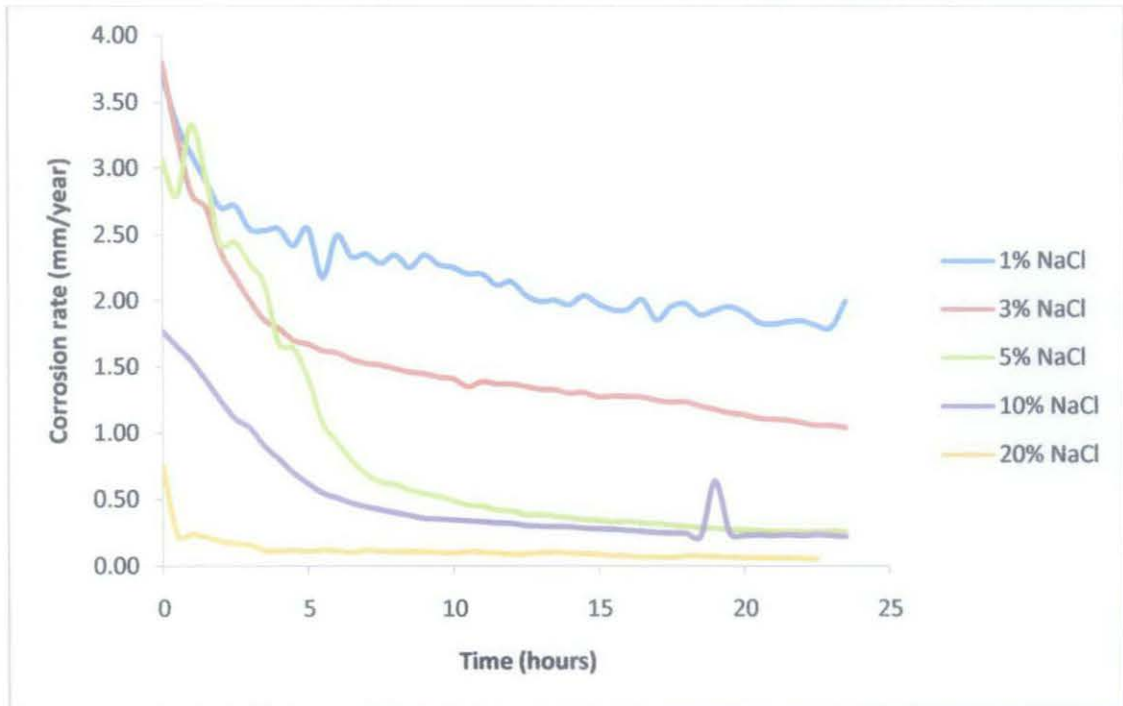


Figure 4.3: Corrosion rate versus time for 50ppm Cl

From Figure 4.3 each test solution shows different levels of corrosion rate. An early observation shows that with the increment of NaCl concentration the corrosion rate decreases. Diverging from the trend that is seen in Laboratory Tests 1 and Tests 2, the lowest corrosion rate for the NaCl concentration is 20% with a corrosion rate of 0.75mm/year than reduced to almost no corrosion rate. This is followed by 10%NaCl test run with a corrosion rate reading of 1.75mm/year, then steadily decreasing to 0.5mm/year. The 5% NaCl test run shows a corrosion rate of 3.0mm/year then also reducing to a corrosion rate of 0.5mm/year. Next is the 3%NaCl test run, yielding a corrosion rate of 3.75mm/year and then reduced to a 1.75mm/year corrosion rate. The last reading is the highest corrosion rate reading after the action of the corrosion inhibitor on the surface of the sample with a reading of 2.5mm/year.

This result is contradicting to the trend observed in Laboratory Tests 1 and Laboratory Tests 2. It seems that the corrosion rate is decreasing with the higher level of NaCl concentration. It is also



observed that the effectiveness of the corrosion inhibitor is reduced with the change of the NaCl concentration. In comparison with Laboratory Tests 2, the corrosion rate of 1%, 3%, 5% and 10%, 20% NaCl was reduced to a relatively same corrosion rate level. In this test run, no such trend is observed. Each test solution has a different corrosion rate and it is increasing with the reduction of NaCl concentration. Possible explanation of the readings and observed trend is that of the effect of the corrosion inhibitor concentration. The dosage used for these test runs is 50ppm while Laboratory Tests 2 injects the corrosion inhibitor with a dosage of 25ppm. The increase of corrosion inhibitor concentration seems to effect the corrosion rate of the carbon steel X52. The corrosion rate is effected in terms of contradicting results for different NaCl concentration and the effectiveness of the corrosion inhibitor is also reduced. An early conclusion is that a higher dosage of corrosion inhibitor compromises the effectiveness of the corrosion inhibitor.

## CHAPTER 5

### CONCLUSION AND RECOMMENDATION

#### 5.1 Conclusion

In conclusion the objective of the this study is achieved that is to investigate the effect of corrosion inhibitor to the corrosion rate of the carbon steel (X52) at different salt concentrations. The variables that are used as constraints for this study are corrosion inhibitor and NaCl concentrations, temperature and pH level. The corrosion inhibitor used is AMTECH manufactured by AMTECH Sdn. Bhd. In this study, fifteen tests were carried out and were divided based on corrosion inhibitor and NaCl concentration. Each test run underwent a preparation process of 1hour for CO<sub>2</sub> purging and the actual test of 24 hours. For each test run, 24 corrosion rate readings are recorded to evaluate the corrosion rate with regards to the four parameters. Breaking down the analysis to uninhibited corrosion rate and inhibited corrosion rate, the uninhibited corrosion test run, the corrosion rate increases with NaCl concentration. Meanwhile for the inhibited corrosion test run, dosages of the CI used were 25ppm and 50ppm. For the 25ppm, the corrosion rate increases with NaCl concentration but is reduced to an acceptable corrosion rate by the corrosion inhibitor. At 25ppm, the corrosion inhibitor manages to reduce the corrosion rate to an acceptable level for each test run. At 50ppm, the corrosion rate decreases with increment of NaCl concentration which is diverging from the trend previously seen in the uninhibited corrosion and 25ppm corrosion inhibitor test run. In addition, the effectiveness of the corrosion inhibitor is also reduced compared to the previous test runs. In conclusion, the optimum CI dosage for the effectiveness of the corrosion inhibitor to the corrosion rate of the carbon steel X52 at different salt concentration is 25ppm. The increase of the NaCl concentration thus corrosion rate increment can still be reduced to an acceptable level by the corrosion inhibitor.

## **5.2 Recommendation**

It is recommended that the test runs be repeated to verify the results, this is to rule out inaccurate results due to errors. Apart from that, it is recommended that the study on corrosion inhibitor is done by also using rotating cylinder electrode (RCE) instead of using static bubble test alone. This is because the static bubble test does not stimulate the real situation in the pipeline due to the low shear wall stress provided by the static bubble test. Linear Polarization resistance measurement alone is not sufficient for the monitoring of the corrosion rate in the laboratory experiments, but more reliable data weight loss method also can be used to determine the corrosion rate of the test. The laboratory test should be conducted with the collaboration of the corrosion inhibitor provider company, for example AMTECH Sdn.Bhd, so that students will be able to obtain confidential data from experiments that had been conducted by the manufacturer of the corrosion inhibitor. It is essential also to be able know the chemical composition of the corrosion inhibitor to better understand the mechanism of the inhibitor. Other operational parameters such as the effect of temperature and pH level to the effectiveness of the corrosion inhibitor to the corrosion rate of carbon steel should be add on to the study to attain a more holistic study.

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