STUDY AND MODELING OF SWEET CORROSION OF MULTIPHASE MIXTURES IN HORIZONTAL PIPELINES

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of the Requirement for the Degree
Master of Science

by
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1. **INTRODUCTION**

Early in the life of an oil well, mostly oil and natural gas are produced. As the well gets older, enhanced oil recovery methods are used. These methods often involve injecting carbon dioxide and seawater to the reservoir. This produces a multiphase mixture of oil, natural gas, carbon dioxide and saltwater as it flows out of the well. Many of the installations are either off shore or in places where extreme weather conditions exist eg. Alaska. Consequently the separation of this mixture takes place miles away from where it is produced. Thus, it has to be transported to separating facilities with the help of pipelines. This multiphase mixture causes severe corrosion problems to these pipelines. The carbon dioxide present in the system dissolves in water to form carbonic acid. This reaction is represented as follows:

\[ \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \]  

(1)

This acid further reacts with the iron present in the system to form the corrosion products, which could be iron carbonates, bicarbonates or carbides.

\[ \text{Fe} + \text{H}_2\text{CO}_3 \leftrightarrow \text{Fe}_2\text{CO}_3 \]  

(2)

\[ \text{Fe} + 2\text{H}_2\text{CO}_3 \leftrightarrow \text{Fe} (\text{HCO}_3)_2 \]  

(3)

To reduce the corrosion damage caused by this multiphase flow, inhibitors, surfactants and drag reducing agents are often introduced into the pipelines. Sometimes, however, these have not been able to alleviate the problem. The inhibitors form a protective
film at the pipe wall. This film, however, can usually withstand shear stresses of the order of 20 - 30 N/m². Zhou²³ (1993), has shown that when a pipeline operates under slug flow conditions, shear stresses of the order of 500 - 1000 N/m² can develop. This may completely destroy the inhibitor film resulting in continued corrosion of the pipeline.

A pipeline can operate in different flow regimes depending upon the flow velocity of gas and liquid. The flow regime in which a pipeline operates is related to the amount of corrosion occurring within a pipeline. Figure 1 shows a lateral view of the flow regimes in a pipeline. Stratified, wavy and rolling wave regimes are seen at low gas and liquid flow velocities (less than 1 m/s). At low gas velocities and higher liquid velocities, plug and slug flow regimes are observed. When, both the gas and liquid velocities are high, pseudo slug and annular flows are observed. Similar flow regimes are seen for 10, 15 and 30 cm internal diameter pipelines. However, these can be very different for smaller 1.25 and 2.5 cm internal diameter pipelines. Thus it is important to conduct research in large diameter pipelines.

Slug flow has been known to severely enhance corrosion damage in flowlines. This is due to the nature of the flow in the slug front. Figure 2 shows a real moving slug in a pipeline. A slug can essentially be divided into four parts. The front of the slug moves with a translational velocity $V_t$. The mixing zone, moves with a velocity $V_m$, and is a highly turbulent zone. This velocity is smaller than the translational velocity and this zone is mainly responsible for the corrosion damage. Corrosion can be caused by wall shear forces or turbulent shear forces or both. The third part is the slug body which is not as highly aerated as the mixing zone. Then there is the slug tail, where the liquid is shed off, behind the slug.
Figure 1. Description of Flow Pattern Classifications (Water-Gas)
This study has used the concept of a stationary slug or hydraulic jump to simulate real moving slugs in a coordinate system moving with the velocity of the slug front. Figure 3 shows a stationary slug or a hydraulic jump. The front of the slug "moves" with a velocity \((V_s - V_t)\) while the gas and film move with velocities \((V_{\text{gas}} - V_t)\) and \((V_f - V_t)\) respectively.

The pipe cross section is shown in Figure 4, in the case of slug flow. D is the internal diameter of the pipeline while h is the liquid film height.
The flow in a slug flow regime is based on the height of the liquid film which is expressed in terms of a dimensionless Froude number.

![Pipe Cross Section](image)

**Figure 4. Pipe Cross Section**

The following method is used to calculate the film Froude number:

\[
A_L = r^2 \left[ \pi - \cos^{-1} \left( \frac{h}{r} - 1 \right) \right] + \frac{(h/r - 1)}{(1 - (h/r - 1)^2)^{1/2}}
\]

\[ (4) \]

\[
h_{\text{eq}} = \frac{A_L}{T}
\]

\[ (5) \]

\[
T = 2r \left( 1 - (h/r - 1)^2 \right)^{1/2}
\]

\[ (6) \]

where:
- \( A_L \) is the Area of the wetted perimeter
- \( r \) is the internal radius of the pipeline
- \( h \) is the height of the gate
- \( h_{\text{eq}} \) is the height equivalent of the wetted perimeter
- \( T \) is the width of the gas liquid interface
Fr = \frac{(V_t - V_f)}{(g h_{eq})^{1/2}} \tag{7}

where: \hspace{0.5cm} Fr \text{ is the Froude Number}

\hspace{0.5cm} V_t \text{ is the translational velocity of the slug}

\hspace{0.5cm} V_f \text{ is the velocity of the film}

\hspace{0.5cm} g \text{ is the acceleration due to gravity}

Since \( V_t \) is identically zero for stationary slugs,

\hspace{0.5cm} Fr = \frac{V_f}{(g h_{eq})^{1/2}} \tag{8}

The Froude number that is to be experimented with gives a value for the film velocity. The volumetric flow rates are then equated, that result in a full pipe flow velocity.

\[ A_L \cdot V_f = A \cdot V \tag{9} \]

where: \( A \) is the cross sectional area of the pipeline

\hspace{0.5cm} V \text{ is the full pipe flow velocity before the gate, necessary to produce a slug at a particular Froude Number}

Some work has been done in vertical flow in the field of corrosion. However, the results from this research cannot be applied to horizontal flow. Since the flow regimes are different research has also been conducted in the field of single phase and two phase flows. This includes transition to slug flow as well as modelling of real moving slugs. To find the corrosion rates using real moving slugs and to get an accurate idea about their effect is a difficult task. This is due to the fact that slugs can flow at high velocities and
are intermittent. There are very few instruments that can be used for these conditions. Thus, stationary slugs were modeled and this made it possible to perform experiments on slug flow as stationary slugs can be easily controlled.

Most of the work done on corrosion is based on experimental results of single phase, water, or two phase, water/gas, systems. This can have only a limited application to the area of multiphase flow related corrosion. It is essential that a second liquid phase be studied. Thus, oil is added into the system to observe the effects of multiphase (oil/water/gas) flow. The oils used for this research are Conoco LVT200 and Arcopac90. At 40 C, the densities and viscosities of Conoco LVT200 and Arcopac90 oils are 800 and 825 kg/m$^3$, and 2 and 15 cp respectively.

This study experimentally determines the corrosion rate in carbon steel pipelines for a wide range of carbon dioxide partial pressures, temperatures, fluid flow velocities and oil concentrations. Full pipe flow and slug flow experiments have been performed. A model has been developed to predict the rate of corrosion of oil/water flow in a horizontal pipeline and involves the carbon dioxide partial pressure, wall shear stress and temperature.
2. LITERATURE REVIEW

The work done towards gaining an insight into the field of corrosion can be divided, depending upon the aspect of corrosion discussed. Measurement, observations, mechanisms, chemistry, kind of flow involved and predictive models could thus form a basis of understanding the process of corrosion. This chapter discusses each of these aspects in detail and also presents citations of relevant work accomplished.

2.1 MEASUREMENT TECHNIQUES

There are different techniques of determining the corrosion rates of fluids in a system. Some of these are electrical resistance, polarization resistance, zero resistance ammetry, electrochemical noise measurement and electrochemical impedance spectroscopy. Of these, the use of weight loss coupons and electrical resistance probes in corrosion testing was discussed by Mckenzie and Vassie \(^\text{14}\) (1985). They found a good correlation between these two techniques. Since the weight loss coupon technique was the standard way to measure corrosion rates, the latter method, because of the good correlation could serve as an alternative.

Even though the electrical resistance probe could be used as an alternative, Bovankovich \(^\text{1}\) (1993) suggested that several existing techniques be used simultaneously to monitor corrosion rates. He was of the opinion that two or more of these techniques chosen judiciously would give complementary results and increase the value of the data obtained. Thus, to monitor corrosion rates the use of more than one technique was necessary.

In this study, the use of linear polarization resistance probes has been
limited to testing saltwater. This technique is only reliable when the solution conductivity is good. The addition of oil increases the resistivity or decreases conductivity of the liquid mixture. Hence, when a multiphase mixture of oil, water and gas is tested, only electrical resistance probes are used.

2.2 GENERAL OBSERVATIONS

It is imperative to experimentally simulate conditions in production wells to determine the extent of damage caused by corrosion. De Waard and Milliams\textsuperscript{3} (1975), performed experiments in stirred beakers to determine corrosion rates by means of weight loss coupons and polarization resistance measurements. They studied the effect of two parameters on corrosion, namely, carbon dioxide partial pressure and the temperature of the system. Their results indicated that the corrosion rate increases with an increase in temperature. From these observations, a model to predict corrosion rates as a function of carbon dioxide partial pressure and temperature was formulated.

Tuttle\textsuperscript{21} (1987) defined types of corrosion and discussed ways to prevent it. He observed four main forms of corrosion. These were material loss, stress corrosion cracking, corrosion fatigue and galvanic corrosion. He described various methods to mitigate these problems, that had evolved over the years. These include inhibition and material selection, cathodic or anodic protection, coatings and control of the environment. Even though significant progress had been made in this area of corrosion protection, much remained to be achieved.

The above had serious limitations since they could not be used in flowing
systems. Nesic and Lunde\textsuperscript{17} (1993), worked on pipe flow to gain an understanding of two phase flow on corrosion. They observed the effect of temperature and carbon dioxide partial pressure on corrosion rates and found that they were similar to the conclusions of De Waard, Lotz and Milliams\textsuperscript{2}. Their research, however, differed from De Waard, Lotz and Milliams\textsuperscript{2} as they performed their experiments in a flow loop instead of stirred beakers and also considered the effect of flow rate on corrosion rates. They showed that the corrosion rates increased with an increase in liquid flow rate.

The importance of using pipe flow to simulate conditions in the oil wells was accentuated by Efird, Wright, Boros and Hailey\textsuperscript{6,7} (1993). They examined corrosion in pipe flow, rotating cylinders and jet impingement systems. They showed that a correlation existed between pipe flow and the jet impingement technique. However, the rotating cylinders always produced a much lower value of corrosion rate when compared to pipe flow. Thus, rotating cylinder electrodes should be used with caution. They showed that for corrosion in pipelines, studies must be done in the real flowing systems.

2.3 MECHANISMS

The knowledge of rate of corrosion in a real world system is not enough, in itself, to define the reason behind the problem. An in-depth understanding of the mechanisms and chemistry involved is also required. Sydberger\textsuperscript{19} (1986) introduced the term “flow induced corrosion”, that was responsible for the corrosive wear of metal surfaces. He discussed the mechanisms responsible for flow induced corrosion. These were convective mass transfer at the metal/fluid interface, phase transport and erosion-corrosion. According to him, the morphology of corroded specimens was not enough to
establish which mechanism played an important role. Thus, more work had to be done, before the dominant mechanism causing flow induced corrosion under certain environmental parameters could be pin pointed.

A study on mass transfer controlled corrosion was conducted by Nesic and Postlethwaite\textsuperscript{16} (1990). They suggested that turbulent intensity could be a factor governing mass transfer controlled corrosion. This high level of turbulence was responsible for disrupting the protective corrosion layer formed which enhanced the oxygen transport and metal loss by corrosion. These observations indicated that the local near-wall intensity of turbulence, instead of wall shear stress was the governing factor for this kind of corrosion. Thus, mass transfer controlled corrosion was shown to be governed by the near-wall intensity of turbulence.

2.4 IMPORTANCE OF IRON IN CORROSION

Once the mechanisms of the process of corrosion have been established, the process chemistry needs to be examined. Equations 2 and 3 show that the final product could be either iron carbonate or bicarbonate. The iron concentration in the solution plays an important part in the reaction chemistry. This was shown by Videm and Dugstad\textsuperscript{22,23} (1989). The results of their research showed that corrosion took place when FeCO\textsubscript{3} is soluble in solution and no protective film formed. The corrosivity of the solution increased when the Fe\textsuperscript{2+} concentration was low. The protection that a Fe\textsuperscript{2+} film offered depended on the temperature of the solution and a stable film formed only at temperatures exceeding 50 C. This film formation increased if the pH value was low and no alkaline substances were present in the solution. However, under extreme high velocity flow conditions, the
corrosion rates were not reduced since the formation of a protective film was hindered. Thus, the extent of corrosion damage depends not only on the environmental parameters, but also on the concentration of iron in it.

The suggestion that iron carbonate film formation has an effect on the final value of corrosion rate was agreed upon by Mishra et al. (1992) and Dugstad (1992). The former performed research to find the environmental parameters that affected protective film formation. These were found to be temperature, pH, carbon dioxide partial pressure, brine content, material composition, flow velocity and time. The latter, however, focussed their study on the influence of temperature on the precipitation kinetics and saturation and supersaturation of iron carbonate. The study of these parameters provided an understanding of the solution chemistry involving Fe$^{2+}$ in the corrosion reaction.

2.5 SLUG FLOW

The reaction mechanisms and solution chemistry were a step towards understanding how corrosion occurred. In addition to that, the effect of the kind of flow pattern within a pipeline and the damage it caused was also of concern. Different flow patterns are observed depending on the flow velocities of the gas and liquid in the system. Green, Johnson and Choi (1989) showed that slug flow is a major cause for concern. This may be due to the intermittency, high flow velocities and shear stresses. Corrosion studies in slug flow are difficult because they travel with such high velocities.

Jepson (1987) proposed that the flow characteristics of horizontal slug flow could be simulated using a stationary slug or hydraulic jump. He studied the
mechanisms involved in the slug body and the velocity and void profiles across the slug cross-section. These flow mechanisms were found to accurately simulate a real moving slug. Hence, the characteristics of a real moving slug could be studied using a stationary slug or hydraulic jump.

Jepson\(^{10}\) (1989) modelled the transition to slug flow in a horizontal conduit. This model assumed that a slug forms due to a hydraulic jump which is sufficient to touch the top wall of the conduit. It also gave necessary and sufficient conditions for the formation of a stable slug. A correlation between the translational velocity and the slug velocity at low and high gas velocities could be obtained with this model. The transition to slug flow could, thus, be predicted using this model.

The theory that real moving slugs could effectively be studied using hydraulic jumps was strengthened by Kouba and Jepson\(^{13}\) (1989). They studied the flow of slugs in horizontal two phase pipelines and related it to hydraulic jumps. They found that the Froude number in the liquid film ahead of the slug was always greater than unity while within the slug it was less than unity. This observation indicated a change from super-critical to sub-critical flow and the presence of a hydraulic jump. It, thus, substantiated the fact that slug flow in a horizontal pipeline is nothing but propagating hydraulic jumps.

Kordyban\(^{12}\) (1990) provided a comparison of the theories that existed for the transition to slug flow in horizontal pipelines. One theory propounded that this transition was thought to be due to the Kevin-Hemholtz instability of waves. However, if this transition was studied on the basis of wave motion equations then it would depend on the wavelength which contradicted experimental data. The other theory used Bernoulli’s
equation to measure the pressure difference across the slug. This method agreed better with experimental data, but it did not predict the wavelength. Thus, neither one of the theories gave a complete explanation for the transition to slug flow.

Fan, Jepson and Hanratty$^8$ (1992) corroborated the fact that a slug was a hydraulic jump and created a model for stationary slugs. They observed the existence of a Benjamin bubble at a minimum volumetric flowrate. They, then suggested that an increase in the Froude number would lead to a lower value of dimensionalized liquid height required for the existence of a stationary slug. A model was developed for stationary slugs which was confirmed by pressure drop measurements over the slug. This made it possible to study real moving slugs as hydraulic jumps.

It was imperative to relate the flow regimes to the corrosion damage caused. Sun and Jepson$^{18}$ (1992) studied the effect of slug flow on corrosion rates in horizontal oil and gas pipelines. They found that the stationary slug front was a highly turbulent region that had large wall shear stresses at the bottom of the pipe. Using a stationary slug, they observed that the corrosion rates at the bottom of the pipe were greater than at the top. These rates were also much greater than those predicted by rotating cylinders or disks. A slug was, therefore, responsible for the increase in corrosion rate in horizontal pipelines. This made it evident that slug flow could be responsible for the high levels of corrosion in a pipeline.

2.6 PREDICTIVE MODELS FOR CORROSION

The work done in striving to understand the complex mechanisms, reactions and flow regimes paved the way to develop predictive models. Based on the knowledge of
these aspects of corrosion and experimental data, De Waard, Lotz and Milliams\textsuperscript{2} (1991) created a model to calculate the “worst case” corrosion rate for systems saturated with the Fe\textsuperscript{2+} corrosion product.

\[
\log V_{\text{nomo}} = 5.8 - \frac{1710}{T} + 0.67 \log (pC_{O2})
\]

(10)

where:

- \( V_{\text{nomo}} \) is the nomogram corrosion rate in mm/yr
- \( T \) is the temperature in K
- \( pC_{O2} \) is the mol \% CO\textsubscript{2} x Total pressure

If the solution is saturated with iron ions then the pH can be calculated using the smaller value of the two equations 11 and 12,

\[
\text{pH}_{\text{sat}} = 1.36 + \frac{1307}{(t + 273)} - 0.67 \log (fC_{O2})
\]

(11)

\[
\text{pH}_{\text{sat}} = 5.4 - 0.66 \log (fC_{O2})
\]

(12)

\[
fC_{O2} = a \times \text{CO}_2 \text{ partial pressure}
\]

(13)

where:

- \( t \) is the temperature in C
- \( \text{pH}_{\text{sat}} \) is the pH value of the saturated solution
- \( fC_{O2} \) is the fugacity of carbon dioxide
- \( a \) is the fugacity coefficient

Their model included a correction factor for the final corrosion rate when
water was saturated with Fe$^{2+}$.

\[
F_{pH} = \begin{cases} 
0.32 \left( pH_{sat} - pH_{act} \right) & \text{if } pH_{sat} > pH_{act} \\
-0.13 \left( pH_{act} - pH_{sat} \right) & \text{if } pH_{sat} < pH_{act} 
\end{cases}
\] (14)

where: \( F_{pH} \) is the correction factor multiplied with \( V_{nomo} \)

This model worked well for low flow velocities of the liquid. However, for high flow velocities the corrosion rates calculated were underestimated. Even though this model had its limitations, “worst case” predictions could be made for corrosion rates.

The model established by De Waard et al.\textsuperscript{2} was based on experimental data from rotating cylinders. Efird, Wright, Boros and Hailey\textsuperscript{6,7} (1993), however, performed experiments on pipe flow to strive to prognosticate corrosion rates. The experimental conditions consisted of different CO$_2$ partial pressures and a range of shear stress values. The analysis of the data showed that corrosion rate correlated with wall shear stress. This correlation made it possible to extend results from small diameter pipe flow experiments to larger diameter pipelines. A correlation between pipe flow corrosion rate and wall shear stress for single phase sweet aqueous systems had, thus, been determined.

\[
R_{COR} = a \tau^b
\] (16)
where: \( R_{\text{COR}} \) is the rate of corrosion in mm/yr

\[
a = 7.5 \pm 0.5 \ (\text{mm/yr})(N/m^2)^{-0.1}
\]

\( \tau \) is the wall shear stress in N/m\(^2\) and

\[
b = 0.1
\]

This correlation is only valid for the conditions tested and is not strictly a predictive model.

A revised correlation between corrosion rate and various parameters like flow velocity, temperature and CO\(_2\) partial pressure was formulated by De Waard and Lotz\(^4\) in 1993. They had not considered the effect of flow velocity of the fluid on corrosion rate in their earlier model (1991). They predicted values of corrosion rates based on a mass transfer and reaction model.

\[
V_{\text{COR}} = \frac{1}{1 + \frac{1}{V_{\text{react}}} + \frac{1}{c V_{\text{mass}}}}
\]  \hspace{1cm} (17)

\[
V_{\text{mass}} = 0.023 \ (D)^{0.7} (U)^{0.8} [H_2CO_3] / (v)^{0.5} (d)^{0.2}
\]  \hspace{1cm} (18)

where: \( U \) is the liquid flowrate in m/s

\( d \) is the hydraulic diameter in m

\( D \) is the diffusion coefficient in m\(^2\)/s

\( v \) is the kinematic viscosity in m\(^2\)/s

\([H_2CO_3]\) is the concentration of H\(_2\)CO\(_3\) and
c is a constant

The temperature dependence of kinematic viscosity is shown as,

\[
\log (v) = \frac{1.3272 (20 - t) - 0.001053 (t - 10)}{t + 105} - 6
\]  

(19)

where: \( t \) is in \( ^\circ \)C

\[ D = (T/v) \times 10^{-17} \]  

(20)

where: \( T \) is in K

\[
[H_2CO_3] = H \times pCO_2
\]  

(21)

\[
H = \frac{1088.76}{T} - 5.113
\]  

(22)

where: \( H \) is Henry’s constant in mol/bar

The reaction part is calculated as follows,

\[
\log (V_{\text{react}}) = 5.8 - \frac{1543}{T} + 0.67 \log (f\text{CO}_2)
\]  

(23)

\[
\log (F_{pH}) = 0.31 (pH_{\text{sat}} - pH_{\text{act}})
\]  

(24)
The value for saturation pH can be calculated using,

\[
\text{pH}_{\text{sat}} = 5.4 - 0.66 \log (\text{fCO}_2)
\]  

(25)

The constant, \( c \), has a value of \( 2.62 \times 10^6 \). This model could be used for higher flow velocities and was not limited to a Reynold’s number value of 10,000. This revised correlation provided a better prediction of corrosion rates than the previous one.

### 2.7 EFFECT OF TEMPERATURE

Many theories have been postulated on the effect of temperature. An accurate description of these can be found in many chemical engineering books. “Chemical Reaction Engineering”, written by Octave Levenspiel (1991) is one such book that has been consulted in this aspect.

For elementary reactions, the rate expression can be written as a product of a temperature dependent term and a composition dependent term. Specifically,

\[
r = f_1 \{ \text{temperature} \} \times f_2 \{ \text{concentration} \}
\]

(26)

\[
= k \times f_2 \{ \text{concentration} \}
\]

(27)

This temperature dependent term for most cases has been found to be well represented by Arrhenius’ law. Thus,
The temperature dependency from collision theory takes the form of,

\[ k = k_0 e^{-E/RT} \]  \hspace{1cm} (28)

This result is generally true for bimolecular collisions between the molecules.

The transition state theory purports that the reactions combine to form intermediate unstable complexes which then decompose spontaneously into products. This theory approximately predicts that,

\[ k = k_1 T^{1/2} e^{-E/RT} \]  \hspace{1cm} (29)

A comparison of the theories shows that the function of temperature can be expressed as,

\[ k = k_2 T e^{-E/RT} \]  \hspace{1cm} (30)

This summarizes the predictions of the different theories for the temperature dependency of the rate constant. For simple reactions the value of the temperature exponent term, \( m \), lies between 0 and 1. For more complicated reactions, however, the value of \( m \) can be as great as 3 or 4.
3. EXPERIMENTAL SETUP

The need to perform experiments to determine corrosion rates in pipe flow is evident from the discussion in the previous chapters. The methods used and the materials required are elucidated in this chapter.

3.1 EXPERIMENTAL SYSTEM

The experimental setup is shown in Figure 5. The system, made of 316 stainless steel, can withstand pressures up to 100 bars and temperatures of the fluid up to 80 C. It comprises a tank, A, which has a capacity to hold 1.2 m$^3$ of liquid. This liquid is pumped by a 7 HP pump into a 7.5 cm diameter pipeline. The flow rate of the liquid is measured using an orifice plate connected to a pressure transducer. The liquid flows from the 7.5 cm internal diameter pipeline into the 10 cm ID pipeline, passing through the test section back into the tank.

Point H, is the gas inlet to the system. Carbon dioxide gas is used to pressurize the system as well as to position a hydraulic jump at the test section. A gate at point G, is used to create a hydraulic jump. A back pressure regulator at point B, controls the system pressure and, if required, the gas is purged at point I. Two heaters at point J, connected to a thermostat maintain the system at a preset temperature. F is the test section where all the corrosion measurements are made.
A. Liquid Tank
B. Liquid Recycle
C. Liquid Feed - 7.62 cm Stainless Steel Pipe
D. Orifice Plate with a Pressure Transducer
E. Flow Height Control Gate
F. Carbon dioxide Feed Line
G. Test Section - 10.16 cm Stainless Steel Pipe
H. Gas Outlet with filters
I. Pressure Gauge with Back Pressure Control
J. Safety Valve
K. Heater
V. Flow Control Valves

Figure 5  Layout of the Experimental System
3.2 TEST SECTION

The test section is shown in figure 6, which is a 10 cm internal diameter pipe section. It has several openings which are used for a variety of purposes. Four main openings at points E and C are used to insert Electrical Resistance (ER) and Linear Polarization Resistance (LPR) probes, made by Rohrback Cosasco, as well as coupons of test material (1018 carbon steel). Any combination of these techniques can be used to measure corrosion rates as these methods compliment each other.

An opening, S, is used to insert a TSI shear stress probe. Since the corrosion rates at the walls are being measured, the probes are flush mounted into the system. The TSI shear stress probes are hot film sensors which is a heat transfer technique that gives the correlation between wall shear stress and the heat transfer rate from the sensor to the fluid. Gas pockets should not cover the probes for prolonged periods of time as this may lead to the burn out of the probes. The voltage signal from the probe is passed to an IFA 100 anemometer system which converts these analog signals through a Metrabyte's model DAS20 AD converter and stores them in a digital form. This is later processed using the TSI anemometry software package.

Several pressure tappings, P, are used to measure the pressure drop across any two points of a stationary slug or a hydraulic jump. ST is a sampling tube which has a dual purpose. It is used to extract samples of fluid to test for the oxygen, iron and carbon dioxide contents as well as the pH. When this is used in conjunction with the void fraction tube V, the void fraction across a radial section of a stationary slug can be measured.
3.3 MEASUREMENT TECHNIQUE & PROCEDURE

3.3.1 MEASUREMENT TECHNIQUE

The electrical resistance probe contains two wires. One is flush mounted on the metal surface while the other, the reference wire, is beneath the surface without any contact with the surface. This method relies on the fact that the DC ohmic resistance will increase in inverse proportion to the cross-section. Thus the progress of corrosion can be monitored from changes in the electrical resistance of the probe, recorded on the ER corrosometer. The LPR probes give a direct value of corrosion rate in mils/yr or mm/yr as desired. However, the dial readings from the ER corrosometer need to be corrected to obtain a value of corrosion rate. The following formula shows how the corrosion rate is calculated.

\[
\text{Corrosion Rate} = \frac{(\text{Change of dial reading}) \times \text{Probe span} \times 24 \times 365}{(\text{Measurement Time, hrs}) \times 1000 \times 40}
\]

where:  
Corrosion Rate is in \(\text{mm/yr}\)  
24 = Hours in a day  
365 = No: of days in a year  
1000 = Maximum probe life  
40 = Conversion factor (mils to mm)

The correction factor depends upon the kind of probe used. Each probe has a different span and depending upon that the value of the rate of corrosion is calculated. The
kinds of probes used are S-10, S-20 and S-40's with probe spans of 5, 10 and 20 respectively. The probe span is directly related to the probe life. Hence, an S-10 probe has a life time of a quarter of an S-40 probe, or would be worn out four times as fast as an S-40 probe under the same conditions tested. The probe span is also a direct measure of the sensitivity of the probe. The smaller the span of the probe, the greater is the sensitivity. However, each one of these probes cost the same amount of money. Thus, prudence suggests the use of ER S-40 probes for long term full pipe flow experiments and ER S-10’s for short duration slug flow experiments.

The corrosion rates calculated from weight loss coupons also require the use of a formula:

\[
\text{Corrosion rate} = \frac{(\text{Weight loss, gm}) \times 24 \times 365 \times 10}{(\text{Density, g/cm}^3) \times (\text{Area, cm}^2) \times (\text{Time, hrs})}
\]  

(33)

where: Corrosion rate = mm/yr
Area = Exposed Surface Area of Coupon
Time = Total time taken for measurement
10 = Conversion from cm to mm
24 = Hours in a day
365 = Days in a year

3.3.2 PROCEDURE

Saltwater is prepared by dissolving ASTM standard sea salt in a measured quantity of de-ionized water. The tank shown in figure 1 is filled with the liquid mixture to
be tested. 100% saltwater, 20% oil - 80% saltwater, 60% oil - 40% saltwater, 80% oil - 20% saltwater or 100% oil, by volume, are the compositions used. The pump is then started, to flow the liquid in the flow loop. Heaters connected to the tanks are switched on and with the help of a thermostat, the system is heated to a constant preset temperature.

The concentration of iron in the experimental system has been shown to play an important role in the determination of corrosion rates. It has been shown that a high iron concentration leads to supersaturation and reduces the observed corrosion rates. Thus, the experimental system is made of 316 stainless steel. This avoids the accumulation of iron in the system which might lead to errors in corrosion rate measurements.

The presence of oxygen, even in small concentrations, can drastically increase the corrosion rates of pipelines. The pipelines and flowlines transporting the crude oil, water and natural gas mixtures have negligible oxygen content. Hence, to obtain a correct estimate of the rate of corrosion of horizontal pipelines under various conditions, the oxygen concentration is kept below 30 ppb.

The oxygen in the system has to be purged to bring it down to acceptable levels. Hence, a deoxygenization procedure is started immediately. The pressure relief valve is partially opened and carbon dioxide is introduced into the system at a constant flow rate. The air and carbon dioxide mixture is allowed to vent freely from the top of the tank. After about 8 hours, regular checks are made for the oxygen levels using CHEMets™ dissolved oxygen test kits. These can accurately determine the amount of oxygen dissolved in the system. If the oxygen level is above 30 ppb, then the procedure is continued and checks made after one hour intervals till it drops down to the acceptable level. A check for
the dissolved iron concentration is also made at that time using similar CHEMets™. It is usually observed that the iron concentration is close to 0 at the start of the experimentation. However, this builds up with each experiment performed and when it is about 10 ppm, the water is removed from the system and replaced with freshly prepared saltwater. The deoxygenization procedure is then repeated and the system pressurized to the desired level to start the experiment.

It has been observed that the deoxygenization procedure is faster with a gate than without one. This is because the stationary slug or the hydraulic jump has the ability to entrain gas and this helps in purging the oxygen with a steady stream of carbon dioxide.

A gate is inserted into the system when slug flow experiments have to be performed. Gas is introduced as the liquid flows beneath the gate and a stationary slug is produced. The position of the stationary slug depends on the gas pressure upstream as well as the back pressure downstream. Since the experiments are performed at a constant system pressure, the upstream pressure is regulated according to the position of the stationary slug. The exact position of the stationary slug is found out using pressure drop readings in conjunction with an ultrasonic technique called the Acoustic Emission Multiphase Flow Monitor, supplied by British Petroleum Research. Pressure tappings, about 0.5 m apart, are connected to a pressure transducer. A large pressure drop is recorded when the slug crosses the first pressure tapping. The pressure drop, which is mostly accelerational, is a clear indication that the slug is located between the two points. The pressure drop also depends on the Froude number being tested. Thus, for higher Froude numbers, a bigger pressure drop is recorded. The latter technique utilizes a Zener Barrier Interface which converts a signal obtained from the sensors and the transducers, into a DC output which is
then seen across an oscilloscope. The sensors are attached to the outside pipe wall. As a slug moves inside the pipe across the sensor position, an output in the form of "noise" is recorded on the oscilloscope.

The measurement time period of any experiments depends upon the kind of probe used as well as the kind of experiment performed. It has been observed that the time period required for an ER S-40 probe to reach an equilibrium value, for full pipe flow experiments is usually more than 15 hours. Thus, most of the full pipe flow experiments have been performed for a time period ranging between 15 and 50 hours. However, for slug flow experiments using ER S-10 probes, the time period required to reach an equilibrium value is approximately 3 hours. The time period for the experiments conducted on slug flow ranges between 2 and 6 hours.

3.4 TEST MATRIX

The test matrix has been designed to gain an understanding of the effect of carbon dioxide partial pressure, liquid flow velocity, fluid composition, flow regime and fluid viscosity on the rate of corrosion of a pipeline or flowline. Three flow regimes, namely, full pipe flow, gas bubbled in, and slug flow were to be tested. The test matrices for full pipe flow, gas bubbled in and slug flow have been shown in Tables 1 and 2.
### TABLE 1. TEST MATRIX FOR FULL PIPE FLOW AND GAS BUBBLED IN

<table>
<thead>
<tr>
<th>Parameters To Be Tested</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide Partial Pressure (MPa)</td>
<td>0.27, 0.45, 0.79</td>
</tr>
<tr>
<td>Liquid Flow Velocity (m/s)</td>
<td>0.18, 0.28, 0.56, 1</td>
</tr>
<tr>
<td>Oil Concentration (%)</td>
<td>0, 20, 60, 80, 100</td>
</tr>
<tr>
<td>Oil</td>
<td>Conoco LVT200, Arcopak90</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>40</td>
</tr>
<tr>
<td>Bubbled Gas Velocity (m/s)</td>
<td>0.2</td>
</tr>
<tr>
<td>Parameters To Be Tested</td>
<td>Values</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>Carbon dioxide Partial Pressure (MPa)</td>
<td>0.27, 0.45, 0.79</td>
</tr>
<tr>
<td>Froude Number</td>
<td>6, 9, 12</td>
</tr>
<tr>
<td>Oil Concentration (%)</td>
<td>0, 20, 60, 80, 100</td>
</tr>
<tr>
<td>Oil</td>
<td>Conoco LVT200</td>
</tr>
<tr>
<td>Temperature (C)</td>
<td>40</td>
</tr>
</tbody>
</table>

**TABLE 2. TEST MATRIX FOR SLUG FLOW**
4. RESULTS

4.1 MEASUREMENT TIME

The use of LPR probes has been very limited to determine the equilibrium value of corrosion rate. The resistivity of the liquid mixture increases as the percentage of oil in the mixture increases. Since the LPR probe is not reliable if the resistivity of the solution increases, data was generated by an LPR probe only when the liquid used was 100% saltwater. The use of an LPR probe was discontinued when the liquid mixture had more than 20% oil.

Figure 7 shows the change of corrosion rate with time under full pipe flow conditions for 100% saltwater, at a partial pressure of 0.27 MPa and a liquid flow velocity of 0.18 m/s. Both, the ER and the LPR probes start of with corrosion rates of 8 and 7 mm/yr, and gradually reach an equilibrium value of 3 and 2.5 mm/yr respectively. These results are similar and show that either the LPR or the ER probe can be used to generate the corrosion rate data.

Figure 8 is a composite graph showing the corrosion rate with time for full pipe flow of 20% Arcopac90 oil and 80% saltwater mixture is tested. For all full pipe flow, at the velocities and pressures considered, it can be seen that the time to reach the equilibrium corrosion rate is 8 - 12 hours. For a flow velocity of 0.28 m/s, the corrosion rates observed at partial pressures of 0.27, 0.45 and 0.79 MPa are 4.2, 7.9 and 11.25 mm/yr respectively. At the same partial pressures and a liquid flow velocity of 1 m/s, the corrosion rates measured are 6.3, 10.25 and 13.4 mm/yr respectively.
Figure 7. Corrosion Rate vs Measurement Time
Full Pipe Flow of 100% Saltwater
CO2 Partial Pressure = 0.27 MPa
Temperature = 40°C
Liquid Flow Velocity = 0.18 m/s
4.2 FLOW EFFECT

The values of the equilibrium corrosion rates for 100% saltwater at three carbon dioxide partial pressures and three flow velocities are shown in Table 3. Tables 4 & 5 contain the data generated for all the other oil and saltwater mixtures tested.

Figure 9 shows the effect of flow velocity on corrosion rate when a 20% Conoco LVT200 oil and 80% saltwater mixture is tested. At a carbon dioxide partial pressure of 0.27 MPa, the corrosion rate increases from 4 to 4.9 mm/yr and from 4.9 to 5.4 mm/yr when the flow velocity is increased from 0.28 to 0.56 and then from 0.56 to 1 m/s respectively. At a carbon dioxide partial pressure of 0.45 MPa, corrosion rates of 6.3, 7.4 and 7.9 mm/yr were recorded for liquid flow velocities of 0.28, 0.56 and 1 m/s respectively. When the pressure was set at 0.79 MPa the corrosion rates measured for the same liquid velocities were 9.2, 10.75 and 11.6 mm/yr. These results indicate that the corrosion rate increases as the flow velocity of the liquid is increased. When the liquid flow velocity is increased the rate of shear also increases and this leads to an increase in the rate of corrosion.

Corrosion rate is plotted against liquid flow velocity for a 60% Conoco LVT200 oil and 40% saltwater mixture in Figure 10. When the carbon dioxide partial pressure is set to 0.27 MPa, the corrosion rates recorded for liquid flow velocities of 0.28, 0.56 and 1 m/s were 4.3, 5.4 and 5.75 mm/yr respectively. At partial pressures of 0.45 & 0.79 MPa, corrosion rates of 6.4, 7.9 and 8.4 mm/yr and 10.8, 14.4 and 15.75 mm/yr were obtained for the same velocities. These results again show that the corrosion rate increases with an increase in flow velocity of the liquid and the result is more pronounced at higher pressures.
Figure 11 shows the effect of liquid flow velocity of a 20% Arcopac90 oil and 80% saltwater mixture on corrosion rate. At a carbon dioxide partial pressure of 0.27 MPa and liquid flow velocities of 0.28 and 1 m/s the corrosion rates recorded are 4.2 and 6.35 mm/yr respectively. At a partial pressure of 0.45 MPa, for the same liquid flow velocities stated above, corrosion rates of 7.9 and 10.25 mm/yr have been observed. At a higher partial pressure of 0.79 MPa and the same liquid flow velocities, the corrosion rates measured are 11.25 and 13.4 mm/yr respectively. These results follow the general trend that has been established using Conoco LVT200 oil instead of Arcopac90 oil. The corrosion rates increased with an increase in liquid flow velocity and this was true for any carbon dioxide partial pressure tested.

Figure 12 is also a graph depicting the change in corrosion rate with liquid flow velocity. This graph has been drawn for a 60% Arcopac90 and 40% saltwater mixture. Values of 4.7 and 6.4 mm/yr have been recorded for the rate of corrosion, at a partial pressure of 0.27 MPa, when the liquid flow velocity is increased from 0.28 to 1 m/s. At partial pressures of 0.45 and 0.79 MPa, the corrosion rates are 9.25 and 11.25 mm/yr for a liquid flow velocity of 0.28 m/s. Corrosion rates of 12.25 and 16 mm/yr were recorded for a liquid flow velocity of 1 m/s and partial pressures of 0.45 & 0.79 MPa respectively. These results too, indicate that the corrosion rates increase with an increase in liquid flow velocity.
<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>Flow Velocity (m/s)</th>
<th>Corrosion Rate (mm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.27</td>
<td>0.18</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>0.28</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4.25</td>
</tr>
<tr>
<td>0.45</td>
<td>0.18</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>0.28</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>8.6</td>
</tr>
<tr>
<td>0.79</td>
<td>0.18</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>11.4</td>
</tr>
</tbody>
</table>

**TABLE 3.** CORROSION RATES OF 100% SALTWATER FULL PIPE FLOW
TEMPERATURE = 40 C
<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>Flow Velocity (m/s)</th>
<th>Corrosion Rate (mm/yr)</th>
<th>20% LVT - 80% Saltwater</th>
<th>60% LVT - 40% Saltwater</th>
<th>100% LVT</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.27 MPa</td>
<td>0.28</td>
<td>4</td>
<td>4.3</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.56</td>
<td>4.9</td>
<td>5.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>5.4</td>
<td>5.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.45 MPa</td>
<td>0.28</td>
<td>6.25</td>
<td>6.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.56</td>
<td>7.4</td>
<td>7.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>7.9</td>
<td>8.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.79 MPa</td>
<td>0.28</td>
<td>9.2</td>
<td>10.8</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.56</td>
<td>10.75</td>
<td>14.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>11.6</td>
<td>15.75</td>
<td>0.25</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 4. CORROSION RATES OF A MIXTURE OF CONOCO LVT200 OIL AND SALTWATER FULL PIPE FLOW TEMPERATURE = 40 C**
<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>Flow Velocity (m/s)</th>
<th>Corrosion Rate (mm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20% Arcopac90 - 80% Saltwater</td>
</tr>
<tr>
<td>0.27</td>
<td>0.28</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>6.35</td>
</tr>
<tr>
<td>0.45</td>
<td>0.28</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>10.25</td>
</tr>
<tr>
<td>0.79</td>
<td>0.28</td>
<td>11.25</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>13.4</td>
</tr>
</tbody>
</table>

**TABLE 5. CORROSION RATES OF A MIXTURE OF ARCOPAC90 OIL AND SALTWATER**
**FULL PIPE FLOW**
**TEMPERATURE = 40 C**
Figure 9. Corrosion Rate vs Liquid Flow Velocity
Full Pipe Flow of 20% LVT200 - 80% Saltwater
Temperature = 40 C
Figure 10. Corrosion Rate vs Liquid Flow Velocity
Full Pipe Flow of 60% LVT200 Oil - 40% Saltwater
Temperature = 40 C
Figure 11. Corrosion Rate vs Liquid Flow Velocity
Full Pipe Flow of 20% Arcopac90 Oil - 80% Saltwater
Temperature = 40 C
Figure 12. Corrosion Rate vs Liquid Flow Velocity
Full Pipe Flow of 60% Arcopac90 Oil - 40% Saltwater
Temperature = 40°C
A comparison of this study with the De Waard, Lotz and Milliams\textsuperscript{2} and the De Waard and Lotz\textsuperscript{4} study is shown in Figure 13. This graph of corrosion rate plotted against liquid flow velocity shows that the studies conducted by the authors mentioned had their limitations to multiphase flow corrosion prediction. At a carbon dioxide partial pressure of 0.27 MPa, temperature of 40°C and pH of 5.7, the study conducted in 1993 consistently underpredicted the results obtained with 100% saltwater. A comparison of the values shows that for a liquid flow velocity of 0.18 m/s, the corrosion prediction is 1 mm/yr while the actual rate of corrosion is 3 mm/yr. When the flow velocity is increased to 1 m/s the prediction again falls short and predicts a value of 3.2 mm/yr for an actual corrosion rate of 4.4 mm/yr. The study in 1991 has not considered the effect of liquid flow velocity at all and underpredicts any data having a flow velocity of 1 m/s or more.

Similar results are obtained at a higher partial pressure of 0.45 MPa and a pH of 5.25. The results are shown in Figure 14. For the study conducted in 1993, a liquid flow velocity of 0.28 m/s, the predicted value is 4 mm/yr while the observed value is 5.6 mm/yr and at a flow velocity of 1 m/s, the predicted value of 8 mm/yr again falls short of the actual value of 8.7 mm/yr. Similarly, the De Waard, Lotz and Milliams\textsuperscript{2} study conducted in 1991, does not consider the effect of flow velocity and greatly underpredicts corrosion rate for flow velocities greater than 0.8 m/s. Thus, at a flow velocity of 1 m/s, the prediction is 5.7 mm/yr for an observed corrosion rate of 8.7 mm/yr.
Figure 13. Corrosion Rate vs Liquid Flow Velocity
Comparison of This Study with DeWaard & Milliams
Full Pipe Flow of 100% Saltwater,
Temperature = 40 C
Figure 14. Corrosion Rate vs Liquid Flow Velocity
Comparison of This Study with DeWaard and Milliams
Full Pipe Flow of 100% Saltwater
Temperature = 40 C
4.3 EFFECT OF OIL VISCOSITY

A comparison of corrosion rates of 20% Conoco LVT200 and 20% Arcopac90 oil mixtures is shown in Figure 15. At a liquid flow velocity of 0.28 m/s and a partial pressure of 0.45 MPa, the corrosion rate for a 20% Conoco LVT200 - 80% saltwater mixture is 6.2 mm/yr while the rate of corrosion for an Arcopac90 oil mixture at the same concentration is 7.9 mm/yr. At a higher pressure of 0.79 MPa and the same liquid flow velocity, the two mixtures have corrosion rates of 9.2 and 11.2 mm/yr respectively. At a higher flow velocity of 1 m/s and a partial pressure of 0.27 MPa, the corrosion rates observed are 5.4 and 6.4 mm/yr respectively for the two mixtures. These results along with the results at higher pressures of 0.45 and 0.79 MPa at a liquid velocity of 1 m/s show that the more viscous Arcopac90 oil mixtures have a higher rate of corrosion than Conoco LVT200 oil mixtures.

A similar comparison is depicted in Figure 16, where the liquid mixture used comprises 60% oil and 40% saltwater. At a carbon dioxide partial pressure of 0.45 MPa and a liquid flow velocity of 0.28 m/s, the corrosion rates observed for Conoco LVT200 oil and Arcopac90 oil mixtures are 6.4 mm/yr and 9.2 mm/yr respectively. At a higher partial pressure of 0.79 MPa and the same liquid velocity, the corrosion rates measured are 10.8 and 12.25 mm/yr respectively. When the flow velocity is 1 m/s and the partial pressure 0.45 MPa, the rate of corrosion is 8.4 and 11.25 mm/yr respectively. Finally, at a higher pressure of 0.79 MPa and the same flow velocity, the corrosion rates are similar at 15.75 and 16 mm/yr respectively. These results follow the general trend laid out by a 20% oil and 80% saltwater mixture. Thus, it can be concluded that a liquid mixture with a higher viscosity has a higher rate of corrosion than a liquid mixture with a lower viscosity. At higher oil compositions, the effect of oil viscosity on corrosion rate is less.
Figure 15. Corrosion Rate vs Liquid Flow Velocity
Full Pipe Flow
Comparison of 20% LVT200 With 20% Arcopac90 Oil
Temperature = 40°C
Figure 16. Corrosion Rate vs Liquid Flow Velocity
Full Pipe Flow
Comparison of 60% LVT200 with 60% Arcopac90 Oil
Temperature = 40°C
4.4 EFFECT OF CARBON DIOXIDE PARTIAL PRESSURE

Figure 17 shows corrosion rate versus carbon dioxide partial pressure for a 20% Conoco LVT200 oil and 80% saltwater mixture. Corrosion rates of 4, 6.3 and 9.2 mm/yr have been recorded for a liquid flow velocity of 0.28 m/s and partial pressures of 0.27, 0.45 and 0.79 MPa respectively. At a flow velocity of 0.56 m/s and the same partial pressures, the corrosion rates are 4.9, 7.4 and 10.7 mm/yr respectively. When the flow velocity is 1 m/s, at the same partial pressures, higher values of 5.4, 7.9 and 11.6 mm/yr respectively have been recorded. These results show that the rate of corrosion increases with an increase in carbon dioxide partial pressure for all the liquid flow velocities tested. This could be due to increased reaction rates at higher carbon dioxide partial pressures. The carbon dioxide dissolves in the water to form carbonic acid and this in turn reacts with the Fe ions present to give the corrosion product which could be Ferrous carbonate or Ferrous bicarbonate. Higher carbon dioxide partial pressures decrease the pH resulting in more acidic solutions, which are more corrosive.

The results for 20% Arcopac90 oil and 80% saltwater are shown in Figure 18. Corrosion rates of 4.2, 7.9 and 11.25 mm/yr have been recorded for carbon dioxide partial pressures of 0.27, 0.45 and 0.79 MPa respectively, at a flow velocity of 0.28 m/s. At a flow velocity of 1 m/s, the corrosion rates measured are 6.4, 10.25 and 13.4 mm/yr respectively for the same partial pressures stated. These results also show that the corrosion rate increases with an increase in carbon dioxide partial pressure.

Figure 19 is a plot of corrosion rate against carbon dioxide partial pressure for a 60% Conoco LVT200 oil and 40% saltwater mixture. At a flow velocity of 0.28 m/s, corrosion rates of 4.3, 6.4 and 10.8 mm/yr have been recorded for partial pressures of
Figure 17. Corrosion Rate vs CO₂ Partial Pressure
Full Pipe Flow of 20% LVT200 - 80% Saltwater
Temperature = 40 C
Figure 18. Corrosion Rate vs CO₂ Partial Pressure
Full Pipe Flow of 20% Arcopac90 - 80% Saltwater
Temperature = 40°C
Figure 19. Corrosion Rate vs CO₂ Partial Pressure

Full Pipe Flow of 60% LVT200 - 40% Saltwater
Temperature = 40°C
0.27, 0.45 and 0.79 MPa respectively. When the flow velocity is 0.56 m/s, the corrosion rates increase from 5.4 to 7.9 to 14.3 mm/yr when the partial pressure is increased from 0.27 to 0.45 to 0.79 MPa. When the flow velocity is 1 m/s, an increase in corrosion rate is also observed as the pressure is increased as stated above. The corrosion rates recorded for the three pressures are 5.75, 8.4 and 15.75 mm/yr respectively. These results are in accord with the ones presented earlier and substantiate the hypothesis that corrosion rate increases with an increase in carbon dioxide partial pressure.

Figure 20 gives the corrosion rates for a 60% Arcopac90 oil and 40% saltwater mixture. Values of 4.7, 9.25 and 12.25 mm/yr have been observed for corrosion rates at pressures of 0.27, 0.45 and 0.79 MPa respectively and a flow velocity of 0.28 m/s. At a liquid flow velocity of 1 m/s, the corrosion rates increase from 6.4 to 11.25 mm/yr when the pressure is increased from 0.27 to 0.45 MPa and, from 11.25 to 16.05 mm/yr as the pressure is increased from 0.45 to 0.79 MPa.

A comparison of this study is made with the work done by De Waard and Lotz\(^4\) and De Waard, Lotz and Milliams\(^2\), and is shown in Figure 21. The rate of corrosion at a carbon dioxide partial pressure of 0.27 MPa for a 20% Arcopac90 oil and 80% saltwater mixture, for this study, has been observed to be 4.2 mm/yr. The predictions offered by the De Waard and Lotz\(^4\) work is 2.2 mm/yr and the De Waard, Lotz and Milliams\(^2\) work is 3.8 mm/yr. Both the studies underpredict the rate of corrosion of this liquid mixture. As the pressure is increased at the same liquid velocity, the two studies predict 4 and 5.7 mm/yr which is less than the value of 8 mm/yr recorded in this study. The corrosion rate of 11.4 mm/yr at a pressure of 0.79 MPa is much more than the rate of 7.4 and 8.5 mm/yr predicted by the two studies mentioned. The work done by De Waard and
Figure 20. Corrosion Rate vs CO₂ Partial Pressure
Full Pipe Flow of 60% Arcopac90 - 40% Saltwater
Temperature = 40 C
Figure 21. Corrosion Rate vs CO₂ Partial Pressure
Comparison of This Study with Dewaard & Williams
Full Pipe Flow of 20% Arcopac90 oil - 80% Saltwater
Temperature = 40 C
Lotz and De Waard, Lotz and Williams underpredicts most of the data obtained in this study and this goes a long way in proving that rotating cylinders may not be used to simulate pipe flow.

4.5 EFFECT OF OIL CONCENTRATION

A plot of Conoco LVT200 oil concentration versus corrosion rate shown in Figure 22, shows that the corrosion rate increases with an increase in oil concentration up to approximately 60%, after which the corrosion rate falls. When the oil concentration is about 80% then the corrosion rate observed is as low as 1 mm/yr, while at 100% oil concentration, the corrosion rate is 0.25 mm/yr. Thus, for a partial pressure of 0.27 MPa and flow velocity of 0.28 m/s, the corrosion rate increases from 3 to 4 mm/yr as the oil concentration increases from 0 to 20%, and then from 4 mm/yr to 4.3 mm/yr as the oil concentration further increases to 60%. At 80% oil concentration, under the same conditions, the corrosion rate drops to 1 mm/yr, while it is negligible at 100% oil.

Figure 23 shows the results for Arcopac90 oil. The results follow the same trend of increasing corrosion with an increase in oil fraction up to 60%, after which the corrosion rate falls quickly. Thus, for a partial pressure of 0.45 MPa and a liquid flow velocity of 0.28 m/s, the corrosion rate increases from 5.6 to 7.9 mm/yr with an increase in oil concentration from 0 to 20%, and from 7.9 to 9.25 mm/yr as the oil concentration increases from 20 to 60%. When the oil concentration reaches 80%, the corrosion rate is less than 0.25 mm/yr and the value remains the same at 100%. The results obtained for both the oils tested, follow this trend and it can be assumed that corrosion rate increases with increasing oil concentration up to 60% after which it drops around 80% because of phase inversion.
Figure 22. Corrosion Rate vs CO₂ Partial Pressure
Comparison of Full Pipe Flow With & Without Gas Bubbled In
20% LVT200 - 80% Saltwater
Temperature = 40°C
Figure 23. Corrosion Rate vs CO₂ Partial Pressure
Comparison of Full Pipe Flow With or Without Gas Bubbled In
60% Conoco LVT200 Oil - 40% Saltwater
Temperature = 40 C
Similar results are obtained for higher partial pressures of 0.45 and 0.79 MPa, and flow velocities of 0.56 and 1 m/s. It has been observed that even when oil is present in the liquid, there is a water layer present at the bottom of the pipe. This stratification of layers, keeps the ER probes in contact with the corrosive water. The explanation for little or no corrosion around 80% oil concentration lies in the fact that phase inversion takes place at high oil concentrations. Thus, oil becomes the continuous phase with water dispersed in it. The oil phase does not allow the water to contact the probes, hence, little or no corrosion is observed at 80% and 100% oil concentrations.

4.6 EFFECT OF BUBBLING GAS

The results presented thus far are those of full pipe flow of liquid. The effect of introducing gas or changing the flow regime in the pipeline has not been addressed. Table 6, gives the results obtained by introducing carbon dioxide gas into the system in the full pipe flow regime.

Figure 24 is a plot of the rate of corrosion against carbon dioxide partial pressure. The liquid mixture used here is 20% Conoco LVT200 oil and 80% saltwater at a liquid flow velocity of 1 m/s and a gas flow velocity of 0.2 m/s. At a partial pressure of 0.27 MPa, the full pipe flow result is 5.4 mm/yr and, when gas is introduced into the system, the corrosion rate increases to 6.2 mm/yr. A similar comparison at a pressure of 0.45 MPa shows that the corrosion rate increases from 7.9 to 8.8 mm/yr when gas is bubbled into the system. At a partial pressure of 0.79 MPa, the corrosion rate is observed to increase from 11.6 to 12.6 mm/yr when gas is bubbled in. These results show that the bubbling of gas into the system increases the rate of corrosion. This could be attributed to the fact that the fluid mixture velocity increases which leads to an increase in shear forces.
<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>Flow Velocity (m/s)</th>
<th>Corrosion Rate (mm/yr)</th>
<th>20% Conoco LVT Oil - 80% Saltwater</th>
<th>60% Conoco LVT Oil - 40% Saltwater</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Full Pipe Flow</td>
<td>Gas Bubbled In (0.2 m/s)</td>
</tr>
<tr>
<td>0.27</td>
<td>1</td>
<td>5.4</td>
<td>6.2</td>
<td>5.75</td>
</tr>
<tr>
<td>0.45</td>
<td>1</td>
<td>7.9</td>
<td>8.8</td>
<td>8.4</td>
</tr>
<tr>
<td>0.79</td>
<td>1</td>
<td>11.6</td>
<td>12.6</td>
<td>15.75</td>
</tr>
</tbody>
</table>

**TABLE 6.** COMPARISON OF CORROSION RATES OF FULL PIPE FLOW AND GAS BUBBLED IN FOR A MIXTURE OF CONOCO LVT200 OIL AND SALTWATER TEMPERATURE = 40 C
Figure 24. Corrosion Rate vs Conoco LVT200 Oil Concentration
Full Pipe Flow
Temperature = 40 C
leading to an increase in corrosion rates. One can also speculate that the local acidity increases due to supersaturation of the liquid with the gas leading to higher reaction rates, hence, higher values of the rate of corrosion.

A comparison of full pipe flow with or without gas bubbled in, for a 60% Conoco LVT200 oil and 40% saltwater mixture is shown in Figure 25. At a liquid flow velocity of 1 m/s, partial pressure of 0.27 MPa and a gas flow velocity of 0.2 m/s, corrosion rates of 7.8 and 5.75 mm/yr were recorded for full pipe flow and gas bubbled in. At a higher partial pressure of 0.45 MPa, the rates were 8 and 10.1 mm/yr and for a pressure of 0.79 MPa, the corrosion rates were 15.7 and 16.9 mm/yr. These results also indicate that the bubbling of gas under full pipe flow conditions leads to an increase in corrosion rate when compared to full pipe flow without gas bubbled in.

4.7 EFFECT OF SLUG FLOW

The effect of a change in the flow regime is observed when slug flow experiments are performed. It has been shown, Sun\textsuperscript{17} (1991) and Zhou\textsuperscript{23} (1993), that slugs enhance the corrosion damage to pipelines and flowlines. Table 7 shows the data generated on slug flow in this study.

Figure 26 plots corrosion rate against carbon dioxide partial pressure for 100% saltwater. It shows that for a Froude number of 6 and partial pressures of 0.13, 0.27, 0.45 and 0.79 MPa the corrosion rates are 2, 5.5, 6.25 and 13.4 mm/yr respectively. At Froude number 9, the corrosion rates for carbon dioxide partial pressures of 0.27 and 0.45 MPa are 5.3 and 6.75 mm/yr. These results show that the corrosion rate increases with an increase in carbon dioxide partial pressure.
Figure 25. Corrosion Rate vs Arcopak90 Oil Concentration
Full Pipe Flow, Temperature = 40°C
<table>
<thead>
<tr>
<th>Film Froude Number</th>
<th>Pressure (MPa)</th>
<th>Corrosion Rate (mm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>100% Saltwater</td>
</tr>
<tr>
<td></td>
<td>0.27</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td>6.25</td>
</tr>
<tr>
<td></td>
<td>0.79</td>
<td>13.4</td>
</tr>
<tr>
<td>6</td>
<td>0.27</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td>6.75</td>
</tr>
<tr>
<td>9</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 7.** CORROSION RATE OF SALTWATER & SALTWATER AND CONOCO LVT200 OIL MIXTURE.
SLUG FLOW
TEMPERATURE = 40 C
Figure 26. Corrosion Rate vs CO₂ Partial Pressure
Slug Flow of 100% Saltwater
Froude # 6 & 9
Temperature = 40 °C
A graph for a mixture of 20% Conoco LVT200 oil and 80% saltwater at a Froude number 6, is shown in Figure 27. The corrosion rate increases from 1.5 to 5.6 mm/yr when the partial pressure is increased from 0.13 to 0.27 MPa. The corrosion rates recorded at pressures of 0.45 and 0.79 MPa, are 7.9 and 9.9 mm/yr respectively. At a Froude number of 9 and partial pressures of 0.13, 0.27 and 0.45 MPa, the corrosion rates are 1.4, 5.3 and 6.5 mm/yr respectively. These results also indicate that the corrosion rate increases with an increase in the partial pressure.

Figure 28 shows the rate of corrosion plotted against Froude number for slug flow of 100% saltwater. At a partial pressure of 0.13 MPa, Zhou\textsuperscript{23} found out that the corrosion rate increased from 2 to 3 mm/yr as the Froude number increased from 5.7 to 10.7. At a pressure of 0.27 MPa, the corrosion rate changed from 5.5 to 5.3 mm/yr when Froude numbers of 6 and 9 were tested. Corrosion rates of 6.25 and 6.75 mm/yr were also recorded at Froude numbers of 6 and 9 when the partial pressure was set at 0.45 MPa. More data needs to be generated before any conclusive statements can be made about the effect of Froude number on corrosion rates. Although it appears, that there is little change in the rate of corrosion when the Froude number is increased from 6 to 9.

Slug flow data for a 20% Conoco LVT200 oil and 80% saltwater mixture is presented in Figure 29. It shows that the corrosion rate changed from 5.6 to 5.3 mm/yr, when the Froude number changed from 6 to 9, at a constant partial pressure of 0.27 MPa. Values of 7.9 and 6.5 mm/yr were also recorded at the same Froude numbers and a pressure of 0.45 MPa. A comparison with the study made by Sun\textsuperscript{17} (1991) shows that for a 20% Arcopac90 oil and 80% saltwater mixture, the corrosion rate changed from 4 to 3.4 mm/yr as the Froude number was increased from 6 to 9.
Figure 27. Corrosion Rate vs CO₂ Partial Pressure
Slug Flow of 20% Conoco LVT200 - 80% Saltwater
Temperature = 40 C
Froude # 6 & 9
Figure 29. Corrosion Rate vs Froude Number
Slug Flow of 20% Conoco LVT200 - 80% Saltwater
Froude # 6 & 9
Temperature = 40 C
Pressure drop readings 30, 60 and 90 cm into the slug were also recorded as slug flow experiments were being performed. Figure 30 shows the variation of pressure drop with a change in Froude number for a 20% Conoco LVT200 oil and 80% saltwater mixture. Pressure drop in a slug is mostly accelerational. The pressure drop 30 cm into a slug changed from 0.19 to 0.32 psia as the Froude number increased from 6 to 9, at a partial pressure of 0.27 MPa. At a Froude number of 6 and partial pressure of 0.27 MPa, the pressure drops recorded 30, 60 and 90 cm into the slug were 0.19, 0.21 and 0.24 psia respectively. The pressure drops recorded 30, 60 and 90 cm into the slug, at a partial pressure of 0.45 MPa and Froude number 9, were 0.32, 0.52 and 0.63 psia. The pressure drop across a slug increases with an increase in Froude number. As the Froude number increases the length of the slug front also increases. Thus, pressure drop would continue to increase substantially if it were measured 30, 60 or 90 cm into the slug at higher Froude numbers.

Pressure drop data can also be used to calculate shear stress. This would give a value of shear stress, 30, 60 and 90 cm across the slug front. This data can be very useful for modeling purposes when shear stress is used as one of the parameters to define the model. Pressure drop data is shown in Table 8.
Figure 30. Pressure Drop vs Froude Number
Slug Flow of 20% Conoco LVT200 - 80% Saltwater
CO₂ Partial Pressures = 0.27 & 0.45 MPa
Temperature = 40 C
<table>
<thead>
<tr>
<th>Composition</th>
<th>Froude Number</th>
<th>Pressure (MPa)</th>
<th>Pressure Drop 30, 60 and 90 cm into the slug</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Saltwater</td>
<td>6</td>
<td>0.27</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.45</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.79</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.27</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.79</td>
<td>0.45</td>
</tr>
<tr>
<td>20% LVT200 - 80% Saltwater</td>
<td>6</td>
<td>0.27</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.45</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.79</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.27</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.45</td>
<td>0.33</td>
</tr>
</tbody>
</table>

**TABLE 8.** PRESSURE DROP 30, 60 & 90 cm INTO THE SLUG, FOR SALTWATER AND 20% CONOCO LVT200 OIL - 80% SALTWATER MIXTURES. TEMPERATURE = 40 C
5: MODELING

The only model available for corrosion rate prediction is the one developed by De Waard et. al. (1991)\(^2\) and (1993)\(^4\). This model is based on data obtained in stirred beakers. Efird et. al.\(^6,7\) (1993) proved that rotating cylinder data cannot be correlated with pipe flow data and that the rate of corrosion was always lesser in the former than in the latter, when tested under the same conditions.

Efird et al. (1993)\(^6,7\) proposed the correlation:

\[
R_{\text{COR}} = a \tau^b
\]

where: \(R_{\text{COR}}\) is the rate of corrosion in mm/yr
\[
a = 7.5 \pm 0.5 \text{ (mm/yr) (N/m}^2\text{)}^{0.1}
\]
\[
b = 0.1 \pm 0.02
\]
\(\tau\) is the shear stress in N/m\(^2\)

Efird et al. (1993)\(^6,7\) performed their experiments at 50 C under various carbon dioxide partial pressures. The values of \(a\) and \(b\), however, are sensitive to the environment tested.

For this study, the rate of corrosion was plotted against the calculated shear stress. Figure 31 is such a graph for full pipe flow of 20\% Conoco LVT200 oil and 80\% saltwater mixture. Different partial pressures of 0.27, 0.45 and 0.79 MPa are used.
Figure 31. Corrosion Rate vs Calculated Shear Stress
Full Pipe Flow of 20% LVT200 - 80% Saltwater
Temperature = 40 C
The equations resulting from such a plot at these pressures are:

At a pressure of 0.27 MPa: \[ CR = 4.8 \times \tau^{0.1} \] (35)

At a pressure of 0.45 MPa: \[ CR = 7.3 \times \tau^{0.1} \] (36)

At a pressure of 0.79 MPa: \[ CR = 10.7 \times \tau^{0.13} \] (37)

These results are quite similar to the ones discussed previously. This encourages us to believe that the corrosion rate may indeed be a function of wall shear stress with an exponent of about 0.1.

Figure 32 is a similar plot for a mixture of 60% Conoco LVT200 oil and 40% saltwater. Under conditions of full pipe flow and a temperature of 40°C, the corrosion rate equations are:

At 0.27 MPa: \[ CR = 5.2 \times \tau^{0.13} \] (38)

At 0.45 MPa: \[ CR = 7.7 \times \tau^{0.12} \] (39)

At 0.79 MPa: \[ CR = 14.0 \times \tau^{0.17} \] (40)

These results too confirm the fact that the exponent of shear stress lies around 0.1. For this study it has been found that a value of 0.1 ± 0.03 for the exponent, best describes the results obtained.
Calculated Shear Stress (N/m²)

Corrosion Rate vs Calculated Shear Stress
Full Pipe Flow of 60% LVT200 - 40% Saltwater
Temperature = 40°C

Figure 32.
Figure 33 and 34 show the results obtained for a mixture of 20% Arcopac90 oil - 80% saltwater and 60% Arcopac90 oil and 40% saltwater. These results too, lie in the domain established earlier and it can be said without doubt, that the value of the exponent of the shear stress is about 0.1.

It has been shown in the previous chapter that there is an increase in the rate of corrosion when the carbon dioxide partial pressure is increased. This indicates that there could be a relationship between the coefficient or the exponent and the carbon dioxide partial pressure, in the corrosion rate equation. Thus either of the following hypothesis was tested;

\[ CR = a(P) \times \tau^b \]  \hspace{1cm} (41)

or

\[ CR = a \times \tau^{b(P)} \]  \hspace{1cm} (42)

It was found that the exponent b did not vary with the partial pressure, hence, no correlation existed between the two. However, the coefficient “a” did have a direct dependence on the carbon dioxide partial pressure. The coefficients obtained from the equations were plotted on separate graphs for different oil and saltwater mixtures. The result was that a power function best expressed the relationship between the carbon dioxide partial pressure and the coefficient “a”.

Thus generally,

\[ a = k \times (P)^c \]  \hspace{1cm} (43)
**Figure 33.** Corrosion Rate vs Calculated Shear Stress
Full Pipe Flow of 20% Arcopac90 - 80% Saltwater
Temperature = 40 °C
Figure 34. Corrosion Rate vs Calculated Shear Stress
Full Pipe Flow of 60% Arcopac90 - 40% Saltwater
Temperature = 40°C
All the graphs plotted showed that the value of the coefficient “k” as well as the value of the exponent “c” varied little with the oil and saltwater composition tested.

These results encouraged a plot, Figure 35, of all the values of the coefficient “a” from different compositions into one graph and the following result was obtained.

\[ a = 15.5 \times (P)^{0.83} \]  

where :  
- \( k \) is the coefficient of the corrosion rate term with a value of 15.5 ± 0.5 expressed in (mm/yr) (N/m²)⁰.¹  
- \( P \) is the carbon dioxide partial pressure expressed in MPa  
- \( c \) is the exponent with a value of 0.83 ± 0.07

The coefficient “a” could then be used in the corrosion rate equation to give a correlation ;

\[ CR = k \times (P)c(\tau)^b \]  

where :  
- \( CR \) is the rate of corrosion in mm/yr  
- \( \tau \) is the calculated wall shear stress in N/m²  
- \( b \) is the exponent of wall shear stress with a value of 0.1  
- \( k, P \) and \( c \) are as described earlier

This correlation can predict the value of multiphase flow related corrosion under the conditions of full pipe flow at 40°C upto and including an oil concentration of 60%. The values predicted are more than the De Waard et al. (1991)² and (1993)⁴ predictions. The values predicted in this study are based on experimental data of pipe flow.
Figure 35. Coefficient "a" vs CO₂ Partial Pressure
Full Pipe Flow of Oil - Saltwater Mixtures
Temperature = 40 C
and it substantiates the findings of Efird et al. (1993)\textsuperscript{6,7}.

The effect of temperature is now considered. Experiments have been carried out at different temperatures to determine that effect. Corrosion rates have been recorded at temperatures of 30, 33, 40, 50 and 60 C. The liquid mixtures tested are 100\% saltwater, 20\% Conoco LVT200 oil and 80\% saltwater and, 60\% Conoco LVT200 oil and 40\% saltwater. An analysis indicated that the corrosion rate increased with an increase in temperature.

Corrosion rates can be predicted using equation 45 only if the operating temperature is 40 C.

The transition state theory is used to incorporate the effect of temperature into the model. A regression analysis is made of all the data generated in this study. The approach taken is to predict the corrosion rate with the parameters known or tested,

\begin{equation}
\text{Since} \quad CR \propto (P)^c (\tau)^b \quad \text{at 40 C} \tag{46}
\end{equation}

or

\begin{equation}
\text{or} \quad CR = k (P)^c (\tau)^b \quad \text{at any temperature} \tag{47}
\end{equation}

where \( k \) is as defined in equation 30, assuming an elementary corrosion reaction

The final expression which includes the temperature dependent term works out to be,
\[ CR = k_1 \ (P)^c \ (\tau)^b \ (T) \ (e^{-E/RT}) \]  \hspace{1cm} (48)

where:
- \( CR \) is the corrosion rate in mm/yr
- \( k_1 \) is a constant
- \( P \) is the carbon dioxide partial pressure in MPa
- \( c \) is the exponent of pressure, 0.83
- \( \tau \) is the shear stress in N/m²
- \( b \) is the exponent of shear stress, 0.1
- \( T \) is the temperature in Kelvin
- \( E \) is the activation energy in Joules/mol
- \( R \) is the gas constant in J/mol K

To make this analysis possible, the actual value of corrosion rate is divided by the predicted value using the known parameters of carbon dioxide partial pressure, shear stress and temperature. The following equation is then obtained,

\[
\frac{CR}{(P)^{0.83} \ (\tau)^{0.1} \ (T)} = k_1 \ (e^{-E/RT})
\]  \hspace{1cm} (49)

Taking the natural log on both sides, we get,

\[
\ln\left(\frac{CR}{CR_p}\right) = \ln(k_1) + E/RT
\]  \hspace{1cm} (50)

where:
- \( CR_p \) is the “predicted value of corrosion rate, \((P)^{0.83} \ (\tau)^{0.1} \ (T)\)” to find
out the value of the activation energy and the constant $k_1$.

The result of this analysis is shown in figure 36. This figure is a graph of $\ln \left( \frac{CR}{CR_p} \right)$ and $1/T$. The resulting equation defines the value of the activation energy and the constant $k_1$. These values are

\[
\begin{align*}
\frac{E}{R} &= 5041 \text{ K} \\
\ln(k_1) &= 12.94
\end{align*}
\]

Substituting them into equation 29 we get,

\[
CR = (P)^c \left( \frac{\tau}{T} \right)^b \left( e^{12.94 - 5041/T} \right)
\]  

(51)

where: $CR$ is the corrosion rate expressed in mm/yr

- $P$ is the carbon dioxide partial pressure expressed in MPa
- $\tau$ is the shear stress expressed in N/m²
- $T$ is the temperature in Kelvin

Values of exponents $c$ and $b$ are 0.83 and 0.1 respectively

This is a predictive equation for corrosion rate using the parameters of carbon dioxide partial pressure, shear stress and temperature being tested. Figure 37 shows the graph of actual versus predicted corrosion rates. The results are quite satisfactory and the predictions are a good representation of the experimental data.

The prediction equation is, however, valid only up to a temperature of 60°C
and can be used for any temperature below that. After 60 C, protective iron scales begin to form on the pipe surface and it becomes difficult to predict the rate of corrosion from this equation. More experiments at higher temperatures need to be performed to figure out this effect. Equation 51 can be used to find out the corrosion rates for oil, water and natural gas flow.
Figure 36. Graph of $\ln (\text{Actual Rate}/\text{Predicted Rate})$ vs $1/T$
Full Pipe Flow of Oil & Saltwater Mixtures
Shear Stresses = 0.1 - 3.5 N/m²
Temperatures = 30, 33, 40, 50 & 60 °C
CO₂ Partial Pressures = 0.27, 0.45 & 0.79 MPa

$y = 12.94 - 5041x \quad R = 0.86$
Figure 37. Predicted vs Actual Corrosion Rate
Shear Stress Values = 0.5 - 4 N/m²
Temperatures = 30, 33, 40, 50 & 60 °C
CO₂ Partial Pressures = 0.27, 0.45 & 0.79 MPa
6. CONCLUSIONS

The following conclusions are based on full pipe flow experiments performed.

The corrosion rates increased with an increase in liquid flow velocity for oil percentages up to 60%. Higher rates of shear and increased turbulence are present at higher velocities and can contribute to the enhanced corrosion rates. Increase in liquid velocities do not increase corrosion rates at concentrations above 80% oil. Corrosion rates at these concentrations are very low.

Increasing the partial pressure of carbon dioxide led to increases in the corrosion rates. This has been shown to be true by many other researchers. Again, this holds for oil concentrations up to 60% oil. Increased reaction rates at higher carbon dioxide partial pressures are responsible for this effect. Above 80% oil concentration, the corrosion rates are very low and increasing the partial pressure has no effect.

For the oils tested, which had viscosities of 2 and 15 cp, at a temperature of 40 C, the corrosion rates were found to increase with an increase in oil concentration. This was true for all oil/water compositions up to and including 60% oil. This can be attributed to the separation and stratification of the oil and water in the pipe which formed a water layer at the bottom of the pipe. However, above 60% oil concentration, the corrosion rate decreased rapidly and tends to zero around 80% oil.

The effect of viscosity was observed when the data for the two oils tested was compared. Higher corrosion rates were recorded for the more viscous Arcopac90 oil.
than for Conoco LVT200 oil, under the same conditions of partial pressure, liquid flow velocity and temperature.

Bubbling gas into the system caused enhanced corrosion to occur, when compared to full pipe flow. The bubbling gas causes increased local turbulence and may also increase the acidity of the mixture due to supersaturation.

The corrosion rates can be expressed as a function of wall shear stress and carbon dioxide partial pressure. This substantiates the work of Efird et al. (1993). A model to predict corrosion rates has been established which shows that corrosion rates are dependent on the wall shear stress, temperature and partial pressure of carbon dioxide. This model can predict corrosion values for low viscosity oils up to 60% oil and 60°C, given the carbon dioxide partial pressure, liquid velocity and oil and saltwater concentration. The corrosion prediction for slug flow can be established when more experimental data is available.

It should be noted that the wall shear stress incorporates both the shear forces and effect of turbulence. The former includes a scouring type of corrosion while the latter can account for the increase in mass transfer rates to and from the wall. The effects of each component cannot be distinguished at this time. However, further work is being carried out to determine the contribution from each mechanism.

The De Waard et al. works of 1991 and 1993 predictions were lower than the experimental values at the same operating conditions. The corrosion prediction model is

\[ CR = (P)^{0.83} (\tau)^{0.1} (T) (e^{12.94-5041/T}) \]
For slug flow, high corrosion rates were observed for 100% saltwater and 20% Conoco LVT200 oil - 80% saltwater mixtures. The data obtained so far is insufficient to make conclusions on the effect of Froude numbers on corrosion rates. However, with an increase in partial pressure of carbon dioxide, the corrosion rates were observed to increase.
REFERENCES


63-67.


ABSTRACT

Previously, work has been done in the field of single phase and two phase corrosion and its control. However, little has been done to address the effect of multiphase flow in pipelines. This research focusses on an experimental study of multiphase flow related corrosion in horizontal high pressure pipelines.

The experimental setup consists of a 316 stainless steel tank with a flow loop, capable of holding 1.2 m³ of liquid. The data is collected in the test section which has an ID of 10.16 cm. Oil compositions of 0, 20, 60, 80 and 100% in the liquid mixture have been experimented with. Two oils, Arcopac90 and Conoco LVT200, have been used for this purpose. The temperature at which these experiments have been performed is maintained at 40°C. The rate of corrosion has been measured at different CO₂ partial pressures and flow velocities of the liquid mixture.

The experimental results presented are for full pipe flow of liquid with and without gas bubbled in. Interesting observations are made when oil is added to the system to study the effect of multiphase flow on corrosion of carbon-steel. The addition of oil enhances the rate of corrosion up to an oil cut of 60% after which the corrosion rate starts to drop. An increase in the flow velocity of the liquid or CO₂ partial pressure, leads to an increase in the corrosion rates. Graphical illustrations are presented to perceive the effect of CO₂ partial pressure, flow velocity of the liquid, liquid mixture viscosity, oil concentration and the effect of bubbling gas on corrosion rates. A model to predict corrosion rates in horizontal pipelines has also been developed.