EFFECT OF ACETATE ION ON CARBON STEEL CORROSION IN THE PRESENCE OF CO$_2$

By

Marc Teyrouz

Submitted in partial fulfillment of the requirements For the degree of Master of Engineering

Major Subject: Petroleum Engineering

At

Dalhousie University

Halifax, Nova Scotia

Decembre, 2012
The undersigned hereby certify that they have read and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled “EFFECT OF ACETATE ION ON CARBON STEEL CORROSION IN THE PRESENCE OF CO₂” by Marc Teyrouz in partial fulfillment of the requirements for the degree of Master of Engineering.

Dated:  Decembre 14\textsuperscript{th}, 2012

Supervisor:  ______________________________________

Reader:  ______________________________________

Departmental representative:________________________
DATE: Decembre 14th, 2012

AUTHOR: Marc Teyrouz

TITLE: EFFECT OF ACETATE ION ON CARBON STEEL CORROSION IN THE PRESENCE OF CO₂

DEPARTMENT OR SCHOOL: Faculty of Engineering, Petroleum Engineering Program

DEGREE: M.Eng. CONVOCATION: October YEAR: 2012

Permission is herewith granted to Dalhousie University to circulate and to have copied for non-commercial purposes, at its discretion, the above title upon the request of individuals or institutions. I understand that my thesis will be electronically available to the public. The author does not reserve other publication rights and the thesis nor may extensive extracts from it be printed or otherwise reproduced without the author’s written permission.

The author attests that permission has been obtained for the use of any copyrighted material appearing in the thesis (other than the brief excerpts requiring only proper acknowledgement in scholarly writing), and that all such use is clearly acknowledged.

______________________________
Signature of Author
DEDICATION

I dedicate this work to almighty God, the source of my knowledge and inspiration.
ACKNOWLEDGEMENTS

This report could not have been written if it were not for the contribution and encouragement of various people.

My first wish is to thank the project supervisor, Dr. Michael Pegg for his advice and support. I am highly indebted to Mr. Mumuni Amadu for his guidance and constant supervision. Special thanks go to Dr. George Jarjoura for providing necessary information regarding the project and also for his support in completing my project.

Special gratitude goes to my friends Andrea Darzi, Joanne Massoud, Maria Bou Rouphael, Jessica Najm and Khalil Azar for their kind co-operation and encouragement.

This report would not have been written without my perseverance. Also, the encouragement and devotion of my family should be mentioned who have helped a great deed.
ABSTRACT

The purpose of this study is to find a new technique that will help engineers decrease corrosion rate and minimize the cost caused by the corrosion of pipelines. It will provide information on the mechanisms, highlight the effect of acetate, and draw attention to areas requiring further research.

Internal pipeline corrosion is still one of the main obstacles that slows and decreases the production of oil and gas. It is primarily associated with the presence of free water, particularly when it reacts with CO₂ and organic acids.

The presence of acetic acid and acetate in the brine can increase the corrosion rate. Some studies have proven that they work as inhibitors. This report will explain in detail the mechanism of corrosion and will verify when acetate works as a buffer as well as the effect it has on corrosion of mild steel pipelines. The findings were backed by researches and papers of authors who have worked on the same topic but with different models and approaches.

The lab-work was done on steel coupons and corrosion rates were calculated using the weight loss technique.
LIST OF SYMBOLS AND ABBREVIATIONS

A Total exposed surface area in in² or mm²
A⁻ Conjugate base
Ac⁻ Acetate ion
CaCl₂ Calcium chloride
CaCO₃ Calcium carbonate
CH₃COOH Acetic acid
CO₂ Carbon dioxide
CO₃⁻ Carbonate ion
e⁻ Electron charge
Fe Iron
Fe²⁺ Ferrous ion
HA Acid
HAc Acetic acid
H⁺ Hydrogen ion
HCl Hydrochloric acid
H₂CO₃ Carbonic acid
HCO₃⁻ Bicarbonate ion
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S</td>
<td>Hydrogen sulfide</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>K</td>
<td>Constant for unit conversion</td>
</tr>
<tr>
<td>LPR</td>
<td>Linear Polarization Resistance</td>
</tr>
<tr>
<td>Δm</td>
<td>Mass of metal in gram</td>
</tr>
<tr>
<td>mₐ</td>
<td>Mass of coupon after exposure</td>
</tr>
<tr>
<td>mₐ</td>
<td>Mass of coupon before exposure</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>Sodium bicarbonate</td>
</tr>
<tr>
<td>O₂</td>
<td>Oxygen</td>
</tr>
<tr>
<td>R corr</td>
<td>Penetration rate in mil/y</td>
</tr>
<tr>
<td>S</td>
<td>Surface area of the metal</td>
</tr>
<tr>
<td>Δt</td>
<td>Total exposure time in hours</td>
</tr>
<tr>
<td>ρ</td>
<td>Density</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS

**DEDICATION** .................................................................................................................. IV

**ACKNOWLEDGEMENTS** ................................................................................................... V

**ABSTRACT** ....................................................................................................................... VI

**LIST OF SYMBOLS AND ABBREVIATIONS** ................................................................. VII

**TABLE OF CONTENTS** ................................................................................................... IX

**LIST OF TABLES** .............................................................................................................. XI

**LIST OF FIGURES** .......................................................................................................... XII

## CHAPTER 1: INTRODUCTION .............................................................................................. 1

1.1 **BACKGROUND** .......................................................................................................... 1

1.2 **CLASSIFICATION OF PIPELINES** ........................................................................... 2

1.3 **TRANSPORTED PRODUCTS** ..................................................................................... 3

1.4 **PIPELINES LEAK DETECTION** .................................................................................. 3

1.5 **SOURCE OF ACETIC ACID AND ACETATE** ............................................................ 4

1.6 **PROJECT SCOPE AND OBJECTIVES** ....................................................................... 4

1.7 **PROJECT ORGANIZATION** ......................................................................................... 5

## CHAPTER 2: LITERATURE REVIEW ..................................................................................... 7

2.1 **DEFINITION OF CORROSION** .................................................................................... 7

2.2 **TYPES OF CORROSION** ........................................................................................... 8

2.3 **FACTORS THAT AFFECT CORROSION** .................................................................... 8

2.4 **PARAMETERS THAT AFFECT CORROSION IN THE PRESENCE OF ACETIC ACID AND CO₂** ................................................................. 10

2.5 **TECHNIQUES TO MEASURE CORROSION RATE** ...................................................... 10

2.6 **CORROSION RATE CALCULATIONS** ........................................................................ 11

2.7 **CORROSION PREVENTION AND REDUCTION** ......................................................... 12

2.8 **TYPES OF WELLS IN RESPECT TO CORROSION** .................................................... 13

2.9 **CORROSION CAUSES** ............................................................................................... 14

2.10 **CONSEQUENCES AND IMPACT OF CORROSION IN THE OIL INDUSTRY** ............... 15

2.11 **CORROSION PROBLEMS DURING PRODUCTION** .................................................. 16

2.12 **CARBON DIOXIDE CORROSION MECHANISM** ....................................................... 17

2.13 **PREVIOUS STUDIES** ................................................................................................ 18

2.14 **EVOLUTION OF CORROSION INVESTIGATION** ...................................................... 20

2.15 **CORROSION RESEARCH IN THE OIL AND GAS INDUSTRIES MODELS USED** .......... 23

   2.15.1 **De Waard Corrosion** ......................................................................................... 23

   2.15.2 **Slight Modification to the De Waard Model** ..................................................... 23

   2.15.3 **Electrochemical Model** ................................................................................. 24

2.16 **EFFECT OF ACETATE AND ACETIC ACID ON CORROSION** .................................. 24

2.17 **BUFFERING EFFECT OF ACETATE** ........................................................................... 26
LIST OF TABLES

TABLE 1: EFFECTS OF THE KEY CHEMICAL CHARACTERISTICS OF CORROSION ..................... 9
TABLE 2: COMPOSITION, MASS AND pH OF THE 14 DIFFERENT SAMPLES .......................... 30
TABLE 3: EFFECT OF SODIUM ACETATE ON THE CORROSION RATE OF THE MILD STEEL COUPONS ......................................................................................................................... 34
TABLE 4: EFFECT OF SODIUM ACETATE ON THE CORROSION RATE OF MILD STEEL COUPONS IN SOLUTIONS SATURATED WITH CO₂ ..................................................................................................................... 35
TABLE 5: EFFECT OF pH ON CORROSION RATE OF MILD STEEL COUPONS IN SOLUTIONS SATURATED WITH CO₂ ......................................................................................................................... 36
TABLE 6: EFFECT OF SODIUM ACETATE AND SODIUM BICARBONATE ON THE CORROSION RATE IN A SOLUTION WITHOUT CO₂ .................................................................................................................. 36
TABLE 7: EFFECT OF SODIUM ACETATE AND SODIUM BICARBONATE ON THE CORROSION RATE IN A SOLUTION SATURATED WITH CO₂ .................................................................................................................. 37
TABLE 8: EFFECT OF CO₂ ON THE CORROSION RATE OF MILD STEEL .................................. 37
TABLE 9: EFFECT OF SODIUM BICARBONATE ON THE CORROSION RATE OF MILD STEEL IN SOLUTION SATURATED WITH CO₂ .................................................................................................................. 38
TABLE 10: THE LAB RESULTS ........................................................................................................ 44
LIST OF FIGURES

FIGURE 1: THE BAYLIS CURVE........................................................................................................................................ 15

FIGURE 2: THE CAPILLARY PRESSURE SYSTEM USED TO SATURATE THE BRINE SOLUTION WITH CO₂.................................................................................................................................................. 32

FIGURE 3: THE CAPILLARY PRESSURE SYSTEM THAT WAS USED TO BUBBLE CO₂ IN THE .................................................................................................................................................. 33

FIGURE 4: pH METER (METLER TOLEDO) USED DURING OPERATION TO CHECK THE VARIATION OF pH.................................................................................................................................... 45

FIGURE 5: pH-INDICATORS USED WHEN TOLEDO WAS NOT AVAILABLE ................................................................. 45

FIGURE 7: COUPON USED FOR THE CORROSION TEST ............................................................................................ 46

FIGURE 8: SAMPLE NUMBER 3 WHERE CORROSION CAN BE SPOTTED ON THE COUPON .......................... 46

FIGURE 9: SOLUTION SATURATED WITH CO₂ ......................................................................................................... 47
CHAPTER 1: INTRODUCTION

1.1 Background

The transportation of the produced oil from its place of recovery to where it is processed and the transportation of the refined product from where it is processed to where it is consumed is a key element in the oil industry and its smooth functioning. Until today, pipeline transportation is the most economical way to transport large quantities of oil and gas and is by far the safest method. Without these pipelines, our world would struggle to satisfy its need of oil and gas. In fact, any substance that is chemically stable can be delivered through a pipeline.

To avoid leakage and any sort of catastrophe, all pipelines should be frequently examined, checked and well maintained. For example, engineers should always check if the cathodic protection levels are at the proper range and if there is any kind of erosion. They should always run cleaning pigs when there is any corrosive element carried in the pipeline to identify the thickness of the metal and eventually determine if the pipeline is deteriorating.

Nowadays, corrosion is a serious matter that is debated and studied around in the field. It is a major concern to the engineers interested in the safety and protection of a good and complete running operating system. "While you read this, 760 kg of iron has been corroded" - this slogan was a poster displayed in an exhibition in 1937 in Brussels that highlighted how much corrosion happens at every moment (Vámos and Petrik, 1937). Because all pipelines are mainly made of steel, and since it is well known that corrosion often occurs in the presence of steel, the main focus is to manage this corrosion. There are many ways to decrease and avoid corrosion but each one has its own and different expense so it is necessary to find an ideal solution with the lowest cost. In that matter, some engineers tried to replace steel pipelines by plastic pipelines, since plastic does not corrode.
But this replacement was ineffective since plastic doesn't normally have the same strength as steel. However, plastic pipelines could serve as a valuable product for low pressure applications such as local distribution lines.

1.2 Classification of Pipelines

There are three categories of pipelines based upon their purpose:

1. The first category is the "gathering pipelines"; this type of pipeline is mainly used to carry natural gas or crude oil, through an interconnected network of smaller pipelines towards a treatment plant. Those pipelines mainly have a small diameter and a length ranging from 100 to 200 metres. Sub-sea pipelines are listed as well under this category.

2. The second category is the "transportation pipelines"; their main role is based on their enormous length in order to move the products from one position to another, for example from one country to another or even more from one continent to another. This comprises, in parallel, many pumps and compressor stations to keep the flow coming.

3. Finally, the third category is the "distribution pipelines"; they have a small diameter so they could lead the product to its final destination, which means the consumer. They distribute the gas, oil, water and chemicals to the cities using a narrowed network.
1.3 Transported Products

The pipelines transport a vast diversity of products and in large quantity. The transported products are mainly gasoline, jet fuel, diesel and natural gas. In addition, many liquids and fuels like crude oil, alcohol and various grades of petrol are also transported. Moreover, water is present in large quantities as a by-product of oil and gas.

1.4 Pipelines Leak Detection

To ensure the reliability of the infrastructure, it is of paramount importance to be able to detect a shortage or a failure in any part of the pipeline system and at the appropriate time. (Yudaya, 2006)

Leaks in pipes where liquid flows can be detected by:
1. Ground producing liquid bubbles.
2. Oil glistening on water.
3. Flames that erupt from the ground.
4. Vapor clouds.

and leaks in pipes where gas is flown can be detected by
1. Blowing sound, hissing, or roaring.
2. Dirt or water that are ejected in the atmosphere.
3. Non-stop bubbling in wet/flooded areas.
4. Ground emerging flames.
5. Vegetation; whether dead or brown found in green fields.
6. Melted snow over the pipeline found during winter time.
1.5 Source of Acetic Acid and Acetate

Oil and gas reservoirs always contain short chain carboxylic acids alongside other corrosive compounds like carbon dioxide (CO$_2$) and hydrogen sulfide (H$_2$S) (Gulbrandsen and Bilkova, 2006). The most abundant of organic acids, which was first discovered in 1944 from oil and gas production and transport lines, is acetic acid (Crolet et al., 1999). Acetic acid can also be written as CH$_3$COOH, and abbreviated HAc. Acetate can also be found in formation waters.

To classify the organic acids, the molecular weight is analyzed. The organic acids with a lower molecular weight are more soluble in water. On the other hand, those of higher molecular weight are only soluble when in their oil phase and solely cause corrosion at elevated temperatures.

1.6 Project Scope and Objectives

Corrosion tests were specified only for brine saturated with CO$_2$ versus pilot tests that exclude CO$_2$. It was important for the experiment that the brine solution be saturated with CO$_2$ so the acetic acid could react with it and start the series of reactions that will be studied later in this paper. Acetic acid and acetate play a significant role on the rate of corrosion that will affect the safety, maintenance and lifetime of the stainless steel pipes that carry the oil and water. The major objectives of this project work were:

1. To study the effects of addition of sodium acetate and sodium bicarbonate in the saturated brine solution on the corrosion of mild steel coupons.
2. To study the effects of carbon dioxide addition on the corrosion of mild steel coupons.
1.7 Project Organization

This paper is based on projects and studies already completed but with different instruments and different materials. In this project, some of the previous studies on the effect of acetate on corrosion in the presence of CO$_2$ will be reviewed. This work project is outlined as follows:

1. **Introduction**: the first chapter is where the reader is introduced to the project. Background information on corrosion, pipelines and the acetic acid as the source of corrosion, as well as the scope and objectives of this project are approached.

2. **Literature review**: past research studies on how acetate causes corrosion of mild steel when found saturated with CO$_2$, is mainly studied in this chapter; in addition to information and calculation equations on how to measure the corrosion rate.

3. **Corrosion background**: some general knowledge about corrosion is introduced in this chapter.

4. **Experimental design**: this chapter includes all the details about the step-by-step procedure used in carrying out the laboratory work for this project.

5. **Results and discussion**: in this chapter, all the results and the observations obtained from the experimental work are listed.

6. **Summary and conclusions**: this chapter summarizes the project with its interpretations and results obtained.

7. **Recommendations**: suggestions and advices that will help in the accuracy and improvement of future works and studies on this topic.

8. **References**: consists of a list of bibliographies used in writing this paper.
Appendix: this chapter consists of some extra data and information that can be helpful in understanding the study. It also includes pictures taken from the lab while doing the experiments.
CHAPTER 2: LITERATURE REVIEW

Corrosion is one of the main challenges that engineers try to overcome every time they have to design a well or a pipeline because it decreases the lifetime of these metal tools. The biggest concern of the engineers is the prevention of corrosion. Because of its high impact on the industry, corrosion control has been a main concern for a long time and is constantly being a center of research in order to improve the efficacy of the metals and to decrease the corrosion of the pipelines. Corrosion can cost a lot of money to the industry if it is not checked and controlled properly. It can also reduce the heat transfer and water flow due to the blockage of pipes and valves.

2.1 Definition of Corrosion

Corrosion is the result of metal reacting with the environment in an electrochemical fashion causing it to lose some of its material (Asrar, 2010). Liquids and gases in contact with metal are chemical causes of this corrosion reaction which could be accelerated by high temperatures, acids and salts (Kanavy and Williams, 2012). The product of this reaction acts as protective layers. If removed, the metallic surface becomes re-exposed and vulnerable to a corrosion reaction once again. Ulick R. Evans, considered as the father of corrosion, talks of this phenomenon which is a three-step electrochemical reaction. First, free oxygen found in the water enters the metallic surface (the cathode), thus causing a reaction with the products (water and electrons) of the oxidation process of metal at the anode side. Then, the hydroxide ion (which is formed by the combination of free electrons, oxygen and water) will come together with the metal ions, products of the oxidation reaction taking place at the anode side, thus leading to the creation of an insoluble metal hydroxide. This leads to metal loss and deposit formation (Bhatia, 2004).
2.2 Types of Corrosion

1. Uniform corrosion: when the corrosion reaction occurs in a uniform fashion over the entire surface area.

2. Pitting corrosion: when the corrosion reaction occurs in a localized point on the surface area.

3. Galvanic corrosion: occurs when the corrosion is caused by the reaction of two dissimilar types of metals in contact with one another.

It is important to note that different types of corrosion are also found in the oil and gas industry. The most important ones are: corrosion fatigue, stress corrosion cracking (SCC), selective leaching and erosion corrosion.

2.3 Factors that Affect Corrosion

There are many factors that are known to affect the corrosion of steel.

The most important ones are:

1. Dissolved oxygen: the total amount of oxygen that is dissolved in the brine plays an important role in allowing the cathodic reaction to occur. Without the presence of oxygen, this reaction does not exist and therefore corrosion does not occur.

2. Alkalinity and acidity: when the alkalinity of water is low, acids are less likely to be buffered out and corrosion will take place.

3. Total dissolved solids: as the concentration of dissolved solids in water increases, the conductivity follows and increases so will the overall corrosion.

4. Microbial growth: accelerates the creation and development of corrosion cells.
5. Flow velocity: when a high velocity flow rate is applied, more oxygen will be transported to some metals. Automatically, a higher corrosion rate will be detected. On the other hand, if the flow rate is very low, a deposition of solids will be noticed at the bottom and a localized corrosion will happen, thereby increasing the corrosion rate.

6. Temperature: the temperature increases the corrosion rate.

The effects of the key chemical characteristics of corrosion like pH and alkalinity are summarized in table 1 just below.

**Table 1: Effects of the Key Chemical Characteristics of Corrosion**

<table>
<thead>
<tr>
<th>Chemical Characteristic</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Low pH may increase the corrosion rate whereas high pH may protect pipes and decrease corrosion rates</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>May help form a protective CaCO₃ coating, helps control pH changes, and reduces corrosion</td>
</tr>
<tr>
<td>Dissolved oxygen (DO)</td>
<td>Increases the rate of many corrosion reactions</td>
</tr>
<tr>
<td>Chlorine residual</td>
<td>Increases corrosion</td>
</tr>
<tr>
<td>Total dissolved solids (TDS)</td>
<td>High TDS increases conductivity and corrosion rate</td>
</tr>
<tr>
<td>Hardness (Ca and Mg)</td>
<td>Ca may precipitate as CaCO₃ and thus provide protection and reduce corrosion rates</td>
</tr>
<tr>
<td>Chloride, sulfate</td>
<td>High levels increase corrosion of iron</td>
</tr>
<tr>
<td>Hydrogen sulfide (H₂S)</td>
<td>Increases corrosion rates</td>
</tr>
<tr>
<td>Silicate, phosphates</td>
<td>May form protective films</td>
</tr>
<tr>
<td>Natural color, organic matter</td>
<td>May decrease corrosion</td>
</tr>
<tr>
<td>Iron, zinc, or manganese</td>
<td>May react with compounds on the interior of a pipe to form a protective coating</td>
</tr>
</tbody>
</table>
2.4 Parameters that Affect Corrosion in the Presence of Acetic Acid and CO$_2$

A number of factors appear to determine the corrosion rate in presence of acetic acid and carbon dioxide. These factors include:

1. Concentration of the reactants and products.

2. Electrochemical kinetics of cathodic reactions (activation control or mass transfer control).

3. Electrochemical kinetics of the anodic reaction (inhibition by HAc, localized or uniform dissolution).


2.5 Techniques to Measure Corrosion Rate

Through time, many measurement techniques were used by many scientists and engineers in order to achieve some studies and get some results concerning corrosion and how acetic acid and acetate can affect the corrosion rate in solution saturated with CO$_2$. Some of these measuring techniques are:

1- Linear Polarization Resistance (LPR): this method relies on a potential current (20mV) that will be applied to a corroding solid sensor where the resulting current response will be measured (Stern and Geary, 1957).

The main advantage for the use of this LPR is the speediness in which it can provide a measurement of the corrosion rate and thus will give an immediate feedback to operators. Moreover, LPR can help determine the tendency for pitting and if this pitting will be shallow or deep.

2- Electrochemical noise measurement: a technique that is based on the fluctuations of current and potential.
3- The potentiodynamic sweep.
4- The electrochemical impedance.
5- Weight loss measurement.
6- The George-De Waard-Nesic (GDN): It is a modification to the de Waard corrosion model.

Each one of these techniques works best in its own suitable conditions. for example, Keith George and Srdjan Nesic stated in their paper “electrochemical investigation and modeling of CO\textsubscript{2} corrosion of carbon steel in the presence of acetic acid” in 2004: “At 100 ppm HAc, the electrochemical model is too conservative in the corrosion rate predicted while the GDN model is in very good agreement with the experimental values. At high concentrations of HAc (1000 ppm) the electrochemical model is in very good agreement with the experimental data while the GDN model under predicts the corrosion rate” (George et al., 2004).

2.6 Corrosion Rate Calculations

To be able to apply a formula to calculate the corrosion rate, some assumptions should be taken into consideration. Primary, we should assume a uniform type of corrosion and secondly a corrosion rate that does not vary with time.

According to some papers, one of the formulas used to calculate the corrosion rate is

\[
R_{corr} = \frac{\Delta m}{S \times \Delta t}
\]  

(1)

Where:

- \(M\) the mass of the corroded metal in grams
- \(R_{corr}\) penetration rate of corrosion in mil/y
- \(S\) the surface area of the metal in in\(^2\) and
The more accurate formula to estimate the corrosion rate in this paper for the calculation is

\[
R = \frac{K \times (m_B - m_A)}{A \times \Delta t \times \rho}
\]  

Where:

- \(A\) total exposed surface area in \(\text{in}^2\)
- \(\rho\) density in \(\text{g/cm}^3\)
- \(K\) constant for unit conversion equal to \(2.23 \times 10^4\)
- \(m_B\) mass of coupon before exposure in gram
- \(m_A\) mass of coupon after exposure in gram
- \(\Delta t\) total exposure time in hours
- \(R\) penetration rate in \(\text{mil/y}\)

2.7 Corrosion Prevention and Reduction

These are the best ways used nowadays to prevent corrosion, or at least try to reduce and control it (Uhlig et al., 1985):

1. Choose the best type of material for the pipelines that will have the maximum resistance to corrosion.

2. Use of corrosion resistant alloys that contain constituents like chromium. The latter has the ability to produce a more effective protective film that resists breakdown. (Shreir et al., 1994).

3. Use some coatings like paints and waxes that will protect the pipes from corrosion due to their higher tendency potential to corrode than the metal they are protecting.
4. Add protective films.


6. Use a cathodic and anodic protection device to protect the pipes from the outside.

7. From the inside, sound operating practices can be used in order to protect the interior from corrosion.

8. Use Smart pigs that are inspection devices to measure things like the pipe thickness and record information about the internal conditions along a pipeline (Fontana, 1986).

9. Chemicals as Corrosion Inhibitors:
   - Chromate: excellent steel corrosion inhibitor, but recently banned by USEPA for environmental issues.
   - Molybdate is the replacement of chromate and is costly.
   - Polysilicate: not often used because hard to formulate but happens to be a very good steel inhibitor at a concentration of 6 mg/L.
   - Polydiol.
   - Ortho-phosphate: only works if there is 50mg of calcium present in the composition
   - Nitrite: has a great ability to be a highly effective steel corrosion inhibitor but a high concentration is needed in the range of 500 -700 mg/L.

2.8 Types of Wells in Respect to Corrosion

There are three (3) types of wells classified according to their degree of corrosivity:

1. Non-corrosive: wells where no corrosion evidences had been spotted over an 8 years period of time, in spite of significant water cut.
2. Corrosive: wells where corrosion problems had been encountered, with short lifetimes, usually less than 3 years.

3. Possibly corrosive: wells where the absence of corrosion problems is still debatable and could not be assumed definitive.

2.9 Corrosion Causes

These are some causes that are known to induce corrosion, amongst which:

1. Water wetting of the pipe wall.
2. High potential corrosivity (high $P_{\text{CO}_2}$, low pH, etc.).
3. An electrical current.
4. Chemical reactions involving water, CO$_2$ and acetic acid.

Moreover, primary factors including alkalinity, pH, hardness, oxidizing agents, CO$_2$, and dissolved solids can also have an effect on corrosion.

Acidic water by definition is water containing a high concentration of (H$^+$) ions. These (H$^+$) ions react with the electrons found at the cathode side increasing the capability of a corrosion reaction. In basic water, meaning water with a high pH, the solubility of calcium carbonate decreases and thus it is more likely to obtain a precipitate consisting in scale.

The pH of water is measured by its level of alkalinity. When the alkalinity of water is high, scale will most probably form even at a relatively low pH. On the contrary, when the alkalinity of water is low, acids are less likely to be buffered out and thus corrosion is more likely to happen.
Figure 1: The Baylis curve (http://water.me.vccs.edu/concepts/corrosioncauses.html).

The Baylis curve shown in Figure 1, describes the relationship between pH, alkalinity and water stability. The area above the curve in blue indicates scale forming water, the grey shaded area is indicative of corrosive water while the white area is that of stable water.

2.10 Consequences and Impact of Corrosion in the Oil Industry

Transportation pipelines are among the main factors of environmental risk during offshore oil developments. One of the main causes of pipeline damage is corrosion. In fact, corrosion is identified as the most common “in-service” cause of failure of pipelines and pipeline spills. Depending on the cause and nature of the damage (cracks, ruptures), a pipeline can become either a source of small and long-term leakage or a sudden blowout of hydrocarbons near the bottom.

Corrosion attacks every component at every stage in the life of every oil and gas field. From casing strings to production platforms, from drilling through to abandonment, corrosion is an adversary worthy of all the high technology and research (Kermani, 1996).
2.11 Corrosion Problems during Production

The entire process starting from oil and gas being produced to the making, transporting and use of the fuel and raw materials for production of certain chemicals is grueling and complicated. This process does not go smoothly without encountering some obstacles one of the major ones being corrosion. The time wasted and the materials that are replaced are costly errors and can be disastrous.

The environmental factors that play a unique role in oil and gas production are the actual environments in which the process occurs and which should be lacking any oxygen if not contaminated. Other unique factors are the temperature and pressures that are found.

The geologic environment that is devoid of oxygen supposedly could be exposed to oxygen contaminated fluids, some of which could be of a corrosive nature while others could carry the potential to be corrosive only when exposed to oxygen.

The problem of corrosion due to oxygen is found mainly in oil production since the process takes place at close to ambient pressures which causes the oxygen leakages through hatches, pump seals and vents to become extremely possible. It is important to note that oxygen, being the powerful oxidant, causes harm even if it is present in the smallest amounts. Another issue found in oil and gas production is mainly the use of carbon and low-alloy steels that are known to have a high corrosion potential.

Another point worth mentioning is hydrogen sulfide which is a weak acid when dissolved in water that has corrosive potential because of the hydrogen ions in it. In oil and gas production, this weak acid behaves as a catalyst in order to stimulate the absorption of hydrogen ions by steel.
2.12 Carbon Dioxide Corrosion Mechanism

CO₂ dissolved in water leads to the formation of carbonic acid (H₂CO₃) (Cai, 2005), which is a weak acid in comparison to mineral acids, as it does not fully dissociate.

In the case of carbon steel in brine, the presence of acetate and carbon dioxide leads to the formation of acetic acid.

Moreover, in many of the brines containing acetate and carbon dioxide, the concentration of acetic acid is far higher than that of free proton (H⁺) and it is this that leads to an enhancement of the rate of corrosion by acetate.

The CO₂ corrosion mechanism that occurs on the metallic surface is affected by several conditions such as temperature, pressure and pH. As Derek Pletcher claimed in 2003; "The speciation of the medium can influence the corrosion of a metal through either the type of film formed on the surface of the corroding metal or through the thermodynamics and kinetics of the anodic and cathodic reactions leading to corrosion" (Pletcher et al., 2003).

The process and mechanism have been studied widely throughout many experiments and are summarized as follows:

Carbon dioxide dissolved in water leads to a hydration reaction, thus producing a weak carbonic acid as shown below:

\[
\text{CO}_2(g) \leftrightarrow \text{CO}_2 \quad \text{(3)}
\]

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \quad \text{(4)}
\]

The carbonic acid (H₂CO₃) produced is then partly dissociated into the bicarbonate ion that may then break down into a carbonate ion by a fast reaction (Pletcher et al., 2002):

\[
\text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \quad \text{(5)}
\]
\[ \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^- \] (6)

As it has been demonstrated in many papers and as generally known by many, carbonic acid solutions are more corrosive than solutions containing strong acids such as HCl to mild steel, at the same pH (Waard and Lotz, 1993). Many hypotheses were suggested in order to answer this controversial debate where Waard had the best explanation, in which he stated that this is because after contact with the metallic surface, there is less dissociation of the carbonic acid molecule. This step is the rate-determining step in the \(\text{CO}_2\) corrosion mechanism. In conclusion, the corrosion rate is directly connected to the concentration of the un-dissociated \(\text{H}_2\text{CO}_3\) molecules in solution.

2.13 Previous Studies

In 1999, Hedges and McVeigh used the rotating cylinder electrodes to investigate the effect of acetate in \(\text{CO}_2\) corrosion. The acetate ions were coming from the decomposition of acetic acid in some experiments and from sodium acetate in others; they noticed that both sources that they used increased the corrosion rates but the acetic acid decreased the pH while acetate increased it where he concluded: “The increased corrosion rates were attributed to the formation of thinner iron carbonate films, since acetate ions have the ability to form iron acetate and transport iron away from the steel surface”. In fact, they didn’t control the pH change in their experimental work. So Hedges and McVeigh argued that: “since HAc dissociation can occur very quickly, it is not possible to distinguish the reduction of hydrogen ions from direct HAc reduction at the electrode surface” (Hedges and McVeigh, 1999).

A paper in 2003 by Garsany, Pletcher and Hedges entitled “the role of acetate in \(\text{CO}_2\) corrosion of carbon steel: studies related to oilfield conditions” used voltammetry on the X65 carbon steel electrodes fabricated from rods, diameter 0.48 cm, to study the effect of
acetate on carbon steel corrosion. The voltammetry was carried out with an EG & G Model 173A potentiostat controlled by a PC operating the Headstart™ software through a Computer Graphics Interface. Voltammograms for the steel samples were recorded as soon as possible after immersion of the steel in the brine and the potential was scanned from the negative limit. At the end, they did many experiments using different conditions like different temperatures and compared the results in Voltammograms. They came up with many conclusions like: “the rate of corrosion increases with temperature. The lower solubility of CO\(_2\) at the higher temperature will lead to a higher pH and a lower conversion of acetate to acetic acid but the increased rates of all electron transfer reaction at 333 K more than overcomes this effect”. Moreover, they have proved that: “a high bicarbonate concentration can lead to a brine pH that is high enough that the conversion of acetate to acetic acid is low and hence the impact of the acetate on steel corrosion can then sometimes be very low” (Pletcher et al., 2003).

Egil Gulbrandsen also studied in one of his paper the effect of addition of acetic acid on CO\(_2\) corrosion and mainly on the formation and protectiveness of corrosion films of iron carbonate (FeCO\(_3\)). His tests were carried out at high temperatures 80°C, 0.5 bar CO\(_2\) and using rotating cylinder electrodes. He has studied corrosion electrochemically using a potentiostat equipped with an eight-channel multiplexer. Corrosion rates were determined from polarization resistance, which was measured by a 0.1 mV/s potential scan vs. the corrosion potential. He concluded that: “It was possible to maintain protective FeCO\(_3\) films at 80°C in presence of up to a least 100 ppm free HAc. Protection was lost below this value” (Gulbrandsen, 2007).
2.14 Evolution of Corrosion Investigation

Crolet and Bonis discussed the role of HAc on the in-situ pH. Their experimental data showed that HAc increased the cathodic limiting currents thus increasing the potential corrosiveness (Crolet and Bonis, 1983).

Hedges and McVeigh tested the effect of HAc on CO₂ corrosion at 60°C. The corrosion rates increased with increasing HAc concentration and with the adding Ac⁻ to a CO₂ system, even if the pH increased since Ac⁻ is converted to HAc by the acidity of CO₂ and since Ac⁻ may be counted as HCO₃⁻. The problem is that they did not take care of the pH in their experiments and the solution not replenished (Hedges and McVeigh, 1999).

Crolet, Thevenot and Dugstad investigated in 1999 the effect of HAc on the anodic dissolution of carbon steel under CO₂ atmosphere. It was found that the corrosion rate was slightly inhibited above 3 mM (180 ppm) HAc. It was also noted that the corrosion rate remained high when the HAc was continuously replenished in corrosion tests (Crolet et al., 1999).

Ueda and Takabe in 1998 investigated the effect of 0.5 % (5000 ppm) HAc on carbon and chromium bearing steels at 60-300°C. They found that the corrosion rate was considerably higher with HAc than with only CO₂. Exception was at 60°C, where HAc gave lower corrosion rate (Ueda and Takabe, 1998).

The effect of HAc has been studied over a wide range of conditions in a series of recent papers from Ohio University:

Sun used rotating cylinder specimens in glass cells bubble tests to investigate the effect of HAc on the part reactions under N₂ and CO₂ atmospheres at room temperature. Polarization curves showed that HAc increased the cathodic current, and that the H₂
evolution from HAc was activation controlled at room temperature. HAc inhibited the anodic part reaction (Sun et al., 2003).

K. George in 2004 used basically the same setup as Sun to further study the effect HAc on the corrosion rate in the temperature range 22-60°C, and developed an electrochemical/hydrodynamic model for the cathodic reaction taking into account the reduction of \((\text{H}^+)\) (from the bulk of the solution), \(\text{H}_2\text{CO}_3\) and HAc. The mass loss rates increased substantially with HAc concentration at 40°C and 60°C but not at 22°C. It was observed that the cathodic current in presence of HAc was reduced in synthetic brine with high salt contents compared to 3 % NaCl (George et al., 2004).

In following papers George, Wang, Nesic and Waard extended the previous experimental work to corrosion loops at higher \(\text{CO}_2\) partial pressures. It was noted that the anodic inhibition observed at room temperature was lifted at 60°C (George et al., 2004).

Nafday and Nesic in 2005 studied the effect of HAc on \(\text{FeCO}_3\) corrosion product film protectiveness at 80°C in 3% NaCl under 0.5 bar \(\text{CO}_2\). No significant effect of HAc on \(\text{FeCO}_3\) layer protectiveness or morphology was found in any of the tests. The corrosion film growth rate, inferred from the rate of decrease of corrosion rate, was determined by the super saturation (Nafday and Nesic, 2005).

Guo studied the effect of HAc and \(\text{Ac}^-\) (50°C, 1 bar \(\text{CO}_2\), and 100°C, 10 bar \(\text{CO}_2\)). The polarization curves showed increased cathodic currents, and some indication of inhibition of the anodic reaction with increasing HAc concentration (0-360 ppm) (Guo et al., 2005).

Hurlen investigated the effect of acetate buffers on the cathodic reaction on iron (\(\text{N}_2\) atmosphere, 25°C). They observed a limiting cathodic current that was dependent on stirring and HAc concentration. However, in the potential region of activation controlled
reaction the HAc had no (or negligible) effect. This was interpreted as an indication that HAc is not a direct reactant in the \( \text{H}_2 \) evolution reaction (Hurlen et al., 1984).

Bech-Nielsen investigated the effect of HAc and Ac\(^-\) on the anodic part reaction on iron (25\(^\circ\)C, N\(_2\) atmosphere, pH 4, 1 M NaClO\(_4\) solution). Inhibition of the anodic part reaction was observed also in this work. The reaction order of the anodic reaction with respect to Ac\(^-\) was -0.7 (Bech-Nielsen, 1974).

Garsany and Pletcher used voltammetry to study the effect of HAc on the cathodic part reaction on platinum and steel in CO\(_2\) environment. They observed a limiting cathodic current in HAc solutions, proportional to the HAc concentration, and to square root of the rotating disc rotation rate. In solutions with both HAc and CO\(_2\) present the cathodic limiting current was the sum of the individual contributions of diffusion limited reduction of solution equilibrium protons, diffusion limited reduction of HAc and reaction limited reduction of \( \text{H}_2\text{CO}_3 \). The relative importance of these reactions depends, amongst many factors, on convection, temperature and concentration of the involved species. It was found that The HAc reduction is activation controlled under CO\(_2\) corrosion conditions. It was also found that the anodic currents were influenced by the presence of HAc or Ac\(^-\) (Pletcher et al., 2003).

Halvorsen and Andresen in 2005 demonstrated that pH-stabilization efficiently reduced the corrosion rates in presence of large amounts of total Ac\(^-\). By increasing the pH of the aqueous phase in the bottom of the line the concentration of HAc was reduced, and hence the partial pressure of HAc over the liquid. This caused a decrease in the concentration of HAc in the condensing liquid, and a reduction in the top-of-line corrosion rate (Halvorsen and Andresen, 2005).
2.15 Corrosion Research in the Oil and Gas Industries Models Used

2.15.1 De Waard Corrosion

De Waard and Milliams first reported a CO$_2$ corrosion model for wet gas pipelines in 1975. The semi-empirical model was based on experimental data (weight loss and LPR measurements) taken from glass cells (Waard and Milliams, 1975). The model is considered to be a “worst case” model due to its conservative estimate for the corrosion rate. The model, through the years, has been revised (1991, 1993 and 1995) to take into account new parameters important to the corrosion process as experimental data became available. For example, in the 1991 model revisions (Waard, 1991) the effect of higher pressures, protective film formation, high system pH, presence of hydrocarbons and water condensation were taken into account. All of the parameters are accounted for in the model through the use of factors which are multiplied by the “worst case” corrosion rate.

The “worst case” corrosion rate was found from the following equation:

$$\frac{1}{V_{corr}} = \frac{1}{V_t} + \frac{1}{V_m}$$  \hspace{1cm} (7)

Where:

$V_{corr}$ the corrosion rate in mil/yr
$V_t$ reaction rate in mil/yr
$V_m$ maximum mass transfer rate of the corrosive species in mil/yr

(Pickett, 1974)

2.15.2 Slight Modification to the De Waard Model

Also called the George-de Waard-Nesic is needed to account for the presence of HAc.

The new equation is:

$$\frac{1}{V_{corr}} = \frac{1}{V_t} + \frac{1}{V_m(H_2CO_3)} + \frac{1}{V_m(HAc)}$$  \hspace{1cm} (8)

Where:

$V_m(H_2CO_3)$ mass transfer rate of carbonic acid
$V_m(HAc)$ mass transfer term for HAc in mil/yr
2.15.3 Electrochemical Model

The second popular model used is the electrochemical model where the nature of the measured cathodic and anodic reactions must be found. Acetic acid can affect the cathodic reaction in CO₂ corrosion according to at least two possible scenarios. The first is HAc acting as a source of hydrogen ions through dissociation and the second is HAc being directly reduced on the metal surface. The model takes into account the electrochemical reactions of hydrogen ion (H⁺) reduction, carbonic acid (H₂CO₃) reduction, direct water reduction, oxygen reduction, and anodic dissolution of iron. The corrosion process was monitored using polarization resistance, potentiodynamic sweep, electrochemical impedance, and weight-loss measurements. The experiments were made under many temperatures ranging from 20°C to 80°C. Experiments in a three-electrode setup were conducted at atmospheric pressure in a battery of eight glass cells. CO₂ gas was bubbled through the cells continuously. Electrochemical measurements were made using a Gamry Instruments potentiostat with an eight-channel multiplexer connected to a personal computer. The glass cells were filled with 3 L of distilled water and a 1 mass% NaCl. In different experiments, CO₂ was bubbled through the electrolyte to saturate the solution. Monitoring of pH and O₂ concentration was used to judge when the solution was in equilibrium. When needed, hydrochloric acid (HCl) or sodium bicarbonate (NaHCO₃) was added to adjust the pH. At the end, more than 50 glass cell experiments were conducted.

2.16 Effect of Acetate and Acetic Acid on Corrosion

The overall acetate concentration and the bicarbonate level (or more precisely the ratio of HCO₃⁻ to CO₂ concentrations) are two main elements that can determine the concentration of acetic acid (and hence its importance in influencing the rate of steel corrosion) (Harrop, 2006).
The level of bicarbonate is likely to influence significantly the acetate/acetic acid ratio and the solution pH (Sidorin, 2005).

At low pH, the un-dissociated form of acetic acid (HAc) is mainly the cause for the rise in the corrosion rate.

When saturated with CO₂ the pH is about 4.5 at room temperature. Therefore, much of the total acetate should be present as acetic acid and the acetate present would be expected to enhance the corrosion of carbon steel. The bicarbonate concentrations are much higher and it is to be expected that the pH remains closer to neutral when saturated with CO₂. Much of the acetate will remain in solution as acetate ion and its influence on the steel corrosion rate will be less. Whether enhanced corrosion is observed will depend on the actual acetate level. It should also be stressed that the measured pH alone is, in practice, an indicator of the bicarbonate level (Pletcher, 2003).

When in the system, HAc is found wavering between the aqueous and the gas forms as seen in reaction (9). The aqueous phase of HAc partly dissociates into hydrogen and acetate ions according to reaction (10):

\[ \text{HAc}_{(g)} \rightleftharpoons \text{HAc}_{(aq)} \]  \hspace{1cm} (9)
\[ \text{HAc}_{(aq)} \rightleftharpoons \text{H}^+ + \text{Ac}^- \]  \hspace{1cm} (10)

In liquid solutions, iron acetate salt can be produced, but it has a higher solubility than that of iron carbonate so an iron acetate precipitate and protective film do not easily form. In 1999, Crolet described that low concentrations of HAc (6 ppm to 60 ppm) can affect the corrosion rates of carbon steel. They stated that the rate of corrosion is faster in the presence of acetic acid because of the inversion of the bicarbonate to acetate ratio (Guo et al., 2005); “It becomes the main source of corrosion in spite of how minimal the amount is present” This is explained by the fact that at this specific point, the acetic acid predominates over the carbonic acid (Crolet, 1999).
Experiments were done to show the role that acetate plays in CO$_2$ corrosion. Both HAc and sodium acetate were used as sources of acetate in different media. Both caused an increase in the rate of corrosion due to less iron carbonate precipitates since acetate ions have the ability to form iron acetate and keep iron away from the metallic surface.

Carbon dioxide (CO$_2$) becomes an issue on corrosion when the concentration of acetic acid in water is higher than 0.1 to 1 mM. In contrast, fields with lower CO$_2$ contents are not corrosive: the corrosion by CO$_2$ disappears at low CO$_2$ pressure, except in the presence of even minute traces of free acetic acid (Yin, 2008).

In Summary, carbonic acid is often used to indicate a solution of dissolved CO$_2$ (carbonated water). CO$_2$ gas dissolves readily in water and forms dissolved CO$_2$(aq). The dissolved CO$_2$ reacts with H$_2$O to form carbonic acid, H$_2$CO$_3$ according to reaction (11).

$$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$$ (11)

The H$_2$CO$_3$ concentration is only a small fraction (ca. 1/600) of the CO$_2$ (aq) concentration. H$_2$CO$_3$ dissociates to form bicarbonate, HCO$_3^-$ according to reaction (12).

$$\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$$ (12)

pKa, an indicative index of the strength of an acid, of HAc is 4.8, and pKa of H$_2$CO$_3$ in equation 6 is 3.5 at 25°C. So, contrary to the general knowledge, carbonic acid is a stronger acid than acetic acid (Crolet, 1983).

Equations (11) and (12) can be added to give reaction (13).

$$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^-$$ (13)

2.17 Buffering Effect of Acetate

A buffer is defined as an aqueous solution that has a highly stable pH, the components of which are either a weak acid with its conjugate base or a weak base with its respective conjugate acid. The pH of a buffer solution is hardly affected if at all by the addition of
either a strong acid or base and therefore is used for the sole purpose of retaining the pH of a solution at a nearly constant value.

It is not possible to distinguish the reductions of acetic acid and free proton (H⁺). Pletcher, Garsany and Hedges pointed out that when dealing with brine solutions which are made up of acetate and saturated with CO₂, we are truly dealing with an acetate buffer. Thus with the addition of CO₂, the brine goes acidic but the change is not significant with the presence of acetate which acts as a buffer thus limiting the change in the pH value (Pletcher et al., 2002).

By converting acetate to an un-dissociated acetic acid, the act of buffering occurs and thus with any increase in pH value there is a corresponding rise in the concentration of proton donor.

2.18 Formation of Ferrous Acetate Complexes at High Temperatures

At high temperatures and neutral pH, if a small amount of HAc is initially added, approximately less than 10% of the Fe (II) is present as a complex FeAc⁺. The creation of this acetate complex is barely noticeable and can be negligible. But when the initial amount of HAc is high, almost 65% of the Fe (II) is existent as acetate complexes and acetate, because their concentration is no more negligible. Furthermore, this complex formation shifts equilibrium of reaction (10) towards the right hand side, more Ac⁻ will form and so lower concentration of free Fe²⁺ will be left in the solution. When this shift happens, the formation of iron carbonate become more difficult.
CHAPTER 3: EXPERIMENTAL SETUP

The experimental work consisted in having an initial solution of concentrated CO$_2$ and studying the effects of the addition of acetate and bicarbonate ions on the corrosion of coupons using the weight loss technique. The different steps of the experiment included the monitoring of the pH change of the solution as well as the measuring of the weight loss due to the above-mentioned additions.

3.1 Materials

This is the list of all equipment and materials used during the experimental work:
- 14 beakers.
- 2 types of pH meter:
  - pH indicators.
  - Mettler toledo (MP 120 pH meter GMbH, serial No. 228476).
- CO$_2$ Tank.
- Capillary pressure system.
- Thermometer.
- Nineteen (19) 1-inch by 1-inch steel coupons (cold rolled steel grade A1008 with a thickness of 0.024 inch).
- Distilled water.
- 15% HCl solution.
- Hygenic gloves.
- Chemicals: Sodium acetate (NaOAc).
  Calcium chloride (CaCl$_2$).
  Sodium Chloride (NaCl).
3.2 Sample Preparation and Procedure

The following step by step procedures were completed during this labwork experiment:

1. The coupons were pre-treated in absolute ethanol followed by acetone in order to be degreased;

2. The degreased coupons were heavily rinsed with de-ionized water;

3. The coupons were dried;

4. Every coupon was accurately weighted and the mass recorded;

5. 100ml of distilled water was placed in each of the 14 beakers in addition to 4g of NaCl and 0.5g of CaCl$_2$;

6. 9 of the 14 solutions were bubbeled for 8 consecutive hours with CO$_2$ using the capillary pressure system;

7. A coupon was placed in each cell containing the brine;

8. Time was recorded throughout the experience and the pH measured with a pH meter (Mettler toledo) (see figure 9 in appendice 1);

9. After 5 days (120 hours), the coupons were removed from the beakers;

10. The coupons were rinsed with de-ionized water followed by 15% HCl to remove the corrosion products, and then rinsed again with de-ionized water;

11. The coupons were then dried-up and weighted to obtain the new mass.

Details of the 14 beakers and their content could be seen in Table 2.
### Table 2: Composition, mass and pH of the 14 different samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition of the sample</th>
<th>Original mass of coupon (g) (±0.0003)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Without CO$_2$ saturation + 100ml brine + coupon</td>
<td>2.9016</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>Without CO$_2$ saturation + 100ml brine + coupon + 1g sodium acetate</td>
<td>2.9011</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>Without CO$_2$ saturation + 100ml brine + coupon + 1.5g sodium acetate</td>
<td>2.8611</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>CO$_2$ saturated + 100ml brine + coupon</td>
<td>2.9006</td>
<td>4.5</td>
</tr>
<tr>
<td>5</td>
<td>CO$_2$ saturated + 100ml brine + coupon + 0.05g (50mg) sodium acetate</td>
<td>2.8875</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>CO$_2$ saturated + 100ml brine + coupon + 0.1g (100mg) sodium acetate</td>
<td>2.9109</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>CO$_2$ saturated + 100ml brine + coupon + 0.3g (300mg) sodium acetate</td>
<td>2.9025</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>CO$_2$ saturated + 100ml brine + coupon + 0.5g (500mg) sodium acetate</td>
<td>2.8962</td>
<td>6</td>
</tr>
<tr>
<td>9</td>
<td>CO$_2$ saturated + 100ml brine + coupon + 1g sodium acetate</td>
<td>2.9062</td>
<td>7</td>
</tr>
<tr>
<td>10</td>
<td>CO$_2$ saturated + 100ml brine + coupon + 1.5g sodium acetate</td>
<td>2.8734</td>
<td>7</td>
</tr>
<tr>
<td>11</td>
<td>Without CO$_2$ saturation + 100ml brine + 1g sodium bicarbonate</td>
<td>2.9110</td>
<td>9</td>
</tr>
<tr>
<td>12</td>
<td>Without CO$_2$ saturation + 100ml brine + 2g sodium bicarbonate</td>
<td>2.9019</td>
<td>10</td>
</tr>
<tr>
<td>13</td>
<td>CO$_2$ saturated + 100ml brine + 1g sodium bicarbonate</td>
<td>2.9003</td>
<td>7</td>
</tr>
<tr>
<td>14</td>
<td>CO$_2$ saturated + 100ml brine + 2g sodium bicarbonate</td>
<td>2.8992</td>
<td>7</td>
</tr>
</tbody>
</table>

#### 3.3 Corrosion Test Methodology

The brine solution was made of distilled water, 4% by weight of NaCl and 0.5% by weight of CaCl$_2$. Another composition could have been used but it was determined that this composition was mostly used and was relevant to the brine formation in the field.

Having a pre-saturated CO$_2$-bubbled solution was a pre-requisite for the experimental work. To obtain this solution, a CO$_2$ tank was connected to the capillary pressure system in order to bubble CO$_2$ into the solution until it reached a saturated state.
Every solution was bubbled with CO₂ for 8 hours to ensure saturation.

It should be duly noted that in the absence of oxygen, no corrosion can occur under any circumstances. Oxygen is responsible for reacting with the hydrogen ions that are released at the cathode due to the electron accommodation. In the lack of oxygen, hydrogen ions accumulate on the cathode and prevent electron accommodation, thus stopping the corrosion process.

3.4 Corrosion Rate from Coupon Mass Loss

When studying and working with coupons, the mass loss is measured and calculated by weighting the specimen before and after exposure, subtracting the two obtained values and converting the result to a penetration rate.

The corrosion rate is estimated according to equation (2).

Assumptions should be made in order to have satisfactory and conclusive results, such as:

1- The penetration is uniform, so the attack will be distributed over the whole surface equally.

2- Areas are unchanged during the period of exposure. When estimating the penetration rate we should assume that the dimensions before and after exposure are still the same.

3- The penetration rate stays the same throughout the exposure period.
Figure 2: The capillary pressure system used to saturate the brine solution with CO$_2$
Figure 3: The capillary pressure system that was used to bubble CO₂ in the solution and saturate it. The beaker containing the solution to be tested was placed inside the grey plastic vessel.
CHAPTER 4: RESULTS AND DISCUSSION

4.1 Analysis of the Results

Experimental results are presented in tables 3 to 9.

Table 3: Effect of sodium acetate on the corrosion rate of the mild steel coupons

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Corrosion rate (mpy)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Without CO₂ saturation + 100ml brine + coupon</td>
<td>22</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>Without CO₂ saturation + 100ml brine + coupon +1g sodium acetate</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>Without CO₂ saturation+100ml brine +coupon + 1.5 g sodium acetate</td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>

From table 3, it can be seen that an increase in the amount of sodium acetate decreases the corrosion rate of the coupons. This decrease could be attributed to the minimization of free (H⁺) ions in solution, according to reaction (10) and (12). It can also be attributed to the ability of sodium acetate forming a protective layer on the surface of the coupons thus decreasing the corrosion rate.
Table 4: Effect of sodium acetate on the corrosion rate of mild steel coupons in solutions saturated with CO₂

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Corrosion rate (mpy)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>CO₂ saturated +100 ml brine + coupon</td>
<td>83</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>CO₂ saturated +100 ml brine + coupon + 0.05g (50mg) sodium acetate</td>
<td>107</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>CO₂ saturated +100 ml brine + coupon + 0.1g (100mg) sodium acetate</td>
<td>110</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>CO₂ saturated +100 ml brine + coupon + 0.3g (300mg) sodium acetate</td>
<td>83</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>CO₂ saturated +100 ml brine + coupon + 0.5g (500mg) sodium acetate</td>
<td>65</td>
<td>6</td>
</tr>
<tr>
<td>9</td>
<td>CO₂ saturated +100 ml brine + coupon + 1g (1000mg) sodium acetate</td>
<td>56</td>
<td>7</td>
</tr>
<tr>
<td>10</td>
<td>CO₂ saturated +100 ml brine + coupon + 1.5g (1500mg) sodium acetate</td>
<td>50</td>
<td>7</td>
</tr>
</tbody>
</table>

From table 4, it can be seen that sodium acetate increases the corrosion rate of the coupons when it is added in low amounts (50-100 mg). This could be due to the sodium acetate providing a partial coverage of the coupon, thus changing the ratio of the cathode to the anode, hence increasing the corrosion rate of the anodic areas. Amounts higher than about 200 mg sodium acetate, has considerable inhibitive effect on the corrosion rate of mild steel coupons. This can be attributed to the ability of sodium acetate to provide a full protective layer on the mild steel and to bind the free (H⁺) ions, resulting from the dissociation of H₂CO₃ in solution.
Table 5: Effect of pH on corrosion rate of mild steel coupons in solutions saturated with CO₂

<table>
<thead>
<tr>
<th>Sample</th>
<th>composition</th>
<th>Corrosion rate (mpy)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>CO₂ saturated +100ml brine + coupon+0.3g (300mg) sodium acetate</td>
<td>83</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>CO₂ saturated+100 ml brine+ coupon+0.5g (500mg) sodium acetate</td>
<td>65</td>
<td>6</td>
</tr>
<tr>
<td>9</td>
<td>CO₂ saturated+100 ml brine + coupon+1g sodium acetate</td>
<td>56</td>
<td>7</td>
</tr>
<tr>
<td>10</td>
<td>CO₂ saturated+100 ml brine + coupon+1.5g sodium acetate</td>
<td>50</td>
<td>7</td>
</tr>
</tbody>
</table>

From table 5, it can be seen that the higher the pH of the solution, the lower the corrosion rate of the coupons. This could be due to the higher concentration of acetate ions reacting with free protons coming from the dissociation of carbonic acid in equation (12). The higher the concentration of acetate, the higher is the consumption of (H⁺) ions due to the direct reaction between acetate and (H⁺) ions to form undissociated acetic acid (equation 8). Less (H⁺) ions will be left in the solution causing a higher pH and a lower corrosion rate, knowing that pH is a function of (H⁺) (pH= - log [H⁺]).

Table 6: Effect of sodium acetate and sodium bicarbonate on the corrosion rate in a solution without CO₂

<table>
<thead>
<tr>
<th>Sample</th>
<th>composition</th>
<th>Corrosion rate (mpy)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Without CO₂ saturation + 100ml brine + coupon</td>
<td>22</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>Without CO₂ saturation + 100ml brine + coupon +1g sodium acetate</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>11</td>
<td>Without CO₂ saturation+ 100 ml brine+1g sodium bicarbonate</td>
<td>5</td>
<td>9</td>
</tr>
</tbody>
</table>

From table 6, one can see that the presence of sodium bicarbonate as well as sodium
acetate has powerful inhibitive effect on the corrosion rate of the steel coupons in solution without CO₂. This can be attributed to the buffering ability of sodium acetate and the ability of sodium bicarbonate to form a protective layer on the surface of the coupons.

**Table 7: Effect of sodium acetate and sodium bicarbonate on the corrosion rate in a solution saturated with CO₂**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Corrosion rate (mpy)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>CO₂ saturated+100 ml brine+coupon</td>
<td>83</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>CO₂ saturated+100 ml brine + coupon+1g sodium acetate</td>
<td>56</td>
<td>7</td>
</tr>
<tr>
<td>13</td>
<td>CO₂ saturated+ 100 ml brine+1g sodium bicarbonate</td>
<td>47</td>
<td>7</td>
</tr>
</tbody>
</table>

The same can be said about the inhibitive effect of both sodium acetate and bicarbonate even with the presence of CO₂ in solution.

**Table 8: Effect of CO₂ on the corrosion rate of mild steel**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Corrosion rate (mpy)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>without CO₂ saturation + 100ml brine + coupon</td>
<td>22</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>CO₂ saturated+100 ml brine+coupon</td>
<td>83</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 8 clearly shows that CO₂ increases corrosion rate when added to a solution and decreases the pH.
Table 9: Effect of sodium bicarbonate on the corrosion rate of mild steel in solution saturated with CO$_2$

<table>
<thead>
<tr>
<th>Sample</th>
<th>composition</th>
<th>Corrosion rate (mpy)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>CO$_2$ saturated+100 ml brine+coupon</td>
<td>83</td>
<td>5</td>
</tr>
<tr>
<td>13</td>
<td>CO$_2$ saturated+ 100 ml brine+1g sodium bicarbonate</td>
<td>47</td>
<td>7</td>
</tr>
<tr>
<td>14</td>
<td>CO$_2$ saturated+ 100 ml brine+2g sodium bicarbonate</td>
<td>46</td>
<td>7</td>
</tr>
</tbody>
</table>

4.2 Corrosion Test Results

The rates of corrosion have been calculated using equation (14):

$$R = \frac{W \times 2.23 \times 10^4}{A \times T \times \rho}$$

(14)

Where:

- $R$ corrosion rate, mil/yr (mpy)
- $W$ coupon weight loss, g
- $A$ total area of exposure = 1 in$^2$ (for all coupons)
- $T$ exposure time, days (5 for all coupons)
- $\rho$ density of metal = 7.85 g/cm$^3$
CHAPTER 5: CONCLUSIONS

The main conclusions drawn from the experimental study can be summarized as follow:

First, sodium acetate increases the corrosion rate of the coupons when it is added in low amounts (50-200 mg) by increasing the corrosion rate of the anodic areas. On the other hand, corrosion rate decreases with increasing acetic acid concentration above 200 mg, due to inhibition of the anodic reaction. In addition, it is confirmed that pH change has a considerable role on the effect of acetate on the corrosion rate: the higher the pH, the lower the corrosion rate. Furthermore, Sodium acetate has buffering capabilities due to powerful inhibitive effect that it has on the corrosion rate of steel coupons. Finally, sodium bicarbonate decreases the corrosion rate by forming a protective layer on the surface of the coupons.
CHAPTER 6: RECOMMENDATIONS

The following recommendations are considered helpful for future studies.

- Conduct the same research using coupons made from steel grades used in the industry.

- Use a coupon holder in order to avoid error caused by coupon sticking to the base of the beaker.

- A longer sampling time for corrosion coupons is recommended for future studies.

- It is recommended that in the future study, more experiments be conducted to determine the effect of pressure, temperature and other down-hole conditions on the corrosion of the coupons, keeping in mind that at 60°C some effect of acetate will be different.
REFERENCES

Asrar N. 2010. Corrosion control of drilling tools through chemical treatments effectiveness and challenges. SPE International Conference on oilfield corrosion


Bhatia A. 2004. Cooling Water Problems and Solutions. Continuing Education and Development,Inc. 9 Greyridge Farm Court Stony Point, NY 10980


Gulbrandsen E, Bilkova k. 2006. Solution chemistry effects on corrosion of carbon steels in presence of CO₂ and acetic acid. San Diego California, USA

Gulbrandsen E. 2007. Acetic acid and carbon dioxide corrosion of carbon steel covered with iron carbonate


Kanavy C, Williams J. April 2012. Strengthening our navy one rust spot at a time

Kermani M. August 1996. The Impact of Corrosion on Oil and Gas Industry. SPE Production & Facilities


Okafor P. June 2009. CO₂ corrosion of carbon steel in the presence of acetic acid at higher temperatures. Journal of Applied Electrochemistry


Pletcher D, Garsany Y, Hedges B. 2003. The role of acetate in CO₂ corrosion of carbon steel: Studies related to oilfield conditions


Vámos I, Szki P. 1997. Measuring the rate of iron corrosion, Budapest, Hungary


West J, Horwood E. 1980. Basic Corrosion and Oxidation, Chichester UK


Yudaya S. 2006. Natural Gas Leak Detection in Pipelines. 1291-A, Cumberland Avenue. West Lafayette, IN 47906
## APPENDIX

Table 10: The lab results

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Original mass of coupon W1 (g) (±0.0003)</th>
<th>Final mass of coupon W2 (g) (±0.0003)</th>
<th>Weight loss (g) W=W1-W2 (±0.0003)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.9016</td>
<td>2.8617</td>
<td>0.0399</td>
</tr>
<tr>
<td>2</td>
<td>2.9011</td>
<td>2.8866</td>
<td>0.0145</td>
</tr>
<tr>
<td>3</td>
<td>2.8611</td>
<td>2.8477</td>
<td>0.0134</td>
</tr>
<tr>
<td>4</td>
<td>2.9006</td>
<td>2.7538</td>
<td>0.1468</td>
</tr>
<tr>
<td>5</td>
<td>2.8875</td>
<td>2.6976</td>
<td>0.1899</td>
</tr>
<tr>
<td>6</td>
<td>2.9109</td>
<td>2.7157</td>
<td>0.1952</td>
</tr>
<tr>
<td>7</td>
<td>2.9025</td>
<td>2.7564</td>
<td>0.1461</td>
</tr>
<tr>
<td>8</td>
<td>2.8962</td>
<td>2.7811</td>
<td>0.1158</td>
</tr>
<tr>
<td>9</td>
<td>2.9062</td>
<td>2.8064</td>
<td>0.0998</td>
</tr>
<tr>
<td>10</td>
<td>2.8734</td>
<td>2.7840</td>
<td>0.0894</td>
</tr>
<tr>
<td>11</td>
<td>2.9110</td>
<td>2.9021</td>
<td>0.0089</td>
</tr>
<tr>
<td>12</td>
<td>2.8019</td>
<td>2.7954</td>
<td>0.0065</td>
</tr>
<tr>
<td>13</td>
<td>2.9003</td>
<td>2.8171</td>
<td>0.0832</td>
</tr>
<tr>
<td>14</td>
<td>2.8992</td>
<td>2.8182</td>
<td>0.0810</td>
</tr>
</tbody>
</table>
Figure 4: pH meter (METLER TOLEDO) used during operation to check the variation of pH

Figure 5: pH-indicators used when Toledo was not available
Figure 6: coupon used for the corrosion test

Figure 7: Sample number 3 where corrosion can be spotted on the coupon
Figure 8: Solution saturated with CO₂