THE UNIVERSITY OF TULSA
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NEW 3-CELL TEST FACILITY TO MEASURE EROSION-CORROSION
INHIBITION EFFECTIVENESS IN A CO₂ SATURATED FLOW LOOP
CONTAINING SAND, HIGH SALT CONCENTRATION, AND OIL

by
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the requirements for the degree of Master of Science
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ABSTRACT

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New 3-Cell Test Facility to Measure Erosion-Corrosion Inhibition Effectiveness in a CO₂ Saturated Flow Loop Containing Sand, a High Salt Concentration, and Oil

Directed by Dr. Siamack A. Shirazi

129 pp., Chapter 6: Summary, Conclusions, and Recommendations

(448 words)

The harsh effects and costly losses due to erosion-corrosion in the oil and gas industry have made studying aspects of erosion, corrosion, and the additive of the two, erosion-corrosion a high priority in recent years. The combination of erosion-corrosion can greatly increase the metal degradation rate and decrease the efficiency of injected chemical inhibitors, used for pipeline protection. This leads to higher than expected corrosion rates, surface pitting, and to material failure. In the past, the detrimental effects of erosion, CO₂ and chloride corrosion, and erosion-corrosion had to be measured in separate tests. Repeating a test multiple times required extra time and raised questions about the consistency of system conditions from test to test. This study introduces a new testing facility that allows the three components to be measured simultaneously, in one test, using a variety of testing techniques. The new facility uses a three plugged-tee test cell configuration designed to measure erosion, corrosion, and combined erosion-corrosion in a single test. Tests were conducted using linear polarization resistance (LPR), electrical resistance (ER), and weight loss (WL) measurement techniques in the three-cell configuration. Results from this
project are being used to more accurately and effectively understand erosion-corrosion prediction for a variety of field conditions.

There are three objectives presented in this research. First, is to establish accuracy and repeatability of measurements for a baseline set of testing conditions in the 3-cell Erosion-Corrosion facility. The 3-cell configuration facility uses three identical, in-line plugged-tee test cells. Test data showed that all three test cells were impacted in the same way by both the fluid and sand particles. The second objective is to use the 3-cell E/C facility to validate previous tests for baseline erosion, corrosion, and erosion-corrosion conditions. The final objective is to experimentally characterize inhibitor effectiveness and identify effects of entrained sand on inhibitor performance in a CO₂ saturated system. Chemical inhibition is widely used in the oil and gas industry to reduce effects of corrosion in the production and transport of corrosive gasses and fluids. Sand particles can prevent proper adsorption of the inhibitor onto the metal’s surface, reducing effectiveness and increasing corrosion rates. A new approach will be utilized to predict inhibited erosion-corrosion for a set of environmental conditions in the presence of sand and oil.

Modified Frumkin isotherms were fitted to experimental inhibited erosion-corrosion data. Results can be integrated into the existing computer program for prediction of inhibited erosion-corrosion rates based on input corrosion variables (pH, temperature, and others) and input erosion variables (particle size, particle shape, material, and others). Accurate erosion-corrosion prediction is imperative because of the difficulty in data collection in many well sites, and is necessary for the reduction of costs and down time.
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CHAPTER 1

INTRODUCTION

Carbon steels are commonly used in the construction of down-hole tubing, drilling, and transport and production pipelines. These materials are chosen because of their relatively low cost when compared to corrosion resistant alloys and because of their ease of manufacture. But, carbon steels are highly susceptible to corrosion damage. Corrosion has become a central problem in the oil and gas industry over the last 30 years. Corrosion and the combined effects of erosion-corrosion have been more prevalent in recent years primarily as a result of a combination of superior oil collection techniques where CO$_2$ is injected into the reservoirs. Increased development of crude with higher quantities of H$_2$S and CO$_2$ and the existence of sweet and sour gas production from drilling in deeper wells$^1$. In the presence of sand, existing corrosion problems are amplified by the formation retardation or complete removal of FeCO$_3$ scale formation as well as by changing the patterns within the flow. High fluid velocity, CO$_2$ or H$_2$S saturated environment, or solid particles trapped in the flow can cause metal loss on the interior wall surfaces of pipelines and tubing$^2$. According to a report funded by the U.S. Congress and completed by the National Association of Corrosion Engineers (NACE, International) and the United States Federal Highway Administration (USFHA), in 2001 the cost of corrosion in the United States was equivalent to approximately 3.1% of the nation’s Gross Domestic Product (GDP) of the time which was about $276 billion$^3$. New estimates, as shown in a report submitted to the U.S. Department of Transportation’s Office of Pipeline Safety by a Houston based private consulting company, gives current expected corrosion costs as of
June 2013 to be over $1 trillion. Previous research conducted by NACE only accounted for the direct costs associated with corrosion. The new report estimated indirect costs, which are the costs accounted for by the consumer, to be equivalent to the direct costs. These findings show the extreme importance of addressing corrosion issues in oil and gas production and transport.

Corrosion prediction based on environmental conditions has, for decades, been the best way to control the corrosion damage that occurs in oil and natural gas pipelines and tubing. Recent advances in research techniques and field studies that have led to improved accuracy for empirical and mechanistic prediction models to account for many environmental parameters, such as the effects of CO\textsubscript{2} pressure, pH levels, a wide range of temperatures, and chloride content. Additional research is also being conducted in the area of chemical inhibitors. This research addresses both the prediction of inhibited erosion-corrosion as well as the inhibitor effectiveness based on environmental conditions.

There are three objectives to this research. The first objective is the evaluation of a new testing system, called the 3-cell E/C test loop. Until now, erosion, corrosion, and the combined effects of erosion-corrosion were measured in three separate tests. Separate tests make it difficult to directly compare results because of the potential error in either the solution composition, setup, or data collection that could lead to disparities in results. The three-cell configuration can be used in a closed flow loop testing facility to measure the effects of erosion, corrosion, and erosion-corrosion in a single test, limiting errors associated with conducting three separate tests. As a first step, a validation study was needed to establish the accuracy and the repeatability a newly-designed test facility.
The second objective was to complete experiments with the 3-Cell E/C Test Loop to validate previous previously held theories on the effects of chloride concentration on corrosion rates\textsuperscript{5,6}. Chlorides are commonly present in deep and offshore drilling. In results in previous work, increased NaCl concentration results in slight decrease in corrosion due to the chloride reducing the solubility of the corrosive agent.

The third (and most important) objective was to study the effects of inhibitor efficiency in an erosion-corrosion environment in a CO\textsubscript{2}-saturated system when sand is part of the flow loop fluids. Carbon dioxide corrosion, also called sweet corrosion, is created when the CO\textsubscript{2} molecules dissolve in water causing an acid to form. This creates H\textsubscript{2}CO\textsubscript{3}, carbonic acid. Carbonic acid is highly corrosive and for constant pH values is actually more corrosive than strong acids, such as hydrochloric or sulfuric acid\textsuperscript{7}. Chemical inhibitors have been widely used in pipeline industries to control the effects of corrosion and erosion-corrosion due to CO\textsubscript{2} and H\textsubscript{2}S corrosion. Various environmental conditions can have a significant effect inhibitor efficiency. Some environmental conditions that contribute to corrosion include temperature, pH, flow geometry, chloride concentrations, water cut, flow velocity, and sand erosion\textsuperscript{8-10}. And, while many inhibitor studies have been completed and prediction models created, there is still little known about the effect that the addition of sand will have on inhibitor efficiency. McMahon, in his testing of corrosion inhibitors used in the oil and gas industry, found that the chemicals inhibiting corrosion can be effected by the presence of sand\textsuperscript{11}. McMahon’s simulations showed that produced sand particles entrained in the flow can have absorbed inhibitor molecules on the surface of the sand, reducing the total inhibitor concentration in the total solution. While a direct correlation between sand concentration and inhibitor effectiveness has not yet been
established, it has been shown through testing that with increased sand concentrations, the inhibitor effectiveness decreases\textsuperscript{5,9,11}. The lack of direct correlation, though, comes from the effect of other parameters. Inhibitor type, environmental conditions, and flow patterns can all contribute to the effectiveness of chemical inhibitors. Nerville and Wang studied the effects of inhibitor presence on sand erosion rates\textsuperscript{12}. They concluded that when inhibitor and sand are present in a system, the adsorption of inhibitor onto the sand particles reduces the erosion rate by reducing the sand impact energy.

Being able to predict inhibitor effectiveness has become ever more important because of new drilling techniques which have allowed for developing deeper wells and because of increased offshore drilling. Accurate prediction models could assist pipeline developers to design the appropriate infrastructure for production and transport of corrosive liquids and gasses. Using the best inhibitor for the present environmental conditions reduces corrosion rates, which reduces costs. Also, effective construction reduces long term costs and environmental hazards associated with repairs, replacement, and spills.

Linear polarization resistance (LPR), electrical resistance (ER), and weight loss (WL) techniques were used in this study to analyze long term test results for metal loss rates of a carbon steel and a stainless steel due to effects of erosion, corrosion, and erosion-corrosion. A previous study developed an approach for the prediction of inhibited erosion-corrosion rates\textsuperscript{5}. The new approach presented here incorporates the use of existing adsorption isotherms combined with mechanistic models derived from experimental results for predicting corrosion and erosion-corrosion rates. The process of adsorption of the inhibitor onto the base metal can be described with the use of the adsorption isotherms. The Flory-Huggins, Frumkin, Temkin, and Langmuir adsorption isotherms were
considered. Also characterized, are inhibitor concentration and effects of erosion-corrosion from sand particles on the carbon steel\textsuperscript{5}. Long term testing was completed in a closed loop testing facility, simulating field conditions to analyze the effectiveness of the adsorption isotherms. Repeat testing was also completed for different NaCl concentrations to confirm correlations used in the mechanistic model for CO\textsubscript{2} corrosion when no scale is present.
CHAPTER 2
BACKGROUND AND LITERATURE REVIEW

2.1 Concepts in CO2 Corrosion

Definition of Corrosion

There are many different categories of metal corrosion. The classifications of corrosion that are most common in transportation and production systems include general or uniform corrosion, localized corrosion such as pitting corrosion or crevice corrosion, stress corrosion cracking, and combined erosion-corrosion\(^3\). Uniform corrosion, often called general corrosion, creates an all-inclusive metal loss pattern across the entire surface of the metal. Uniform corrosion is the most common type of corrosion, especially in transport pipelines where there is a uniform structure with few changes in flow direction or environmental conditions. Localized corrosion exists in a central area, instead of on the entire surface area, where conditions are more suitable for corrosion or because a reduction in corrosion protection occurs. Pitting, which is a very dangerous type of attack due to concentrated chloride ions, is the worst type of localized corrosion due to the difficulty detection. Crevice corrosion happens between joints in the pipelines where corrosion protection measures often fall short. Stress corrosion cracking is a brittle fracture of the metal caused by harsh environmental conditions. Failures due to stress corrosion cracking result in high costs primarily because the surface of the metal often appears unaffected while large cracks can be growing under metal surface. The brittle fractures mean that there is little time to detect possible failure before it occurs. Erosion-corrosion is the combined
effects of corrosion and erosion and can be increased by either high flow velocities or the inclusion of solid particles entrained in the flow. All classifications of corrosion mentioned share the same definition. They cause a degradation of material, in this case metal, through an electrochemical reaction. The material disintegrates resulting from a chemical reaction to its surroundings in an effort to return to its elementary atoms\(^{13, 16}\). Corrosion is often determined by the type of environment the area is subjected to, such as H\(_2\)S corrosion, CO\(_2\) corrosion, or acid corrosion. H\(_2\)S and CO\(_2\) are the most common and most damaging types of corrosion that companies in the oil and natural gas industries face, primarily because of the new need to be able to transport wet, untreated gases through areas that are not easily accessible like offshore pipelines\(^{14}\). It is difficult to monitor and treat pipelines in these rural or inaccessible areas, driving industrial demands for increased research in the area of localized and uniform CO\(_2\) corrosion. New production and transport methods have created a need for development of new corrosion prediction and monitoring techniques.

**Impact of Corrosion Costs**

As was discussed in Chapter 1, in 2013, the current accepted estimate for the direct costs of corrosion have now surpassed 500 billion US dollars per year\(^4\). In the 2001 study conducted by NACE, International and the United States Federal Highway Administration (USFHA), a lower estimate of about 276 billion dollars a year is given for the direct expenses due to corrosion related damage. The pie chart in Figure 1 shows the estimated breakdown given in the NACE report for the direct corrosion costs, separated based on industry within the United States. Most corrosion in the oil and gas industry occurs internally within the production wells, transportation pipelines (especially for water wet
gases), and pre-refined storage tanks where water, oxygen, and chlorides are often present. Developing an understanding of what causes corrosion is crucial for future efforts in corrosion control and prevention. Basic prevention practices for extending the lifetime of pipeline and well components include: proper material selection, adequate design, and excellent system fabrication. The study also estimates that 25% to 30% of corrosion related costs are preventable. Production and transportation costs are continuing to increase, the industry must be proactive in controlling corrosion in an effort to reclaim some of the over 80 billion USD a year in preventable costs. Table 2.1 gives an estimated value for the yearly amount spent to combat corrosion in the US. The table was submitted in the NACE, International 2001 report and estimates the total prevention cost at about $121.43 billion. Besides the cost of repairs, replacement, and downtime, there is also the added safety risk. Improved safety is another factor that can be affected by severe corrosion complications due largely to earlier than expected component failure leading to catastrophic disasters.
Figure 2.1: Division of Yearly Costs Due to Corrosion Based on Industry

Table 2.1: Annual Amount Spent on Corrosion Prevention

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<td>Corrosion Resistant Alloys</td>
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</tr>
<tr>
<td>Corrosion Inhibitors</td>
<td>1.1</td>
</tr>
<tr>
<td>Engineering Plastics &amp; Polymers</td>
<td>1.8</td>
</tr>
<tr>
<td>Cathodic &amp; Anodic Protection</td>
<td>1.0</td>
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<tr>
<td>Corrosion Control Services</td>
<td>1.2</td>
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<tr>
<td>Research &amp; Development</td>
<td>.02</td>
</tr>
<tr>
<td>Education &amp; Training</td>
<td>.01</td>
</tr>
<tr>
<td><strong>Total Cost</strong></td>
<td><strong>121.43</strong></td>
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Electrochemistry Concepts for Corrosion

Corrosion rates in the field either depend on the electrochemical reactions, the flow pattern, the mass transport process, or a combination of the three. In the oil and gas industry the most common cause of corrosion is an electrochemical reaction that occurs between a metal and an electrolyte solution. In this case, the corrosion rate is determined by the state of reaction between the anodic reaction and the cathodic reaction\textsuperscript{16,17}. The anodic reaction process starts with the oxidation of the metal resulting in a release of electrons ($e^-$). The anodic reaction is represented by Equation 2.1. Equation 2.2 is the anodic reaction that occurs on carbon steel in a CO\textsubscript{2} saturated system.

\begin{equation}
    M \rightarrow M^{n+} + ne^- \tag{2.1}
\end{equation}

\begin{equation}
    Fe \rightarrow Fe + 2e^- \tag{2.2}
\end{equation}

The cathodic reaction is a reduction reaction where hydrogen or oxygen molecules are reduced, removing electrons from the surface of the metal. A single reaction equation cannot be used to describe the cathodic reaction because there are several reaction types taking place. The four types of reactions considered are hydrogen evolution, oxygen reduction, metal deposition, and metal ion reduction. The most common cathodic reaction is oxygen reduction. The following equations show four cathodic reactions considered. Equation 2.3 shows the cathodic equilibrium between the acid solutions and the hydrogen gas, Equation 2.4 shows the oxygen reduction reaction for acid solutions, Equation 2.5 shows the oxygen reduction reaction for a basic solution, and Equation 2.6 shows the metal ion reduction.

\begin{equation}
    \text{Equation 2.3}
\end{equation}

\begin{equation}
    \text{Equation 2.4}
\end{equation}

\begin{equation}
    \text{Equation 2.5}
\end{equation}

\begin{equation}
    \text{Equation 2.6}
\end{equation}
When the anodic and cathodic reactions are in equilibrium then the flow of electrons from the two reaction equations is balanced. When this happens there is no net electron flow, meaning that there is no electrical current\textsuperscript{16-17}.

Anodic and cathodic reactions have limited transfer rates creating an abundance of electrons on the metal surface. The potential at the surface of the metal then becomes more negative because of extra electrons accumulating at the interface of the metal and the interacting solution. The change to a negative potential is called cathodic polarization. If there are insufficient electrons on the metals surface then a change to a positive potential is created, called an anodic polarization. For an increasingly positive potential at the metal to solution interface, the oxidizing power of the solution rises due to the anodic polarization being greater\textsuperscript{16, 18}.

\textit{Effect of Environmental Factors on Corrosion}

The largest influence propelling internal pipeline corrosion in the oil and gas industry is the environmental factors to which the surface of the metal is subjected. Environmental factors have varying influences on internal corrosion rates, but combined factors lead to more severe corrosion as compared to each factor individually. Some of the
critical environmental elements that influencing corrosion rates in the oil and gas industry are internal temperature, the fluid flow velocity, CO\textsubscript{2} partial pressure, pH, the material selection, and the amount of dissolved oxygen present\textsuperscript{14}.

Temperature is a very important factor that must be considered for corrosion control. Corrosion rates generally will approximately double for every 10° C (50° F) rise in internal temperature for a chemically stable solution. A counter example exists when oxygen is present in the solution. For a metal submersed in water that is open to ambient room temperature water, corrosion rates are much higher than they are when that same water is heated to its boiling temperature. This is primarily due to the byproducts that are created on the metal’s surface as corrosion occurs. At lower temperatures where oxygen is present, hematite (Fe\textsubscript{2}O\textsubscript{3}) will rapidly form on the surface of the metal. When placed in a solution of boiling water, a black film called magnetite (Fe\textsubscript{3}O\textsubscript{4}) is formed which provides a protective layer on the metal’s surface, reducing corrosion rates. The best way to avoid high corrosion rates is to avoid large temperature fluxes across the surface of the metal\textsuperscript{19}.

The flow velocity can also have a significant impact on the corrosion rate. The impact of flow velocity on local corrosion rates is dependent on other factors such as the material selection and local environmental conditions. Neglecting additional conditions, a high flow velocity will have the most significant effect on the corrosion rate. Electrochemical interactions between solution components and entrained particles are common in production and transportation systems and must therefore be considered. For a steady state solution with controlled polarization, the flow velocity has little to no effect. However, under cathodic reaction conditions the corrosion rate increases with flow velocity. When solid particles are captured in the fluid solution the flow velocity has
limited effect until a threshold velocity is reached. After this point the corrosion rate increases drastically through combination of erosion-corrosion\textsuperscript{16}.

Corrosion due to the presence of CO\textsubscript{2} gas is boosted by the interaction with the water molecules, creating an electrochemical oxidation reaction. The partial pressure alone has a limited effect on the corrosion rate but when combined with other environmental factors, such as temperature, the partial pressure can have a significant impact\textsuperscript{6-8}. Figure 2.2 shows the CO\textsubscript{2} partial pressure versus the corrosion rate at four different temperatures. Each test was held at a constant temperature and started at a partial pressure of 40 psi then was increased to 65 psi and finally to 115 psi. For all four cases the corrosion rate increased as the partial pressure was increased, but at different rates. For the system in Figure 2.2, at low temperature ranges, minimal corrosion rate increase is seen, even as the pressure is increased. Shown is that the corrosion rate increased from about 275 to 465 mills per year (mpy). Even at 140\textdegree{} F the corrosion does not increase much until the pressure is nearly tripled from its starting point. Figure 2.2 shows though, that with increased temperatures the corrosion rate increases faster with the increasing partial pressure. For a temperature of 194\textdegree{} F the corrosion rate increased from an initial 985 mpy to a final corrosion rate of 2087 mpy at a partial pressure of 115 psi\textsuperscript{20}.
Figure 2.2: Effect of Partial Pressure on the Corrosion Rate with Increasing Temperature

The solution pH has a significant effect on corrosion rates. Solution pH is a measure of the hydrogen ions (H⁺) in the test solution and range on a log scale from 0 to 14. A pH value of 7 signifies the solution is in its neutral state, if the pH is greater than 7 then it is a basic solution and if it measures below 7 then the solution is acidic. A high acidity level in the solution typically means elevated corrosion rates. Even if the solution is basic, corrosion can still exists due to the occurrence of dissolved oxygen in the solution.

Dissolved oxygen in the solution can be very detrimental to oil and gas infrastructure. For corrosion to occur there must be an oxidizing agent. Oxygen in the
solution causes increased corrosion rates by working as a recipient for electrons and by removing the film of hydrogen at a cathode. The presence of CO$_2$ or H$_2$S gases cause an acceleration of the corrosion process. The corrosive behavior of an active passive metal is divided into three regions: active, passive, and transpassive. In the active region the metal behavior is normal; as the oxidizing agent increases so does the corrosion rate. When an excess of oxidizing agent forms then the passive region is entered. Excess oxidizing agent causes the development of a passive layer which in turn causes a decrease in corrosion by protecting the metals surface. If the oxidizing agent is increased still further, the result is a minor increase in the corrosion rate. This region is the transpassive layer and it requires a high oxidizing concentration or a strong oxidizing agent to achieve$^{17,21}$.

**Corrosion Rate Measurement Techniques**

Corrosion rate can be monitored using several different types of measurement processes such as weight loss or electrochemical measurement techniques. Since most metal corrosion occurs by an electrochemical process, the use of electrochemical measuring techniques gives the best picture of what is occurring in the corrosion process. For this techniques, a specimen is submersed in a solution that simulates field conditions and measurements are taken across the specimen surface. Electrochemical studies are ideal because measurements taken from a specimen with a surface area of just a few square centimeters can be used to model a much larger system$^{17}$. The specimens used are electrodes; made up of a working electrode and a reference electrode that are electrically isolated from each other. Some of the more common techniques utilized are Tafel Extrapolation, Linear Polarization Resistance (LPR), Electrochemical Frequency
Modulation (EFM), and Electrochemical Impedance Spectroscopy (EIS). The corrosion rate depends on the current flow between the anodic and cathodic reactions. When the anodic and cathodic reactions are in equilibrium there is no net flow of electrons across the metal surface limiting corrosion. The rates of anodic and cathodic reactions operate as functions of the potential and the voltage of the corroding metal. Tafel Extrapolation and LPR methods are further defined below.

In corrosion measurements, it is not possible to directly measure the corrosion rate. To solve this, Tafel Extrapolation is used to measure the net current across an electrode’s surface and extrapolate a corrosion rate. The potential and current are measured at an equal distance on either side of the corrosion potential \( E_{corr} \) and plotted on a graph. The total current is plotted versus the potential showing the extrapolation and giving the corrosion current value, \( I_{corr} \). An example plot is shown in Figure 2.3. The anodic and cathodic reactions are shown in Figure 2.4. The graph in Figure 2.4 shows the absolute current along the horizontal axis on a logarithmic scale versus the potential along the vertical axis. The top curved line is the sum of the cathodic and anodic currents, or the total current, calculated from the theoretical anodic and cathodic currents as shown by the labeled straight lines. In LPR testing a controlled potential is applied to the electrode specimen surface with use of a potentiostat. The change in current across the surface specimen is then measured and through additional calculations, a metal loss rate or corrosion rate can be determined. The intersection of these lines depicts the changing point where the system goes from anodic to cathodic or vice versa. The absolute current is shown in a log format because of the large range of currents that are gathered during a corrosion experiment. Tafel Extrapolation does have several limitations in that real-time monitoring is not
possible and the method is unsuitable for systems containing more than one reduction process. Linear polarization is the more effective method for these types of systems.

Figure 2.3: Anodic and Cathodic Current Components in the Corrosion Process

Figure 2.4: Plot of Total Current ($i_T = i_o + i_c$) versus Potential
Linear Polarization Resistance, LPR for short, is the slope of the curve for the potential-current density at the free corrosion potential, which gives a value for the polarization resistance ($R_p$). Figure 2 gives the linear polarization plot for polarization versus the current density. Unlike the Tafel Extrapolation method, LPR can be used for more than one reduction process to give corrosion measurements in real time. The corrosion rate is calculated from the measured resistance potential. A small overpotential is applied to an electrode or series of electrically isolated electrodes and the corresponding current is measured.

![Figure 2.5: Linear Polarization Curve](image)

Equation 2.7 shows the Stern-Geary equation which relates the polarization resistance to the corrosion current:
\[
R_p = \frac{B}{i_{corr}} = \frac{\Delta E}{(\Delta t)\Delta E \to 0}
\]

- \(i_{corr}\) is the corrosion current
- \(R_p\) is the polarization resistance
- \(B\) is the proportionality constant and can be determined empirically or calculated by the anodic and cathodic Tafel constants

Equation 2.8 shows the process for calculating a value for \(B\) from the Tafel constants (\(\beta_a, \beta_c\))\textsuperscript{22-24}.

\[
B = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)}
\]

The range for an anodic Tafel constant is between 0.06 and 0.12 volts/decade. The range for a cathodic Tafel constant is 0.12-infinity. For this study it is assumed that the anodic and the cathodic Tafel constants have equal values of 0.12 volts/decade. For these values Equation 2.8 can be simplified as shown in Equation 2.9. The Tafel constants can also be determined experimentally using polarization plots. Examples from literature are shown in Figures 2.6 and 2.7\textsuperscript{24}.

\[
R_p = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c) \cdot i_{corr}} = \frac{0.026}{i_{corr}}
\]
Figure 2.6: Polarization Diagram with Anodic and Cathodic Branches

Figure 2.7: Polarization Diagram for Current Density versus Potential for Anodic and Cathodic Branches
The resistance potential ($R_p$) readings given by the LPR measurements can be used to calculate the corrosion current ($I_{corr}$) as shown by Equation 2.10. For uniform corrosion the corrosion current values obtained can then be used to then calculate the corrosion rate in terms of metal loss per year at set time increments over the length of a test. Equation 2.11 is used to calculate the corrosion rate at each resistance potential measured\textsuperscript{22-25}.

\[
I_{corr} = \frac{B}{R_p} \tag{2.10}
\]

\[
CR = \frac{I_{corr} \cdot K \cdot EW}{\rho \cdot A} \tag{2.11}
\]

- CR is the corrosion rate in either mm/year or mpy
- $I_{corr}$ is the corrosion current in amps
- K is an units based constant, (for mm/year $K= 3,272$, for mpy $K = 1.288e5$)
- EW is the equivalent weight in grams
- $\rho$ is the density in grams/cm$^3$
- A is the electrode surface area in cm$^2$

**Corrosion Control**

The three main ways that corrosion is controlled in oil and gas production are fluid flow control, material selection, and the use of chemical inhibitors. Because of the various types of corrosion that exist different methods are needed to account for them. The best way to approach corrosion problems in a system are to look at the environmental conditions and other factors that are specific to that particular system\textsuperscript{18}. The proper material selection as well as the use chemical inhibitors has drawn a lot of attention in research fields in recent
years. The ultimate goal for the industries affected by corrosion is to find the most cost
efficient method for preventing or at least controlling the damage created by corrosion.
The three main corrosion control methods are explained in more detail below.

One method for corrosion control is to control the fluid flow velocity. Corrosion
rates are often easily controlled by the formation of a magnetite or, an even more protective,
iron carbonate layer that forms on the internal surface of pipe walls. However, the
protective film that forms can be destroyed by high velocity or turbulent flow. Entrained
solid particles flowing at a high velocity will erode away any film that forms. More
importantly, corrosion rates increase with increased flow velocity, especially with low pH
levels. A study published P.V. Sheers considered the interaction of pH and flow velocity
on the corrosion rate. Figure 2.8 shows experimental data of what can happen with
increasing flow velocities for different pH values. For all pH values, as the velocity is
increased the corrosion rate also increases. The largest effect is seen at a pH value of 3
where the corrosion rate increased drastically as the flow velocity was increased$^{25-27}$. The
accepted cause for the increase in corrosion rate is an increased rate at which corrosive ions
are being delivered to the metal surface of the electrode.
Another important factor is material selection. Corrosion causes extensive damage to metal infrastructure in the oil and gas industry. The best way to reduce costs is to install appropriate materials to be able to handle the environmental conditions in the system. Each system faces different obstacles due to corrosion, so each system requires individual analysis to determine the best materials to use. Testing results have shown that the worst materials for corrosion prevention in CO$_2$ saturated systems are hard steels and cast iron. The better material choice are corrosion resistant alloys that have been coated with nickel, chromium, or other elements$^{7,16}$. But while these corrosion resistant alloys will typically be sufficient to protect against corrosive damages, they can be extremely expensive. Materials such as 22Cr, 25Cr, and titanium are examples of materials that offer impressive corrosion resistance, especially in CO$_2$ saturated systems. Chromium 13, on the other hand,
has been found to be one of the more cost effective alloys that can effectively reduce corrosion in a system containing CO₂ corrosion. Although carbon steel is highly susceptible to corrosion it is still the most widely used material in the oil and natural gas industry. Carbon steel is very low in cost in comparison to any available alloyed steels\textsuperscript{17}.

The other leading method for corrosion control is the use of chemical inhibitors. Chemical inhibitors are chosen specifically for the environmental conditions present in each system. The primary function of inhibitors is to adsorb onto the metal surface of an electrode to protect against corrosion\textsuperscript{12}. Ideally a chemical inhibitor is chosen for maximum protection for the minimum concentration. In choosing an inhibitor, experience is typically key which comes from years of field experience. The factors that affect the effectiveness of an inhibitor are temperature, solution chemistry, metal used, system pH, and flow conditions. Ultimately chemical inhibitors, when used appropriately, are an effective form of corrosion control\textsuperscript{11, 16}.

2.2 Concepts in Erosion

\textit{Definition of Erosion}

Solid particle erosion can be defined as a mechanical process of the material removal that is caused by the impacting of solid particles entrained in a fluid flow on the surface of a material. In the oil and gas industry, erosion primarily occurs due to the presence of sand particles entrained in liquid and gas flow. Figure 2.9 shows how high flow velocities increase sand erosion rates causing material on tubing, pipelines, and other infrastructure to sustain extensive damage. The graph shows that as the impact velocity is increased the weight loss, which corresponds to material loss, also increases. The increase
in weight loss becomes drastic at high impact velocities. The graph gives results for impact angles of 5, 30, 60, and 90 degrees. Because of expanded drilling sites to onshore and offshore sand beds and with the use of deeper wells, sand erosion is a serious concern for production and transport companies. Sand production also has a major impact on corrosion rates. Sand erosion can cause a rise in localized corrosion by creating pits or divots which increase the exposed surface area of the material. Erosion can also impact corrosion rates by removing the sometimes brittle protective films that are used in the oil and gas industry to protect the surface of the metal from corrosion.

Figure 2.9: Weight Loss for Steel Based on Impact Angle and Impact Velocity
Factors Affecting Erosion

The factors that affect sand erosion rates most fit into categories of sand characteristics, fluid flow characteristics, and characteristics of the material used. Sand characteristics that affect erosion rates are particle size, particle shape, density, particle impact velocity, and particle impact angle. For example, Figure 2.9 shows that impact angles of 30 and 60 degrees have the highest erosion rates. Dundar, Inal, and Stringer reported that the erosion rate will decrease as the particle size decreases to a point of zero particle erosion for particle sizes of 1-2 µm in ductile materials. And at high velocities, impacting sand particles can create depressions in the metal increasing erosion and erosion-corrosion rates. Particle impact velocity can be calculated by the simple power law shown in Equation 2.12, where ER is the erosion ratio. The erosion ratio is the ratio of the mass of the material lost divided by the mass of the weight of solid particles impacting the metal.

\[ ER = A \times V_p^n F(\alpha) \]  

Equation 2.12

A and n are constants specific to material properties; n falls in the range of 2-3 for ductile materials and up to 6 for brittle materials. \( V_p \) represents the impact velocity of the solid particles and depends heavily on flow conditions, system geometry, and solid particle properties, such as particle size and density. \( F(\alpha) \) depends on the impact angle and ranges between 0 and 1. Solid particle concentration generally does not change the erosion rate for concentrations low enough that the particles do not interact. The erosion ratio decreases at higher sand concentrations due to particles interfering with each other.

The fluid characteristics that affect sand erosion rates are fluid density, flow velocity, fluid viscosity, and system geometry. For example, erosion in smooth pipes is generally negligible for controlled flow velocities at most pipe sizes, but becomes a large
factor for geometries with numerous bends, reducers, or fittings. There is an increase of
two orders of magnitude for the rate of solid particle erosion in a gas-sand mixture as
compared to a liquid/sand mixture in an elbow geometry. There is an increase in erosion
rate for gas/sand mixtures because the transfer of momentum from the fluid to the solids is
less sufficient. The solid particles impact the material wall at a greater angle in gas than in
liquid and referring to Figure 2.9 this shows that the erosion rate will be greater. In
liquid/sand mixtures, especially as fluid density and viscosity increase, the solid particles
are more likely to follow streamlines.

Material characteristics that affect solid particle erosion include the material
hardness and the material ductility. Materials with a high harness value and also good
ductility are the more resistant to solid particle erosion. Brittle and low hardness materials
are most effected by particle erosion.

Erosion Prediction and Control

The importance of being able to model and predict solid particle erosion rates is
increasing as sand production in oil and gas wells continues to increase. Accurate erosion
modelling can help reduce costly repairs as well as reduce downtime in production and
transport of oil and gas. The Erosion/Corrosion Research Center at The University of
Tulsa, through the use of literature review, Computational Fluid Dynamics simulation data,
and experimental testing, has created a mechanistic model for the prediction of erosion
rates called the Sand Production Pipe Saver (SPPS). The model is designed to predict the
rate of penetration of carbon steel by sand particles for a variety of different field simulated
parameters. Some of the parameters considered in SPPS are pipeline geometry, fluid
density, sand production rates, CO₂ partial pressure, pH, and other environmental and system factors. Equation 2.13 includes the parameters that are considered in the equation are the Brinell hardness of the material, the impact velocity and angle, and the particle shape where f(θ) is a function of the impact angle as shown in Equation 2.14 \textsuperscript{34}. Additional factors are listed below:

\begin{equation}
ER = C (HB)^{-0.59} F_s f(\theta) V_p^n
\end{equation}

\begin{equation}
f(\theta) = 1.4234 \theta^5 - 6.328 \theta^4 + 10.9327 \theta^3 - 10.1068 \theta^2 + 5.3983 \theta
\end{equation}

- ER is the erosion ratio
- C is a constant value 2.17e-6
- n is a constant value of 2.41
- HB is the Brinell hardness of the material
- F_s is the sand shape factor (0.5 for OK #1 sand)

Once the SPPS model is used to approximate erosion rates, control methods can be used to reduce the predicted erosion rates. The three primary ways to control sand erosion are similar to those used to control corrosion and are the flow velocity, the sand rates, and material selected.

The erosion rate is directly affected by the particle impact velocity and therefore related to the fluid flow velocity. When controlling the flow velocity is not possible other parameters can be changed such as infrastructure design changes that result in reducing the
angle at which particles impact interior metal surfaces. This can only be accomplished when an erosion prediction model is available to highlight potential erosion complications.

The second method for reducing solid particle erosion is to control the amount of sand that is being produced. Currently, focus is centered on prediction of erosion caused by sand production. Emphasis is also being put on monitoring sand production and adjusting prediction models for an increase or decrease in sand production. To reduce sand production gravel packs and sand screens are used at the reservoir entrances downstream of the production well. By these methods, sand size and concentration can be effectively controlled and the particles producing the highest amount of erosion can be removed from the system before entering piping systems.

Another important way to control erosion rates is metal selection. Prediction models are assessed to determine the material type that would be best for each specific well and transport system. Materials are based on their ductility, hardness, mechanical strength, fatigue resistance, and their composition.

2.3 Concepts in Erosion-Corrosion

Importance of Erosion-Corrosion Research

It is necessary to differentiate between erosion, corrosion, and erosion-corrosion to be able to understand the interactions that are causing total metal loss. The complexity of erosion-corrosion occurs in an additive or potentially synergistic process between erosion and corrosion. In oil and gas production erosion enhanced corrosion is a complicated issue that leads to costly damages. According to the corrosion standard DIN 50900, erosion-
corrosion is defined as the “combination of the mechanical removal of a surface (erosion) and corrosion, where the corrosion is initiated by the destruction of protective layers as a result of erosion.” This definition only accounts for the mechanical damage caused by wear. Lotz and Heitz combined corrosion standard DIN 50900 with wear standard DIN 50320 to classify the types of mechanical/chemical attacks that occur in erosion corrosion. The claim is that in addition to thermal/chemical attack, there is also a mechanical/chemical attack. It can be classified as follows:

- Wear at the phase boundary
- Stress and fatigue corrosion and forms of mechanical/chemical/thermal attack in the material
- Transport-determined corrosion in the liquid medium

For a situation where there is pure wear occurring, whether the loss is occurring due to mechanical removal of the passive layer or removal of the base material itself would not greatly affect total erosion rates. But, under corrosive conditions, damage in the surface layer may cause significant differences in final weight loss. As solid particle erosion removes the protective surface layers exposing the base metal to attack by both the erosion component as well as the corrosion component, making erosion-corrosion more severe of an issue than either erosion or corrosion considered independently.

Ultimately, the greatest issue to be addressed is the accelerated corrosion rate of carbon steels or low alloy steels when there is removal of the protective oxide or chemical inhibitor layers. How accelerated the damage is determines the degree of the corrosion. For carbon steels and low alloy steels, protective layers are necessary to separate highly
corrosive conditions from coming into contact with the bare metal surface. This form of attack is important when the thickness of the oxide or inhibitor layer is a primary factor against corrosion development\(^{37}\).

As noted above, some materials are more susceptible to corrosion than others making material selection important in any production or transport system. Alloy hardness has been shown to be a factor in preventing or enabling erosion-corrosion to occur. Soft alloys are more susceptible to erosion-corrosion than steels with a higher hardness. But, the relative hardness properties of an alloy can be misleading because the hardening process can have an effect of its resistance to erosion-corrosion\(^{37}\).

ASTM proposes a “Standard Guide for Determining Synergism between Wear and Corrosion.” The guide takes into account the synergistic interaction that occurs in a system where both wear and corrosion exist to calculate the increased erosion-corrosion metal loss rate. Four types of tests are proposed to obtain values for the following:

- \( T \) – Total material loss
- \( \omega_0 \) – Pure erosion material loss
- \( C_o \) – Pure corrosion material loss
- \( C_w \) – Penetration rate in corrosion wear conditions

The total material loss (\( T \)) accounts for the pure wear and the pure corrosion along with the synergistic term. \( C_w \) tends to be higher than \( C_o \) because of mechanical wear interaction and can be measured by an electrochemical technique\(^{38}\).

Erosion-corrosion is further associated with production velocities. Because the erosion rate is highly dependent on flow velocities, so is the erosion-corrosion rate.
Through research conducted at the Erosion/Corrosion Research Center three erosion-corrosion regimes have been identified for a carbon steel elbow geometry. Tests were conducted in a closed flow loop that circulated a CO$_2$ and chloride saturated solution with iron carbonate scale forming conditions and the addition of sand. For low fluid velocities a protective layer of iron carbonate scale formed on the internal surface of the elbow. The entire exposed surface was covered and as a result metal loss rates were low. When the flow velocity was increased, scale formation was prevented and metal loss rates were much higher. Even more problematic was the development of pitting at the particle impingement points where no scale was able to form. Pitting increases the erosion and the corrosion rate. The third regime, the intermediate flow velocities, saw limited scale formation at the impingement points but did not see total scale removal. The flow velocities separating the three erosion-corrosion regimes were called the “threshold velocities$^{39}$.”

**Erosion-Corrosion Prediction and Control**

Like with the individual components of erosion and corrosion, combined erosion-corrosion rates can be affected by several different factors in the system. In the last decade rising costs of damages due to erosion-corrosion has led to an effort to develop predictive models for CO$_2$ erosion-corrosion rates. Several empirical laboratory models, empirical field models, and mechanistic models have been developed in this area taking into account many different parameters$^{5,40}$. Some of the parameters taken into account are the effect of CO$_2$ pressure, temperature, pH, and chloride content among others. The problem with these models though is their accuracy comes into question when sand is produced in the system.
One way of controlling erosion-corrosion rates is by engineering design. During initial design stages care should be taken to analyze potential risk related to the specific conditions for that system. Proper design can reduce the effects of erosion-corrosion. Appropriate selection of pipe size, shape of fittings, and geometry all have to be taken into account in the design process. One example of a design consideration is that by increasing the diameter of pipes and fittings and by reducing the number of bends reduces the points of impact.

Material selection is another parameter to be considered for proper erosion-corrosion resistance. While corrosion parameters have to be taken into account, other factors also have to be considered. When choosing a material the strength, ductility, machinability, and cost are all taken into consideration. The rate of metal loss due to erosion-corrosion is dependent on the electrochemical and the mechanical properties of a material. One way to get better corrosion and erosion-corrosion resistance is by alloying the steel. Chromium is an effective alloy in reducing corrosion rates and therefore reducing erosion-corrosion rates. Chromium also helps the steel respond better to the heat treatment process improving the materials hardenability and strength. Stainless steels offer the best protection against corrosion and erosion-corrosion due to their high chromium content but are more expensive than carbon steels\textsuperscript{41}.

A common practice in the oil and gas industry is the application of chemical inhibitors to control erosion-corrosion rates in highly corrosive environments. Successful erosion-corrosion control with inhibitor use is dependent on using the most cost effective corrosion inhibitors to optimize performance. Typically a continuous injection of an inhibitor into the corrosive environment is used to reduce erosion-corrosion rates. Ideally
an inhibitor will provide a protective film on the metal surface and have the ability to absorb the sand in the inhibited solution, slowing sand particles down and reducing erosion rates\textsuperscript{41}. When sand is present in the system it can reduce the rate of absorption of the inhibitor onto the surface of the pipe walls. Therefore, systems with high velocity sand can retard the effectiveness of inhibitor. Ultimately, for an inhibitor to be effective it must be able to reduce the erosion-corrosion rates for a given set of system conditions to be able to increase the length oil and gas infrastructure.

Another popular method for the reduction or prevention of corrosion is cathodic protection. Cathodic protection is used by forcing metal to act as a cathode. This is done by using an impressed current or by anode attached externally to the pipe wall. It reduces the anodic corrosion reaction by creating an electric field at the external surface of the metal forcing the net flow of current into the metal\textsuperscript{6, 16}.

The appropriate erosion-corrosion control method comes from first using a prediction model to analyze the severity of erosion-corrosion risk for each system. Studies were completed at the Erosion/Corrosion Research Center on erosion-corrosion behavior in a carbon steel elbow geometry\textsuperscript{42}. The study considered a CO\textsubscript{2} saturated chloride solution with the addition of sand in closed flow loop system. Tests were conducted in thirteen different groups of environmental conditions in an effort to simulate a variety of field conditions. Temperature, CO\textsubscript{2} pressure, pH, and sand concentration were some of the parameters considered. The results from these test sets were used to create a semi-empirical model for the prediction of erosion-corrosion rates and the threshold velocity for an elbow pipe geometry. The goal of the testing was to quantify a relationship for the erosion-corrosion resistance of a material under specific environmental conditions. The
erosion-corrosion resistance (ECR) is the highest erosivity that a system can tolerate without reducing effects of protective layers of iron carbonate scale or inhibitor. The following three behaviors were identified for determining ECR: 1- low erosivity, which allows scale formation with little to no penetration; 2- intermediate erosivity, which results in high penetration rates and pitting as a result of partial scale removal; 3- high erosivity, uniform corrosion results from high scale penetration rates that cause complete scale removal\textsuperscript{43, 44}. With these results a threshold velocity can be determined since there is a direct relationship between impingement velocity and erosion rate. The goal in any system is to achieve low erosion rates.

2.4 Corrosion and Erosion-Corrosion Inhibition

\textit{Chemical Inhibitor Application}

Chemical inhibitors are a widely used corrosion prevention method in the oil and gas industry. A chemical inhibitor is defined as a soluble substance that can be injected into a corrosive system without effecting the reaction to effectively reduce the corrosion rate. Figure 2.10 shows the direct costs of corrosion prevention in the U.S. for oil and gas production companies. Corrosion reducing chemical treatments make up the largest portion of costs at nearly 80\% \textsuperscript{44}. 
Chemical inhibitor effectiveness in protecting the metal surfaces in corrosion environments is looked at in the form of its inhibitor efficiency. The inhibitor efficiency is the percent reduction in corrosion rate when inhibitor is injected compared to a system where no inhibitor exists\(^45\). An ideal inhibitor efficiency is at least 80\%. The inhibitor efficiency is calculated with the following equation:

\[
E = \frac{R_0 - R_i}{R_0} \times 100\% 
\]

\[2.15\]

- \(E\) is the inhibitor efficiency (\%)
- \(R_0\) is the uninhibited corrosion rate
- \(R_i\) is the inhibited corrosion rate
Inhibitors are applied to production systems in one of two methods. The first is continuous treatment. Continuous treatment of the inhibitor necessitates a constant injection rate of the inhibitor applied directly into the liquid product being transported. This type of system has several requirements:

- Must have proper phase behavior
- Must be easy to handle
- Must have a low vapor pressure
- Must be non-scale forming
- Must be able to be dehydrated
- Must have sufficient sulfur solubility

in order to be considered successful. Inhibitor types most suitable for continuous injection are water soluble, water dispersible, or oil soluble\(^5\).

The second inhibitor injection method is batch treatment. In batch treatment large quantities of inhibitors are applied to the annulus or into the well tubing. This also requires that the well be shut down until the inhibitor, trapped in the production fluid, can reach the bottom of the well, displacing the fluid from the production tubing\(^4\). Batch treatment is primarily used in areas that create difficulty in injecting downhole to protect production tubing. When the chemical inhibitor is injected into the downhole tubing, the inhibitor absorbs to the exposed surfaces of equipment to form a film that protects the surface of the well from corrosion attacks. It is important that chemical inhibitors are delivered to the correct location at the right times to ensure maximum corrosion and erosion-corrosion protection. The rate at which batch treatments are injected depends on the flow velocity,
environmental conditions, and the chemistry of the production fluid. If the flow velocity is too high, the inhibitor film on the metal surface could get stripped off by mechanical shear stresses applied to the protected metal by the flow.

**Types of Inhibitors**

There are three divisions of inhibitors: cathodic, anodic, and mixed. All three divisions have the same general ingredients for use in the oil and gas industry. A typical inhibitor will contain: carboxylic acids, active inhibitor intermediates, demulsifier and/or surfactant in aromatic solvents, and alcohols. The inhibitor intermediate is the active component attributed to corrosion protection. Compounds containing nitrogen are present in most inhibitor intermediates in oil and gas production. Nitrogen atoms contain a free pair of elections which can be adsorbed onto the metal surface as well as their hydrocarbon chain make these compounds excellent inhibitor types. Different inhibitor intermediates occasionally can be manufactured from the same raw materials by varying reaction conditions. Raw materials are typically low cost materials with impurities and the resulting inhibitor intermediates are not high purity products.

Active inhibitor intermediates available on the market include: Imidazoline, amide, amine, and amidoamide. They are introduced into commercial products based on consumer performance needs which varies based on the process in which the chemical is produced. Amine base inhibitors are not useful in high temperature systems exceeding 300° F. Imidazoline has a high viscosity as compared to amide, which is a solid wax making is easier for formulating corrosion products. Because of this, imidazoline used in
products is a mixture of imidazoline and amide with ratios varying from 1:1 to 9:1 depending on consumer needs and manufacturing process\textsuperscript{47}.

The three divisions of inhibitors are divided based on the chemical reaction that occurs to slow down the corrosion process. Environmental conditions influence which inhibitor type is used in a specific system. Examples of cathodic inhibitors include phosphates, polyphosphates, and zinc salts. Cathodic inhibitors are used to change the cathodic reaction potential. These type of inhibitors are generally less effective than the anodic and mixed categories. When cathodic inhibitor is injected into corrosive environments, it attacks cathodic sites. The sites of cathodic reaction are eliminated thus reducing the corrosion rate. Figure 2.11 depicts the cathodic inhibitor reaction with and without the addition of inhibitor\textsuperscript{48}.

![Figure 2.11: Cathodic Inhibitor Polarization Curve With and Without Inhibitor\textsuperscript{48}](image-url)
Anodic inhibitors are most aggressive of the three categories of inhibitors. Examples of anodic inhibitors can include: nitrite, ferricyanide, silicates, and orthophosphate. Anodic chemical inhibitors are injected into a corrosive system to increase the anodic reaction and, which in turn, decreases the overall corrosion rate. When the inhibitor is inserted into the corrosive system it forms a shallow layer on the surface of the metal to increase the anode potential. The anodic polarization curve for an anodic inhibitor showing an increase in potential when inhibitor is added is shown in Figure 2.12.

![Figure 2.12: Anodic Inhibitor Polarization Curve With and Without Inhibitor](image)

Figure 2.12: Anodic Inhibitor Polarization Curve With and Without Inhibitor

The category of mixed inhibitors accounts for most of the organic inhibitors used in the oil and gas industry. Mixed type of inhibitors have can influence either the anodic or the cathodic reactions in a system in order to reduce the corrosion rate. Figure 2.13 shows the polarization curve for the mixed inhibitor. It can be seen from the graph that the
mixed category of inhibitor acts in the same way as either the anodic or the cathodic curves, ultimately causing a reduction in the total corrosion rate.  

![Figure 2.13: Mixed Inhibitor Polarization Curve With and Without Inhibitor](image)

**Figure 2.13: Mixed Inhibitor Polarization Curve With and Without Inhibitor**

*Inhibitor Effectiveness in Erosion-Corrosion Environment*

Extensive studies have considered different inhibitors and their effectiveness. These studies have resulted in several inhibitor prediction models, like the Sand Production Pipe Saver (SPPS) program created by the University of Tulsa, but there is still limited prediction capabilities for inhibited erosion-corrosion rates. Erosion-corrosion is a complicated problem to predict and the physical and chemical interactions with inhibitors make this prediction more complicated. Currently, the best prediction method is to consider each condition (environmental, materials, and others) for each system and try to pair the best inhibition techniques for that particular system. The effectiveness of an
injected inhibitor has been found to decrease when sand is also present in the system\textsuperscript{5, 49, and 50}. The key factor causing the erosion-corrosion rates to decrease and to what severity are still left to be defined. Because inhibitor use in the oil and gas industry is so important, improving inhibitor efficiency to account for all conditions, including sand, is essential to reducing corrosion and erosion-corrosion damage.
CHAPTER 3
EXPERIMENTAL FACILITY AND PROCEDURES

3.1 Research Approach

As described in chapter 1, there are three objectives for this research. These objectives include: i) validating test Loop #3 and test Loop #4 (both called the 3 cell E/C test loop) for accuracy and repeatability, ii) validate previous erosion, corrosion, erosion-corrosion results both with and without inhibitor, and iii) to explore inhibitor effectiveness for systems with sand and oil environments.

The research objectives will be accomplished using three measurement techniques: weight loss (WL), electrical resistance (ER), and linear polarization resistance (LPR). The use of different testing techniques in the three cell configuration allows test data to be validated by comparison of data (for example erosion, corrosion, or erosion-corrosion rates) that are obtained by different techniques from the same test at the same time. LPR and ER measurements give real time data while the weight loss measurements show the difference between before and after test measurements. Testing methods were used to analyze effects of temperature, pH, sand concentration, and inhibitor concentration on erosion, corrosion, and erosion-corrosion rates of AISI 1018 carbon steel and SAE 316 stainless steel. The methods used are described in further detail in this chapter.

Initially, tests were conducted to establish a baseline model for comparison, as well as to test and validate the newly-designed 3-cell E/C test loop. The baseline tests included:
pure erosion, pure corrosion, and erosion-corrosion. The use of different testing facilities can result in dissimilarities in the data that is produced. For this reason a baseline set of data had to be established for the 3-cell E/C test loop. All tests completed had the same conditions for pH, temperature, CO$_2$ or N$_2$ pressure, flow velocity, and test duration. Two major parameters were altered during baseline testing. These included the weight percent of chloride (3 and 18 weight percent) and sand weight percent (1.0 and 0.3 weight percent). All tests were run under non-scale forming conditions. Once a baseline was established, tests from previous studies were repeated to validate previous research and compare results to baseline testing for the 3-cell E/C test loop. Inhibitor was injected to monitor effects in systems measuring erosion, corrosion, and erosion-corrosion. Two different inhibitor injection procedures were used. The first procedure was to operate the flow loop under corrosive conditions until a stabilized corrosion rate was reached (as determined by baseline results), then the inhibitor was injected to measure the impact on the corrosion rate in a system already exposed to corrosion damage. The second procedure involved adding inhibitor to the test solution at the beginning of a test. In the latter case, the inhibitor forms a protective layer on the specimen surface before corrosive damage can occur. Sand was also injected in a similar fashion. The first procedure of injection was to wait 1-2 hours after the system was in operation to allow a layer of inhibitor to form on the metal’s surface. Sand was added through the feeder at the top of the tank and flowed through the entire system. The second procedure was to introduce the sand immediately after the inhibitor was injected into the system. Numerous tests were conducted under a variety of conditions in an effort to simulate actual encountered field conditions.
3.2 Measurement Techniques

Erosion, corrosion, and erosion-corrosion results were measured using LPR, WL, and ER methods. These three methods are among those widely accepted in the oil and gas industry as valuable measurement techniques. In industry, a corrosion risk assessment is completed to assess the need for corrective action in a facility either before it begins production or while the facility is in operation. For high corrosion risks a mitigation strategy is employed based on the system conditions and location of the corrosion problem in order to prevent or reduce corrosion damage from occurring. Reduction in corrosion means improved safety, which is especially important for older infrastructure that have a higher failure risk. It also means a reduction in operating costs such as maintenance, inspections, and shutdowns, as well as reduced risk of having a negative environmental impact\textsuperscript{49, 50}.

Linear Polarization Resistance (LPR) is a common corrosion measurement technique in both research and industrial applications. It is a direct measurement method and can be installed in an area to monitor the active corrosion rate. However, using LPR also has some disadvantages, such as: corrosion rate trends rather than absolute values, the requirement of a conductive media with a continuous aqueous phase, results are reliant on the quality of the test electrodes, and LPR fails to give adequate results describing localized corrosion\textsuperscript{49}.

The LPR test probes used herein were constructed at the Erosion/Corrosion Research Center. Figure 3.1 shows a detailed schematic of the testing probe used in the 3-cell E/C test loop. The LPR probe has a working electrode made of AISI 1018 carbon steel
and a reference electrode which is made of SAE 316 stainless steel; the 316 stainless steel
3-cell E/C test loop serves as the counter or grounding electrode. The working and
reference electrodes have outside diameters of 1.25 and 0.065 inches and are separated by
a non-conductive epoxy layer that is 0.20 inches in diameter. The assembly of the reference
and working electrode are mounted in heat shrink insulation. The impingement jet has an
inner diameter of 0.256 inches and is aligned to impact the center of the face of the
working/reference electrodes. To ensure only the desired surface area is impacted, an
epoxy paint is coated on the exterior of the carbon steel that could be exposed to the
corrosive system. The electrochemical probe is enclosed in a 1.5 inch plugged-tee fitting,
keeping the probe submerged and at equilibrium with the system pressure and temperature
(Figure 3.8). The electrochemical probe is connected to a Gamry Instruments potentiostat
for taking LPR readings.

![Figure 3.1: Expanded View of Electrochemical (LPR) Probe](image)

Running a test using LPR first starts with the test inputs setup page. Key parameters
to include in the software setup include: the surface area of the test specimen, the voltage
range, the sample period, the equivalent weight, the specimen density, the test length, the repeat time, and the anodic and cathodic Tafel beta constants. Figure 3.2 shows an example input screen where all test parameters are included. The scan rate determines the speed of the potential sweep during its data acquisition period. Scan rates higher than 100 mV/second yield unreliable data. This occurs because the scanning and the filter processes come into competition with each other. The total number of points that the test will produce can be estimated by dividing the scan time by the sample period\textsuperscript{51, 53}. Table 3.1 gives a summary of the input values used specifically for this research. The surface areas were the same for the LPR, WL, and ER test specimens.

Figure 3.2: Gamry Instruments Echem Analysis Sample Input Screen\textsuperscript{22}
Table 3.1: LPR Input Parameters

<table>
<thead>
<tr>
<th>LPR Input Parameters</th>
<th>±0.01 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial and Final E</td>
<td>±0.01 V</td>
</tr>
<tr>
<td>Scan Rate</td>
<td>0.2 mV/s</td>
</tr>
<tr>
<td>Sample Period</td>
<td>0.2</td>
</tr>
<tr>
<td>Sample Area</td>
<td>7.92 cm²</td>
</tr>
<tr>
<td>Density</td>
<td>7.87 gr/cm³</td>
</tr>
<tr>
<td>Equivalent Weight</td>
<td>27.92</td>
</tr>
<tr>
<td>Repeat Time</td>
<td>15 min</td>
</tr>
<tr>
<td>Tafel Constants</td>
<td>0.12 V/Dec.</td>
</tr>
</tbody>
</table>

Since the corrosion current ($I_{corr}$) cannot be measured directly, the LPR method can be used to estimate $I_{corr}$ from a Tafel plot of the current versus the voltage data. The current can be measured as a small potential of 10 mV is applied across the LPR probe. From this, a curve of the log current versus the potential can be plotted. Measured data can be fitted to a theoretical model. Models used typically assumes that the rates of both the anodic and cathodic processes are controlled by the electron transfer at the metal surface. An electrochemical reaction under kinetic control obeys the Tafel equation shown by Equation 3.1. This equation gives the behavior of an isolated reaction:

$$I = I_0 \exp \left( \frac{2.303(E-E_0)}{B} \right)$$  \hspace{1cm} 3.1$$

where,

- $I$ is the current resulting from the reaction;
- $I_0$ is a reaction dependent constant called the exchange current;
- $E$ is the electrode potential;
- $E_0$ is the equilibrium potential
B is the Tafel Constant (refer to Eq. 2.8).

In a corrosion system there are two opposing reactions, the anodic reaction and the cathodic reaction. For a full understanding of the chemical reactions taking place, the Tafel equations for both the anodic and cathodic reactions are needed. The total reaction equation creates the Butler-Volmer equation and is shown by equation 3.2:

\[
I = I_{corr} \exp \left( \frac{2.303(E-E_{corr})}{\beta_a} \right) \exp \left( -\frac{2.303(E-E_{corr})}{\beta_c} \right) \quad 3.2
\]

- \( I \) is the measured cell current (amps)
- \( I_{corr} \) is the corrosion current (amps)
- \( E \) is the electrode potential (volts)
- \( E_{corr} \) is the corrosion potential (volts)
- \( \beta_a \) is the anodic Tafel Beta constant (volts/decade)
- \( \beta_c \) is the cathodic Tafel Beta constant (volts/decade)

The Butler-Volmer Equation can be simplified by restricting the potential to a value very near to that of the \( E_{corr} \) value. When close to \( E_{corr} \), the current versus voltage curve becomes a straight line. The slope of this line gives a value for the polarization resistance, \( R_p \) (Figure 2.3). This value can be applied to Equations 2.7-2.9 to achieve the corrosion current. Manipulating equation 2.9, the equation for calculating the corrosion rate at each collected \( R_p \) value is shown in Equation 3.3:

\[
CR \ (mm/yr) = \frac{3272 \times EW \times I_{corr}}{A \times \rho} \quad 3.3
\]
where

- CR is the corrosion rate (mm/year)
- EW is the equivalent weight (grams)
- Icorr is the current density (μA/cm²)
- A is the area (cm²)
- ρ is the density (grams/cm³)

Equation 3.3 has units of mm/year. The industry unit for measuring corrosion rate is mils per year (mpy). Converting, Equation 3.4 gives the corrosion rate in mpy.

\[
CR \text{ (mpy)} = \frac{CR_{\text{mm/yr}} \times 1000}{25.4} \tag{3.4}
\]

LPR measurements were used herein to characterize corrosion effects for different environmental conditions as well as to characterize inhibitor effectiveness in the presence of sand. Since LPR can only be used to measure the corrosion rate, the weight loss method be used along with LPR to get a more complete picture of the erosion and the erosion-corrosion effects caused by flow velocity and solid particle. To use a WL method the test specimen is to be properly prepared and weighed prior to and after each test. Proper preparation of the test specimen is key to achieving accurate measurement results. Specimen preparation is described in Appendix A. If the total time duration of the test is known, then the weight loss measurement can be used to calculate the erosion rate or erosion-corrosion rate in mpy and mm/year. Equation 3.5 is used to calculate the penetration rate of the steel in mpy.
\[
\text{mpy} = \frac{534\times WL}{\rho \times A \times t}
\]  \hspace{1cm} 3.5

where

- WL is the measured weight loss in milligrams
- A is the surface area in \(\text{in}^2\)
- T is the time duration in hours
- \(\rho\) is the density in grams/cm\(^3\)

Conversion to mm/year is the same as shown in Equation 3.4.

One technique for direct thickness loss measurement is electrical resistance. ER probes measure the change in electrical resistance across a metal surface area in reference to the probe’s reference plate and then relates this value to a change in cross-sectional area of the metal surface. Equation 3.6 shows the process for measuring the electrical resistance. ER probes have a much higher sensitivity than LPR probes but a typical ER probe has a surface metal thickness ranging from 10 \(\mu\text{m}\) to 120 \(\mu\text{m}\) which translates to a short probe life. Advantages of ER probes include: instantaneous measurement of thickness loss, can be used in any type of environment, can be used to monitor erosion, corrosion, and erosion-corrosion depending on the metal type used in the probe, and can be used for taking either intermittent or continuous readings. The ER probes used in this study were 1.25 inch, large flush probes obtained from Metal Samples (Munford, Alabama, U.S.). Figure 3.3 shows a diagram of Metal Samples retractable probe that was used and 3.4 shows a picture of the impacted surface of the probe. Average probe life for each probe was how long it took to remove 20 \(\mu\text{m}\); the number of tests depended on the type of test
conducted. Equations 3.7 can be used to calculate the metal loss in mils. Equation 3.8 is used to obtain a corrosion rate over the span of the test:\textsuperscript{54}

\[ R = r \frac{L}{A} \]  

3.6

where

- R is the resistance
- \( r \) is the specific resistance
- L is the element length
- A is the cross sectional length (from View A-A)

Figure 3.3: Schematic of the Metal Samples Probe\textsuperscript{56}
Figure 3.4: Picture of the Impingement Surface of the ER Probe

\[ M = \frac{S \times P}{1000} \]  

Where

- \( M \) is the total metal loss
- \( S \) is proportional to the element’s metal loss
- \( P \) is the probe life

\[ C = \frac{P \times 365 \times (S_2 - S_1)}{\Delta T \times 1000} \]  

- \( C \) is the Corrosion rate
- \( \Delta T \) is the time lapse between points \( S_1 \) and \( S_2 \)
Key parameters in selecting the proper type of ER probe to use include: element thickness, geometry, and predicted corrosion rate. Selecting the proper probe can extend its total life and therefore give the best results in corrosion monitoring.

3.3 Testing Facility

*Single phase Flow Loop (Loop #3)*

Two 3-Cell E/C test loops (Loop #3 and Loop #4) were built in order to conduct single phase erosion, corrosion, and erosion-corrosion experiments. A complete description of testing procedures is provided in Appendix A. The loops were used to circulate a CO$_2$ saturated brine solution to the three, in-line impingement test cells. Due to need for resistance to high temperatures, corrosion, and pitting effects, both loops were constructed of 316 stainless steel. The loop can operate at maximum operating conditions of temperature of 200 °F, (93 °C), pressure of 150 psig (1.13 MPa), and a nozzle velocity of 32.6 fps for a nozzle diameter of 0.236 inches. Figure 3.5 shows a schematic of the two flow loops used. Both loops have sand feeders located at the top of the tank and an inhibitor application valve located in the bypass section of the loop. Loop #3 is designed for the brine solution only. Loop #4 has an additional valve on the tank, as seen in Figure 3.5, to allow for an oil/brine mixture. A photograph of Loop #3 is shown in Figure 3.6. The major components of Loop #3 and Loop #4 are identical and include: three cell test section, sand injector, tank, inhibitor injection site, and circulation pump. An expanded view of the 3 in-line impingement test cells is shown in Figure 3.7. The test section is designed to hold three 1.25” LPR, ER, and/or WL probes during a single test. Figure 3.8 shows a schematic
of one of the three test cells holding an LPR probe. There is 0.5 inches between the impingement nozzle and the impact surface of the LPR probe. Tests using LPR and WL measurement techniques were run for 24 hours. Tests using ER probes lasted 9 hours due to increased probe sensitivity; the test results were scaled to compare with LPR and WL measurements.

Figure 3.5: Schematic of 3-Cell E/C Test Loop
Figure 3.6: Photo of Test Loop #4

Figure 3.7: Expanded View of the 3-Cell E/C Test Section\textsuperscript{5}
Test Preparation and System Parameters

Test preparation begins with de-aerating the test solution. The purpose of de-aeration is to remove the dissolved oxygen from the test solution. A dissolved oxygen of less than 10 ppb is required for a valid test. Test solution is circulated through the system using a Wanner Engineering D-10X Hydra-Cell diaphragm pump. The pump has a maximum flow capacity of 7.8 GPM. Referring to Figure 3.5, the test solution flows from the tank to the pump and then exits and impacts the 3-cell test section before returning to the tank. The solution is held at a constant temperature and pressure throughout the test. Temperature is monitored and controlled with a band heater which is mounted to the exterior of the stainless steel tank along with a temperature gauge. The solution pH can be monitored in the bypass section of the system at the tank output. The pH probe is calibrated then used to measure the system pH before and after each test. Based on prior research
conducted by Hassani, the output value from the pH meter needs to be corrected for high chloride concentrations. Figure 3.9 shows the correction factor that Hassani obtained\(^5\). In order to acquire the desired pH, hydrochloric acid or sodium hydroxide was injected into the bypass of the system until the appropriate pH is reached. Sand concentration can be tested throughout the test and additional sand can be added as needed through the sand feeder located at the top of the tank. Concentration rates are measured at the discharge of the pump. To inject sand into the tank, the feeder must first be de-aerated, then pressurized to about 25 psig; the CO\(_2\) injection pressure must be high enough to overcome the system pressure. The sand circulates from the tank, through the pump, and then impacts the test section shown in Figure 3.7 before returning to the tank.

\[ Y = 0.017X + 3E-5X^3 \]
\[ R^2 = 0.995 \]

Figure 3.9: pH Correction Factor vs NaCl wt% Concentration\(^5\)
The first research requirement was to complete baseline testing on both Loop #3 and Loop #4. This was done in order to i) validate that the new 3-cell system configuration is capable of measuring identical results in all three cells and ii) ensure that Loop #3 and Loop #4 were truly identical and produced the same results. A baseline set of erosion, corrosion, and erosion-corrosion results were established at non-scale forming conditions before studying inhibitor effects. An inhibitor study was completed to identify the effect that different inhibitor concentrations can have on corrosion rates both with and without sand. Table 3.2 gives composition values for the test solution preparation for baseline tests. The additives listed in the table were added in a five gallon container of distilled water before being pulled into the system tank. Table 3.3 shows testing parameters for Loop #3 and Loop #4. Baseline results did not include the addition of inhibitor in the test solution.

Table 3.2: Composition of Test Solution

<table>
<thead>
<tr>
<th>Additive</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>3% and 18% by weight</td>
</tr>
<tr>
<td>NaHCO3</td>
<td>200 ppm</td>
</tr>
<tr>
<td>CaCl2</td>
<td>50 ppm</td>
</tr>
</tbody>
</table>
Table 3.3: Testing Parameters for Single Phase Flow

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Non-scale Forming Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>135 °F (57.2 °C)</td>
</tr>
<tr>
<td>pH</td>
<td>4.8</td>
</tr>
<tr>
<td>Superficial Gas Velocity</td>
<td>32.6 fps</td>
</tr>
<tr>
<td>Pressure</td>
<td>20 psig $\text{CO}_2$</td>
</tr>
<tr>
<td>NaCl Concentration</td>
<td>3.0 and 18 wt%</td>
</tr>
<tr>
<td>Material</td>
<td>AISI 1018, 1010, and X65 Carbon Steel</td>
</tr>
<tr>
<td>Available Measurement Tech.</td>
<td>LPR, EIS, PDYN, WL, ER, and 3D profilometry</td>
</tr>
<tr>
<td>Sand Size (µm)</td>
<td>150 µm</td>
</tr>
<tr>
<td>Sand Rate</td>
<td>Low Sand Concentration (&lt;0.5 wt%)</td>
</tr>
<tr>
<td>Inhibitor Concentration</td>
<td>Range between 0-200 ppm</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>Less than 10 ppb</td>
</tr>
<tr>
<td>Geometry</td>
<td>3 Plugged Tee test cells in series (E,C,E-C)</td>
</tr>
</tbody>
</table>

Water/Oil Flow Loop (Loop #4)

The purpose of having two identical loops is to keep one loop free of oil contamination. Once oil is introduced into a system, it can be very difficult to remove. A thorough cleaning procedure is necessary to remove any presence of oil and inhibitor. In order to accomplish this, a non-foaming commercial grade detergent is used. The activation temperature of the detergent is 130 °F, therefore hot water and soap are mixed and circulated through the test loop with use of the band heater. The water/soap mixture
is circulated through the system as needed until all oil and inhibitor is removed. Clean hot water is then used to remove the soap. Clean tap water is flushed through the system to remove any additional contaminants. The cleanliness of the system can be tested by collecting a sample from the running system in order to check its clarity.

Referring to Figure 3.5, testing Loop #4 has an additional valve that allows for an oil/water mixture. Testing conducted in Loop #4 used the same conditions and the same solution as those listed in Tables 3.2 and 3.3 but with the addition of oil at 20% and 40% water cuts. Oil has the potential to reduce corrosion rates, but it does not reduce the corrosion rates to an acceptable level. Therefore, the addition of chemical inhibitors is still necessary to reduce corrosion rates to a safe level. The inhibitor used herein was a water soluble, oil dispersible imidazoline-based solution resulting in higher corrosion rates than with a non-oil solution. Testing was used in order to model inhibitor effectiveness in an oil/water mixture. A complete test matrix showing variable parameters is in Table 3.4.
### Table 3.4: Test Conditions

<table>
<thead>
<tr>
<th>Test Type</th>
<th>NaCl (wt%)</th>
<th>Inhibitor (ppm)</th>
<th>Water Cut (wt%)</th>
<th>Sand Conc.</th>
<th>Test T (hr)</th>
<th>Probe (C1)</th>
<th>Probe (C2)</th>
<th>Probe (C3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ER</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CR</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>E-C</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ER w/ inh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CR w/ inh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-C w/ inh</td>
<td></td>
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<tr>
<td>ER w/ oil</td>
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<tr>
<td>CR w/ oil</td>
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<td>E-C w/ oil</td>
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<td>ER w/ oil &amp; inh</td>
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<tr>
<td>CR w/ oil &amp; inh</td>
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<td>E-C w/ oil &amp; inh</td>
<td></td>
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</tr>
</tbody>
</table>
CHAPTER 4
EROSION-CORROSION INHIBITION MODEL

4.1 Modeling Inhibitor Performance

It is widely accepted that the basic mechanism for inhibitor protection is adsorption of imidazoline-based inhibitors to the surface of a metal, thereby blocking electrochemical action at the metal surface. The adsorption depends on the adsorption/desorption equilibrium of a particular inhibitor for a particular substrate, and the degree of chemical and or physical absorptivity of inhibitor to surface atoms on a particular metal surface depends on temperature, test solution composition, and the electrochemical potential at the metal/solution interface.

Many different inhibitor adsorption isotherms have been developed for studying predicting the mechanism of corrosion inhibition. Such methods include the Flory-Huggins, Frumkin, Temkin, Langmuir, Bockris-Swinkels, Hill-de Boer, Parsons, Damaskin-Parsons, and Kastening-Holleck models. These isotherms use the same general form as shown by Equation 4.1. Inhibitor prediction models have been widely studied for predicting the worst case scenario for corrosion effects in oil and gas production and transportation systems. The use of these models though is limited when complex effects such as H₂S and CO₂, protective scale formation, and water entrainment exist. Work completed by Nesic et al. provides a model for predicting the critical velocity for entraining free water by flowing oil phase as well as the effect of the key variables. However, this model does not account for the complexity of the interaction of oil and inhibitor.
\[ K_a C_{\text{inh}} = G(\theta, n) e^{-f\theta} \]  

4.1

where,

- \( G(\theta, n) \) is the configurational factor
- \( C_{\text{inh}} \) is the inhibitor concentration
- \( \Theta \) is the fraction of surface coverage by inhibitor
- \( f \) accounts for the interaction between adsorbed particles
- \( n \) ratio of the inhibitor molecule coverage to the water molecule

The results presented in this thesis expand on a recently developed model from Hassani for understanding the effects of inhibitor effectiveness in the presence of an oil/water mixture, as well as with the presence of sand particles. Hassani found that the Frumkin isotherm most accurately modeled inhibitor effectiveness for systems with oil/water mixture and sand. Figures 4.1 and 4.2 show an example of the Frumkin and Temkin isotherm results and show why the Frumkin isotherm was chosen for this study\(^5\).

Inhibitor adsorption isotherms are defined by the interaction of inhibitor particles with the metal surface. The Frumkin isotherm is can be used for coverage prediction when a mutual interaction of the inhibitor molecules is important\(^5\). A Frumkin isotherm can be used for developing a relationship between inhibitor concentration and corrosion rate. The Frumkin isotherm is shown in Equation 4.2
Figure 4.1: Frumkin Isotherm Fitted to WL Corrosion and Erosion-Corrosion Data.

Test conditions: pH=5.0, T=93°C, 100% water cut, U=9.4 m/s, 0.5 wt% sand

Figure 4.2: Temkin Isotherm Fitted to WL Corrosion and Erosion-Corrosion Data.

Test conditions: pH=5.0, T=93°C, 100% water cut, U=9.4 m/s, 0.5 wt% sand
where $K_{ad/d}$ is the adsorption/desorption constant. When inhibitor molecules that are absorbed on the surface of the impacted metal attract each other a negative value for “f” is assumed. A positive value is used when the absorbed molecule repel each other. The value for the surface coverage can be calculated by applying equation 4.3 to the corrosion rates measured at different inhibitor concentrations.

$$\theta = 1 - \frac{CR_{\theta}}{CR_{\theta=0}}$$ \hspace{1cm} 4.3

where,

- $CR_{\theta}$ is the inhibited corrosion rate
- $CR_{\theta=0}$ is the uninhibited corrosion rate

Two types of absorption interactions between organic inhibitor and a metal surface are physical adsorption and chemisorption. The Gibbs free energy can be used to determine the type of adsorption. Equation 4.4 shows the Gibbs free energy equation

$$K_{ad/d} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^o}{RT}\right)$$ \hspace{1cm} 4.4

where $\Delta G_{ads}^o$ is Gibbs free energy, $R$ is the universal gas constant, and $T$ is the temperature. Values of $\Delta G_{ads}^o$ between 0 and -20 kJmol$^{-1}$ specify physical type of adsorption (physisorption). Values in this range have a low activation energy. Values of $\Delta G_{ads}^o$ between -21 and -40 kJmol$^{-1}$ result in a combination of both physisorption and chemisorption. $\Delta G_{ads}^o$ values of -40 kJmol-1 or less designates a chemisorption process which involves a transfer in charge from the inhibitor molecules to the metal surface.
Conditions tested here resulted in $\Delta G^0_{\text{ads}}$ values ranging from -2.254 to -12.135. This indicates physisorption and that the adsorption of the inhibitor onto the metal surface is a spontaneous process. Adsorption of nitrogen atoms onto the metal’s metallic surface block the active sites, generating a physical barrier to restrict the corrosion process\textsuperscript{5, 57}.

Frumkin isotherms were then used to predict the inhibited corrosion rates as a function of inhibitor concentration for different environmental conditions. The isotherm is used to calculate the amount of metal coverage that is achieved by the inhibitor. This value represents how well the inhibitor works to protect the target metal from corrosion damage. These values can be applied to the Erosion/Corrosion Research Center model for the prediction of inhibited corrosion, SPPS: CO\textsubscript{2}. Applying the isotherm to the SPPS: CO\textsubscript{2} model resulted in good correlation between the experimental data and the program prediction.

4.2 Inhibited Erosion-Corrosion Prediction

Erosion-Corrosion takes into for different effects: i) the pure erosion ii) the pure corrosion iii) the erosion affected by corrosion, as well as, iv) the corrosion affected by erosion. This study includes inhibited erosion-corrosion prediction for conditions where there is no iron carbonate scale formation. Erosion-Corrosion rates, especially at higher flow velocities, tend to be higher than the adding of the pure erosion and the pure erosion rates. Dave et al. found that at higher flow velocities there is no buildup of corrosion products and therefore a higher corrosion rate\textsuperscript{58}. This occurs for both systems with and without sand, but when sand is present, corrosion rates are accelerated. This happens because the sand causes an increase in surface roughness and therefore, an increase in the
total surface area. Dave et al. also found that corrosion can accelerate the erosion rate. Corrosion can cause pitting and other surface irregularities which create a desirable surface for increased erosive action\textsuperscript{58}.

Inhibited erosion-corrosion is more complicated to predict than inhibited systems of pure corrosion. Sand particles remove iron carbonate layers and can affect the synergistic effects between erosion and corrosion. It has been seen in results presented here in Chapter 5, as well as, by Dave et al., and Hassani that for solutions with inhibitor concentrations greater than about 25 ppm no protection layer is produced\textsuperscript{5, 58}. This results in more uniform corrosion across the surface creating a smoother surface that restricts the erosion rate. Sand, therefore, does not contribute to the corrosion rate. As the inhibitor concentration increases the effect of erosion caused by corrosion decreases rapidly. Sand still impacts the corrosion rate in an inhibited system by slowing down the absorption process of the inhibitor onto the metal surface and, to some extent, by adsorbing inhibitor molecules on the surface of the sand. Referring to Figure 4.1, the surface coverage achieved for an erosion-corrosion solution varies by a factor of about two at an inhibitor concentration of 10 ppm and decreases to a factor of about 1.25 at an inhibitor concentration of 100. For higher inhibitor concentrations where the solution is heavily saturated by the inhibitor, sand has less impact on the inhibitor efficiency as well as the erosion-corrosion rate. To study inhibited erosion-corrosion rates an assumption is made that the inhibited erosion-corrosion rate consist of only two parts: the erosion part of erosion-corrosion and the corrosion part of erosion-corrosion. The erosion part of the calculated inhibited erosion-corrosion rate reduces to approximately the same as the pure erosion rate. The equation assumes that the erosion rate is equal to that of the pure erosion
rate. These assumptions are shown by Equation 4.5. The corrosion part of erosion-corrosion can be estimated based on the Frumkin isotherms as a function of the inhibitor concentration.

\[
[E - C]_{\text{inhibited}} = [\text{Erosion part of } E - C] + [\text{Corrosion part of } E - C]
\] 4.5

The corrosion part of erosion-corrosion is a function of the environmental conditions as well as the inhibitor concentration. To predict the inhibited corrosion rate Frumkin isotherms can be used to account for different conditions and varied inhibitor concentrations. The isotherms must be modified to account for the effects of erosivity. This makes the corrosion part of erosion-corrosion a combination of both the pure corrosion rate and the corrosion caused by erosion.

The determination of the Frumkin isotherm is based on the \( f \) and \( K_{a/d} \) values. Referring back to Equation 4.2, \( f \) represents the mutual interaction of inhibitor molecules and \( K_{a/d} \) is the adsorption/desorption constant. The value for \( K_{a/d} \) is a function of the entropy change that occurs during the adsorption/desorption process. Entropy in a system is a measure of the disorder or measure of the system’s progression towards thermodynamic equilibrium. This value can be affected by system conditions that create a change in the inhibitor adsorption/desorption process, such as environmental changes like an increasing temperature or the addition of sand. Equation 4.6 gives the relation for \( K_{a/d} \).

\[
k_a \propto e^{-\frac{\Delta S_{ads}}{R}}
\] 4.6
where,

- $\Delta S_{ads}$ is the adsorption entropy change
- $R$ is the universal gas constant

This study assumes that the adsorption/desorption constant, $K_{a/d}$, is affected by environmental changes and sand erosion, but that constant $f$ is not necessarily subject to a significant effect by those factors. Because of this, Equation 4.2 can be modified for $K_{a/d}$ to account for the erosion rate and the temperature. This empirical equation is based on experimental data for changing temperatures and changing erosivity collected in this study, as well as, the work by Hassani$^5$ and Dave et al.$^{58}$. This study shows modified Frumkin isotherms developed for the prediction of erosion-corrosion rates for temperatures $135^\circ$ F and $200^\circ$ F, and erosivity rates between 120 and 160 mpy. An additional environmental condition will include the effect of solution water cut, for water cut values of 20% and 40%. The final form of the modified Frumkin isotherm for the prediction of inhibited erosion-corrosion is shown in Equation 4.7.

$$
\left[ k_a \left( ER, \Delta T \right) \right] C_{inh} = \left( \frac{\theta}{1-\theta} \right) e^{-f\theta} \quad 4.7
$$
CHAPTER 5
RESULTS AND DISCUSSION

5.1 Validation of Test Facility

The first objective of this research was the construction and validation of the 3 cell E/C test loop. The test loop had to be evaluated for cell-to-cell interchangeability, this is ensure that erosion, corrosion, and erosion-corrosion can be measured from any of the three test cells. Also tested was the reproducibility of measurements to ensure a low standard deviation from test to test. Table 5.1 shows a summary of the results testing probe interchangeability. Test Cell 1 held a 316 stainless steel weight loss probe, cell number 2 held an AISI 1018 carbon steel weight loss probe, and cell number 3 held an AISI 1018 carbon steel weight loss probe. A five gallon test solution was prepared with conditions shown in Table 5.2. The system was vacuumed before each test for at least two hours to remove dissolved oxygen form the system and then pressurized with nitrogen gas. Nitrogen gas, at a partial pressure of 20 psig was used to prevent a corrosion reaction from taking place at the target surface of the carbon steel electrode. As shown in Table 5.1, the weight loss values from all three cells are within a close range of standard deviation proving cell interchangeability and reproducibility of test data.
Table 5.1: Summary of Erosion Tests Measuring Probe Interchangeability and Reproducibility

<table>
<thead>
<tr>
<th>Material Tested</th>
<th>Erosion Cell 1</th>
<th>Erosion Cell 2</th>
<th>Erosion Cell 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material Tested</td>
<td>316 SS</td>
<td>1018 CS</td>
<td>1018 CS</td>
</tr>
<tr>
<td>Measurement Technique</td>
<td>WL</td>
<td>WL</td>
<td>WL</td>
</tr>
<tr>
<td>Average ±Stn. Dev. (mpy);(n=3)</td>
<td>324 ± 15</td>
<td>328 ± 24</td>
<td>333 ± 29</td>
</tr>
</tbody>
</table>

Table 5.2: Summary of Erosion Test Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Test Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>135°F</td>
</tr>
<tr>
<td>Gas Velocity</td>
<td>32.6 fps</td>
</tr>
<tr>
<td>NaCl Concentration</td>
<td>18.0 wt%</td>
</tr>
<tr>
<td>Partial Pressure</td>
<td>20 psig N₂</td>
</tr>
<tr>
<td>Average Sand Size</td>
<td>150 µm</td>
</tr>
<tr>
<td>Sand Rate</td>
<td>1.0 wt %</td>
</tr>
</tbody>
</table>

Additionally, test accuracy was measured. Accuracy was determined using both results from the first sets of tests shown in Table 5.1 as well as Table 5.3. Data from Table 5.1 were compared to previous testing to ensure accuracy of results. Experiments conducted by Hassani at the E/CRC showed that at a sand concentration of 0.5 wt%, the measured erosion rate was 160 mpy. For tests conducted at 1.0 wt% sand concentration, the erosion rate was measured to be 325 mpy. Accuracy of results can also be established from results shown in Table 5.3. Table 5.4 shows the system conditions that were used to conduct these three tests. For all three tests, the solution was drawn into the system and
the oxygen was removed by vacuuming the system for at least two hours. In uninhibited erosion-corrosion experiments for non-scale forming conditions the total erosion-corrosion rate should equal approximately the additive of the pure erosion and the pure corrosion components. In the test results summarized in Table 5.3, the erosion component was measured in cell number 1 with a 316 stainless steel probe and resulted in an average value of 322 mpy for three tests. The corrosion component was measured in cell number 2 with a 1018 carbon steel LPR probe and gave an average value of 532 mpy for three tests. The total erosion-corrosion value was measured in cell number 3 with a 1018 carbon steel weigh loss probe and resulted in an average measured value of 804 mpy for three tests. Adding results from Cell 1 and Cell 2 gives approximately the same value as that measured in Cell 3, proving the accuracy of the system in its ability to measure erosion, corrosion, and erosion-corrosion in a single test for this case where synergy between erosion and corrosion is not expected.

**Table 5.3: Summary of Erosion-Corrosion Tests to Measure Data Accuracy**

<table>
<thead>
<tr>
<th>Material Tested</th>
<th>Erosion Cell 1</th>
<th>Corrosion Cell 2</th>
<th>E-C Cell 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material Tested</td>
<td>316 SS</td>
<td>1018 CS</td>
<td>1018 CS</td>
</tr>
<tr>
<td>Measurement Technique</td>
<td>WL</td>
<td>LPR</td>
<td>WL</td>
</tr>
<tr>
<td>Average ±Stdev (mpy); (n=3)</td>
<td>322 ± 27</td>
<td>532 ± 48</td>
<td>804 ± 28</td>
</tr>
</tbody>
</table>
Table 5.4: Summary of Test Conditions for Erosion-Corrosion Validation Tests

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Test Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>135° F</td>
</tr>
<tr>
<td>Gas Velocity</td>
<td>32.6 fps</td>
</tr>
<tr>
<td>NaCl Concentration</td>
<td>18.0 wt%</td>
</tr>
<tr>
<td>Partial Pressure</td>
<td>20 psig CO₂</td>
</tr>
<tr>
<td>Average Sand Size</td>
<td>150 µm</td>
</tr>
<tr>
<td>Sand Rate</td>
<td>1.0 wt %</td>
</tr>
</tbody>
</table>

5.2 Baseline Results

Baseline Erosion Results

Baseline erosion tests were completed on Loop #3 and Loop #4. Erosion tests were conducted at a low erosion rate of 120 mpy which corresponds to a sand concentration of 0.3 wt%. Testing conditions used include those listed in Table 5.4 and also included a NaCl concentration of 3.0 wt% and a sand concentration of 3.0 wt%. The erosion rate of 120 mpy was selected in order to simulate possible erosivity situations in oil and gas production. Figure 5.1 shows an example of the test results from the erosion testing. For this example a 316 SS probe was used in Loop #4 and the probe was located in Cell 3. The test in Figure 5.1 ran for twenty-four hours with a data point collected every 140 seconds. In total there were eight tests completed using WL and ER test methods. The eight tests produced an average erosion rate of 119 mpy with a standard deviation of ±12. Figure 5.2 shows a complete summary of results for erosion testing for both sand concentrations and
both NaCl concentrations. The chart includes error bars to show the standard deviation for each set of results. Test results showed that the NaCl concentration did not have an effect on the erosion rate.

![Erosion Rate vs Time](image)

**Figure 5.1: ER Probe Results for Erosion Rates versus Time**
Baseline Corrosion Results

LPR, WL, and ER methods were used to measure baseline corrosion rates. Test conditions selected for corrosion testing was based on erosion results. Testing parameters for non-scale forming conditions are as listed in Table 5.5 and represent those commonly seen in the oil and gas industry. Table 5.6 shows a summary matrix of the corrosion tests with different testing types used. This matrix gives a short summary of the results that were measured. A test matrix was used to catalog all results, calculate averages, and comparing testing methods. The Metal Samples ER probes were obtained for this research. The new probes were tested alongside an LPR and a WL probe to compare accuracy of the new ER probes. It was found that the ER probes preformed as expected, giving nearly identical corrosion rates as the LPR and WL probes. Figure 5.3 shows an example of LPR results for baseline corrosion testing using a NaCl concentration of 18.0 wt%. The
average corrosion rate calculated for a set of six tests was 580 mpy with a standard deviation of ±42 mpy.

Table 5.5: Summary of Test Conditions for Baseline Corrosion Tests

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Test Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>135(^\circ) F</td>
</tr>
<tr>
<td>Gas Velocity</td>
<td>32.6 fps</td>
</tr>
<tr>
<td>NaCl Concentration</td>
<td>3.0 and 18.0 wt%</td>
</tr>
<tr>
<td>Partial Pressure</td>
<td>20 psig CO(_2)</td>
</tr>
<tr>
<td>pH</td>
<td>4.8</td>
</tr>
<tr>
<td>NaCl (wt%)</td>
<td>Cell 1</td>
</tr>
<tr>
<td>-----------</td>
<td>--------</td>
</tr>
<tr>
<td>10.0%</td>
<td>33.91</td>
</tr>
<tr>
<td>18.0%</td>
<td>16.79</td>
</tr>
<tr>
<td>30.0%</td>
<td>15.09</td>
</tr>
<tr>
<td>45.0%</td>
<td>15.09</td>
</tr>
</tbody>
</table>

Table 5.6: Matrix of Corrosion Baseline Test Results
A low NaCl concentration of 3.0 wt% and a high NaCl concentration of 18.0 wt% were tested in order to measure the effect that chloride concentration has on corrosion rates. Previous testing conducted by Hassani suggested that at low chloride concentrations the corrosion rate is higher. Figure 5.4 shows the LPR results comparing the two different chloride concentrations tested. For a NaCl concentration of 3.0 wt%, the average corrosion rate was 595 mpy with a standard deviation of ±26. As shown above, tests at a NaCl concentration of 18.0 wt% resulted in an average corrosion rate of 580 mpy with a standard deviation of ±42. The measured results for the two NaCl concentrations fell within the calculated standard deviation. Therefore, the NaCl concentration has little to no effect on the corrosion rate at these conditions.
Baseline Erosion-Corrosion Results

The third set of baseline tests measured in the new 3-cell E/C test loop was the total erosion-corrosion rate using all three test cells. Table 5.7 gives a summary of results for tests comparing all three measurement techniques, sand concentrations of 1.0 and 0.3 wt%, and NaCl concentrations of 3.0 and 18.0 wt%. Non-scale forming test conditions included: temperature of 135° F, a flow velocity of 32.6 fps, CO₂ pressure of 20 psig, and pH of 4.8. Erosion-corrosion test results were again used to analyze data from the three testing techniques, LPR, WL, and ER, and evaluate the comparability between the three techniques. From the test matrix shown in Table 5.6 it can be seen that the NaCl concentration did not have an effect on the erosion, corrosion, or the total erosion-corrosion rates. The average erosion-corrosion rate 3 weight percent was 722 mpy and the calculated
average for 18 weight percent NaCl was mpy 695. This results matches results presented
in baseline erosion and baseline corrosion results. The three sets of results show that for
non-scale forming conditions, the NaCl concentration has insignificant effect on the
measured erosion, corrosion, and erosion-corrosion rates.

Figure 5.5 shows results for erosion-corrosion tests for sand concentrations of 1.0
wt% and 0.3 wt %. From the graph it can be seen that the 316 stainless steel WL and the
316 stainless steel ER probe values are nearly the same and fall within the error bars. This
shows accurate and comparable results for the erosion component. LPR was used to
measure the corrosion component. Values in these test matched those obtained from the
pure corrosion baseline testing. The third measurement obtained was the total erosion-
corrosion rate. This is shown in the far right columns of the two sand concentration
categories. Test results showed that the erosion component added with the corrosion
component is nearly the same as the measured erosion-corrosion value. It is expected that
for non-scale forming, uninhibited conditions that the total erosion-corrosion rate is the
summation of pure erosion and pure corrosion components.

Figure 5.5 also shows erosion-corrosion results for two sand concentrations, 3.0
wt% and 1.0 wt%. These results proved that for non-scale forming conditions with no
inhibitor, there is not a significant interaction between the erosion component and the
corrosion component. Evidence of this is seen, first, by the comparing the corrosion rate
at the two sand concentrations. The corrosion rate does not change between 0.3 wt% and
1.0 wt% sand concentrations. This implies that for non-scale forming conditions the
corrosion component effected by erosion is minimal. Second, it can also be seen that the
erosion rate at 1.0 wt%, shown to the left side of the graph is about three times higher than the erosion rate at 0.3 wt%, shown to the right side of the graph, which is to be expected. From these results it can be seen that the erosion component effected by corrosion is insignificant for these conditions. These results hold true that for uninhibited, non-scale forming conditions the total erosion-corrosion is equal to the additive of the erosion component and the corrosion component.
| 580 | 839 | 115 | 733 | 2201 | 301 | 1977 | 2018 | 2018 | 2018 | 2018 | 2018 | 2018 | 2018 | 2018 | 0.3% | 0.3% | 0.3% | 0.3% | 0.3% | 0.3% | 0.3% |
|-----|-----|-----|-----|------|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 761 | 721 | 185 | 626 | 118 | 737 | 418 | 738 | 418 | 738 | 418 | 738 | 418 | 738 | 418 | 316 | 316 | 316 | 316 | 316 | 316 | 316 |
| 443 | 401 | 111 | 679 | 517 | 718 | 45 | 718 | 45 | 718 | 45 | 718 | 45 | 718 | 45 | 1018 | 1018 | 1018 | 1018 | 1018 | 1018 | 1018 |
| 702 | 645 | 181 | 831 | 431 | 92 | 831 | 431 | 92 | 831 | 431 | 92 | 831 | 431 | 92 | 316 | 316 | 316 | 316 | 316 | 316 | 316 |
| 657 | 609 | 123 | 561 | 454 | 782 | 392 | 782 | 392 | 782 | 392 | 782 | 392 | 782 | 392 | 1018 | 1018 | 1018 | 1018 | 1018 | 1018 | 1018 |
| 741 | 642 | 152 | 685 | 443 | 106 | 685 | 443 | 106 | 685 | 443 | 106 | 685 | 443 | 106 | 316 | 316 | 316 | 316 | 316 | 316 | 316 |
| 418 | 772 | 360 | 829 | 515 | 702 | 515 | 702 | 515 | 702 | 515 | 702 | 515 | 702 | 515 | 1018 | 1018 | 1018 | 1018 | 1018 | 1018 | 1018 |
| 695 | 823 | 313 | 760 | 276 | 719 | 313 | 760 | 276 | 719 | 313 | 760 | 276 | 719 | 313 | 1018 | 1018 | 1018 | 1018 | 1018 | 1018 | 1018 |
| 778 | 843 | 293 | 793 | 206 | 599 | 293 | 793 | 206 | 599 | 293 | 793 | 206 | 599 | 293 | 1018 | 1018 | 1018 | 1018 | 1018 | 1018 | 1018 |
| IPR | LMP | CI | C1 | C2 | mpy | CI | C1 | C2 | mpy | CI | C1 | C2 | mpy | CI | C1 | C2 | mpy | CI | C1 | C2 | mpy | CI | C1 | C2 | mpy |

Table 5.7: Matrix of Erosion-Corrosion Baseline Test Results
5.3 Inhibited Corrosion Rates

*Inhibited Corrosion*

Chemical inhibitors are commonly used in the oil and gas industry to protect against corrosive environments. Test parameters used are the same as baseline corrosion tests except using only a single NaCl concentration of 3 weight percent (Table 5.5). Corrosion rates at these conditions were collected in the 3-Cell E/R test loop using LPR and WL measurement techniques. Average corrosion rates for each inhibitor concentration are summarized in Table 5.8 and shown graphically in Figure 5.6. To show the maximum
measured inhibitor effectiveness, the results used in Table 5.8 and Figure 5.7 were from tests that had the inhibitor injected at the beginning of the test. It was found that when corrosion was allowed to occur without chemical treatment for several hours, the inhibitor was less effective once it was injected. Figure 5.7 shows what occurs when the inhibitor is administered after the corrosion rate has been allowed to increase to high rates. After 11 hours, 100 ppm of inhibitor was injected into the system. The average corrosion rate at the end of the test was 22 mpy. Comparing this value to the average corrosion rate 10 mpy given in Table 5.8 shows that the inhibitor is more effective when applied at the beginning of the test versus in the middle after the corrosion rate has been allowed to climb.

Table 5.8: Inhibitor Concentrations and Their Measured Corrosion Rates

<table>
<thead>
<tr>
<th>Inhibitor Concentration (ppm)</th>
<th>Corrosion Rate (mpy)</th>
<th>Surface Coverage (θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>580</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>390</td>
<td>.26923</td>
</tr>
<tr>
<td>10</td>
<td>248</td>
<td>.53846</td>
</tr>
<tr>
<td>25</td>
<td>96</td>
<td>.81538</td>
</tr>
<tr>
<td>40</td>
<td>55</td>
<td>.91346</td>
</tr>
<tr>
<td>50</td>
<td>46</td>
<td>.93077</td>
</tr>
<tr>
<td>75</td>
<td>17.5</td>
<td>.96635</td>
</tr>
<tr>
<td>90</td>
<td>15</td>
<td>.97308</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>.98269</td>
</tr>
<tr>
<td>150</td>
<td>6.5</td>
<td>.98750</td>
</tr>
<tr>
<td>200</td>
<td>4.5</td>
<td>.99327</td>
</tr>
</tbody>
</table>
Figure 5.6: Average Corrosion Rates for Conditions Listed in Table 5.8

Figure 5.7: Corrosion Test Results with Inhibitor Added at Midpoint
The Frumkin isotherm, described in Chapter 4, was applied to the inhibited corrosion results. Hassani compared the Langmuir and the Frumkin isotherms in his research. Hassani found that the Frumkin isotherm provided the best fit to measured experimental data. It is more accurate than the Langmuir model because of its consideration of the adsorption/desorption of inhibitor molecules. To use the Frumkin isotherm, a value for $f$ and $K_{ad}$ must be determine. These two values are adjustable parameters that are dependent on the environmental conditions. A least squares method was applied to a Microsoft Excel VBA program to fit the $f$ and $K_{ad}$ parameters for the environmental testing conditions used. The value obtained for $f$ was 2.046 and the value for $K_{ad}$ at zero erosivity was .0397. Figure 5.8 shows the Frumkin isotherm for the corrosion rates versus each inhibitor concentration as shown in Table 5.8. The corrosion rates are represented by a theta value which corresponds to the inhibited corrosion rate at each inhibitor concentration as compared to the uninhibited corrosion rate. This model can be implemented in an already existing computer model (SPPS) to predict inhibited corrosion rates.
Despite the widespread use of chemical inhibitors in the oil and gas industry to mitigate corrosion rates inside production and transportation equipment, their effectiveness is often compromised by environmental conditions. One significant factor that affects an inhibitor's ability to perform is the generation of sand particles. At high flow velocities, sand particles can disrupt and slow the absorption process of the inhibitor onto the metal surface. Moreover, sand can transport some of the inhibitor through the pipe, hindering its adherence to the pipe walls. This reduction in inhibitor absorption necessitates an increased application of inhibitor to achieve the desired effectiveness. Predicting the minimum inhibitor concentration needed is crucial for companies employing a chemical inhibitor in erosion environments to optimize their performance.

\[ K_{a/d} [C_{inh}] = \left( \frac{\theta}{1 - \theta} \right) e^{-f\theta} \]

**Figure 5.8: Frumkin Isotherm for Inhibited Corrosion Results**

*Effect of Sand on Inhibited Corrosion Rates*

Although chemical inhibitors are often utilized in the oil and gas sector to lower corrosion rates inside production and transportation equipment, they are frequently affected by the environmental conditions. A major factor impacting an inhibitor's ability to perform is the production of sand particles. Especially at high flow velocities, sand particles disrupt and decelerate the absorption process of the inhibitor onto the metal surface. The sand can also transport some of the inhibitor through the pipe, preventing its ability to adhere to the pipe walls. A reduction in inhibitor absorption results in a need for increased application of inhibitor to achieve the same effectiveness. Prediction of the minimum inhibitor concentration needed is imperative for companies employing a chemical inhibitor in erosion environments because of the
high cost of using inhibitors. Not only are the chemicals themselves very expensive but they also have to be separated before the oil or gas product makes it to the consumer. The refining process is very expensive, so the less inhibitor that a company is required to use the more money they save.

Table 5.9 expands from Table 5.8 to include inhibited erosion-corrosion at a sand erosion rate of 120 mpy. System conditions were the same as those used in the inhibited corrosion testing with the addition of 0.3 weight percent sand which is equivalent to an erosion rate of about 120 mpy. Figure 5.9 shows the previously graphed Frumkin isotherm with an additional fit for the addition of sand. Included in the Figure 5.10 is data results produced in previous work completed by Hassani. Hassani tested inhibited erosion-corrosion rates using a similar testing techniques in a single test cell system for an erosion rate of 160 mpy, or 0.5 weight percent sand concentration. Test conditions for Hassani’s tests were: flow velocity of 30.8 fps, temperature of 135°F, pH 4.8, and NaCl concentration of 18 weight percent. The $K_a/d$ parameter in the Modified Frumkin isotherm equation (Equation 4.7) is a function of the sand rate and the temperature. This requires a new $K_a/d$ value for each of the erosion rates (0, 120, and 160 mpy) presented. Since recalculating the value of $K_a/d$ takes into account the changing sand rate and none of the remaining system conditions change, this research assumes that the value of $f$ remains the same for the development of isotherms for erosion rates of 0 and 120 mpy. Results from Hassani are presented with the $K_a/d$ and $f$ values found in literature. Table 5.10 presents the values for both $f$ and $K_a/d$ for each of the three erosion rates tested.
Figure 5.11 and Figure 5.12 demonstrate that there is a large shift to the right and downward as more sand is added to the system, as shown by the arrows. For example, looking at Figure 5.12, at an inhibitor concentration of 50 ppm, the surface coverage value (θ) for a system operating with an erosion rate of 0 mpy is .92069, the surface coverage value (θ) at an erosion rate of 120 mpy decreases to .8256, and the surface coverage (θ) at an erosion rate of 160 mpy plunges even further to a value .75611. The resulting decrease is about 18 percent in inhibitor effectiveness when comparing an erosion rate of 0 mpy and an erosion rate of 160 mpy. Figures 5.9 and 5.10 best illustrate why it is necessary to understand the effect of sand production on inhibitor effectiveness. Sand plays a large role in an inhibitor’s ability to absorb onto a metal surface, making corrosion rates more difficult to predict and control. The Frumkin isotherm prediction models can be used to more accurately predict the necessary inhibitor concentration that is needed over a widespread range of environmental conditions and sand concentrations in order to adequately protect internal pipeline walls and prolong the life of the drilling and transportation tools used in the oil and gas industry.
Table 5.9: Summary of Inhibited Corrosion and Erosion-Corrosion Experimental Results and Their Corresponding Theta (θ) Values

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>CR Rate</th>
<th>Surface Coverage (θ)</th>
<th>E-C Rate</th>
<th>Surface Coverage (θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>580</td>
<td>0</td>
<td>625</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>390</td>
<td>0.26923</td>
<td>513</td>
<td>0.1792</td>
</tr>
<tr>
<td>10</td>
<td>248</td>
<td>0.53846</td>
<td>396</td>
<td>0.3664</td>
</tr>
<tr>
<td>25</td>
<td>96</td>
<td>0.81538</td>
<td>249</td>
<td>0.6016</td>
</tr>
<tr>
<td>40</td>
<td>55</td>
<td>0.91346</td>
<td>144</td>
<td>0.7696</td>
</tr>
<tr>
<td>50</td>
<td>46</td>
<td>0.93077</td>
<td>109</td>
<td>0.8256</td>
</tr>
<tr>
<td>75</td>
<td>17.5</td>
<td>0.96635</td>
<td>67.5</td>
<td>0.892</td>
</tr>
<tr>
<td>90</td>
<td>15</td>
<td>0.97308</td>
<td>54</td>
<td>0.9136</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>0.98269</td>
<td>34</td>
<td>0.9456</td>
</tr>
<tr>
<td>150</td>
<td>6.5</td>
<td>0.98750</td>
<td>23</td>
<td>0.9632</td>
</tr>
<tr>
<td>200</td>
<td>4.5</td>
<td>0.99327</td>
<td>16</td>
<td>0.9744</td>
</tr>
</tbody>
</table>

Table 5.10: $f$ and $K_{a/d}$ Values for Varying Sand Erosion Rates

<table>
<thead>
<tr>
<th>Sand Erosion Rate (mpy)</th>
<th>Parameter</th>
<th>0</th>
<th>120</th>
<th>160</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_{a/d}$</td>
<td>.03965</td>
<td>.0215</td>
<td>.0162</td>
</tr>
<tr>
<td>$f$</td>
<td></td>
<td>2.0458</td>
<td>2.0458</td>
<td>1.301</td>
</tr>
</tbody>
</table>
Figure 5.9: Frumkin Isotherms Showing Decreasing Inhibitor Effectiveness with the Addition of Sand Particles
5.4 Effect of Oil on CO₂ Corrosion Rates

**Effect of Oil/Water Mixture on Corrosion Rates**

Oil was introduced into the system at water cuts of 20% and 40% to evaluate the effect that the addition of oil has on CO₂ corrosion rates. A three gallon brine solution was mixed with two gallons of mineral oil to produce an oil/water mixture. Valves located on the tank were adjusted to achieve the proper oil water mixture (Figure 3.5). The oil and water travelled to the circulation pump where they was mixed together to create the oil/water emulsion that then impacted the three-cell test section. The water cut was
measured after the discharge side of the pump. A clear glass beaker was used to capture 200 milliliters of the emulsion. The beaker was placed on top of a level table for five to ten minutes to allow the fluid to separate into the individual water and oil layers. The volume of each fluid layer was measured in order to calculate a percentage of water to oil. This process was repeated until the desired water cut percentage was reached.

Test solution composition was the same for the tests with oil. These included: temperature 135°F, velocity 32.6 fps, pH 4.8, and NaCl concentration 18 weight percent. Using LPR measurements, the average measured corrosion rate for the 40% water cut was 514 mpy and the average measured corrosion rate for the 20 water cut was 502 mpy. The corrosion rate for a 100% water cut solution was 580 mpy. The differences in measured corrosion rates implies that the corrosion rate decreases with decreased water cut. To more accurately assess the effect that oil concentration has on CO₂ corrosion rates, a student’s t test was used to measure the statistical difference between each of the three cases. A student’s t test is a tool used to determine the statistical difference between two arrays of data. A one-tailed, 95% student’s t test was used, requiring that the P value to be less than .05 (5%) in order to show statistical difference in the corrosion rates. The equation for calculating statistical difference is shown in Equation 5.1. Table 5.1 summarizes the results of LPR measurements and includes results from the t test. From the results in Table 5.11, Test #1 and Test #2 prove that when oil/water emulsion is present at a water cut of 40% or lower, there is a reduction in the CO₂ corrosion rate. But, Test #3 has a P value significantly greater than .05, suggesting that there is no statistical difference between the measured LPR values for water cuts of 40% and 20%. Therefore, there is not a reduction in corrosion rate as the water cut is reduced from 40% to 20%.
\[
t = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}
\]

5.1

where,

- \( \bar{x} \) is the sample mean (mpy)
- \( s \) is the sample variance
- \( n \) is the sample size

Table 5.11: CO\textsubscript{2} Corrosion Rate Statistical Analysis for Water Cuts of 100\%, 40\%, and 20\%

<table>
<thead>
<tr>
<th>Calculated Results</th>
<th># 1 - 100% vs 40%</th>
<th># 2 - 100 % vs 20%</th>
<th># 3 - 40% vs 20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average CR\textsubscript{inh=0}</td>
<td>580</td>
<td>514</td>
<td>502</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>4204</td>
<td>3208</td>
<td>4302</td>
</tr>
<tr>
<td>P (T&lt;t) 1 Tail</td>
<td>.046</td>
<td>.037</td>
<td>.385</td>
</tr>
</tbody>
</table>

Rincon et al. suggests that oil reduces the corrosion rate by one of two ways. First, the oil could be absorbed onto the metal surface after being dissolved in the aqueous state. Or, when the water and oil form an emulsion it creates a lower conductivity than a brine solution, reducing the corrosion rate\textsuperscript{61}. It was seen upon removing test probes from the test cells at the end of a test that an oil layer is formed on the surface of the probe. The oil layer that is formed causes a decrease in the anodic reaction by impeding the highly conductive brine solution from contacting the metal surface. Figure 5.11 shows LPR results for
measured corrosion rates for 20% and 40% water cuts. Comparison of corrosion rates for 100%, 40%, and 20% water cuts are shown in Figure 5.12.

![Corrosion Rate vs Time](image)

**Figure 5.11: LPR Corrosion Results for Two Different Water Cuts (20% and 40%)**
Inhibited Oil/Water Corrosion Rates

Inhibited CO$_2$ corrosion rates were measured at inhibitor concentrations of 0, 10, 25, 50, 75, 90, 100, 150, and 200 ppm at a 40% water cut using the LPR technique. The LPR results of corrosion tests versus the inhibitor concentration used is shown in Figure 5.13. From the graph, it can be seen that at a 40% water cut, the inhibitor is less effective than in the system at 100% water cut. The imidazoline-based inhibitor used in this study is water soluble and oil dispersible. As shown above oil/water emulsions can create a layer of oil on the metal surface. Because the inhibitor used in this study is water soluble, some of the inhibitor molecules are displaced from the metal surface by the oil layer. This causes a reduction in inhibitor absorption of the inhibitor onto the metal surface allowing for prolonged exposure to the highly conductive brine solution and keeping corrosion rates higher than desired. Therefore, for systems production a water/oil emulsion, the presence
of oil decreases the inhibitor effectiveness and results in a need for increased inhibitor concentration.

![LPR Corrosion Rate Averages vs Inhibitor Concentration](image)

**Figure 5.13: Corrosion Rate Averages for Increasing Inhibitor Concentrations at 40% and 100% Water Cuts**

Shown above is that oil reduces the effectiveness of inhibitor. This creates a need for a model to predict inhibitor effectiveness over a range of inhibitor concentrations and for a range of environmental conditions. Therefore, a Frumkin isotherm can be used as to model and predict inhibitor effectiveness for a given set of environmental conditions. Figure 5.14 shows the effect of adding inhibitor to an oil/water system. The least squares method, described previously, was used to determine new values for the constants $f$ and $K_{a/d}$. $f$ was found to be 1.124 and the value of $K_{a/d}$ was .051. With the exception of 10 ppm inhibitor concentration, the oil caused an average of 4% reduction in surface coverage.
value at a water cut of 40%. In general, adding oil to a system causes a reduction in inhibitor effectiveness by retarding the ability of the inhibitor to adhere to the metal surface.

Figure 5.14: Frumkin Isotherm Relationships for Two Water Cuts (100% and 40%)

\[ K_{a/d}[C_{inh}] = \left( \frac{\theta}{1 - \theta} \right) e^{-f\theta} \]
CHAPTER 6
SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

6.1 Summary and Conclusions

The focus of this thesis was the validation of a newly built 3-Cell E/C Test Loop to test erosion, corrosion, and erosion-corrosion components simultaneously in a single test and use the newly developed facility to investigate the impact that sand erosion and oil has on inhibitor efficiency. Testing was completed using linear polarization resistance, weight loss, and electrical resistance measurement techniques. Results from the 3-Cell E/C Test Loop were used in the Modified Frumkin absorption isotherm equation to develop prediction models for erosion rates of 0, 120, and 160 mpy. The Modified Frumkin Isotherm was also used to develop a model for a 40% water cut.

Baseline testing was completed to measure erosion, corrosion, and erosion-corrosion rates. Baseline erosion conditions included: \( V_{sg} = 32.6 \text{ fps}, N_2Pp = 20 \text{ psig}, T = 135^\circ \text{F}, \) sand concentrations of 1.0 and 0.3 weight percent, and NaCl concentrations of 3 and 18 weight percent. Erosion rates were measured at 320 mpy for a sand concentration of 1.0 weight percent and 118 mpy at 0.3 weight percent using ER and WL techniques. High NaCl concentration was predicted to increase erosion rates due to an increase in fluid density and viscosity, but results showed no identifiable correlation between NaCl concentration and the measured erosion rate. Corrosion conditions included: \( V_{sg} = 32.6 \text{ fps}, \)
fps, pH 4.8, CO$_2$ Pp = 20 psig, T = 135°F, and NaCl concentrations of 3 and 18 weight percent. The average measured corrosion rate at 18 and 3 weight percent NaCl were 580 mpy and 595 mpy using LPR and WL methods. Corrosion measurements also showed no statistical difference due to a high NaCl concentration. The average baseline erosion-corrosion rate at NaCl and sand concentrations of 18 and 0.3 weight percent was 704 mpy. Baseline erosion-corrosion results obtained from ER and WL measurements showed no synergistic effect between erosion and corrosion in an uninhibited system. This implies that the erosion-corrosion rate for a non-scale forming, uninhibited system is equal to the additive of the pure erosion and the pure corrosion components.

The Modified Frumkin isotherm was used to model inhibitor effectiveness as a ratio of inhibited corrosion for a specific inhibitor concentration to the uninhibited corrosion rate. The modification to the original Frumkin isotherm equation allowed the $K_{a/d}$ parameter to be adjusted for temperature and sand erosion rate. Inhibited corrosion rates were measure for inhibitor concentrations of 0, 5, 10, 25, 40, 50, 75, 90, 100, 150, and 200 ppm. It was found that inhibitor concentration above 90 ppm showed little change in corrosion rate. Adding sand to the solution caused a drastic decrease in inhibitor efficiency for inhibitor concentrations below 100 ppm. For inhibitor concentrations of 100 ppm and above, the solution was sufficiently saturated with inhibitor to counter most impact to the absorption rate due to sand erosion. Inhibited erosion tests showed that there was no change to erosion rates due to the presence of inhibitor. In inhibited systems, increasing the sand rate can increase the corrosion component of erosion-corrosion by accelerating the rate at which the inhibitor layer is removed for the metal surface.
At a pH of 4.8 and temperature of 135°F water cuts of 20% and 40% were found to reduce the corrosion rate compared to a system with a 100% water cut. Introducing oil to the system reduces the surface area being wetted by the water and retards the solution conductivity, thereby reducing the corrosion rate. Water cuts of 20% and 40% produced nearly the same corrosion rate and it was found that their values were statistically identical.

The Modified Frumkin isotherm showed that a 40% water cut solution resulted in a decrease in inhibitor effectiveness. Inhibited oil/water tests had conditions of: T= 135°F, V_{sg} = 32.6 fps, 4.8 pH, and 18 weight percent NaCl. Hassani found that in post testing measurements, 10% of the inhibitor from the system dissolves into the oil phase. Absorption of some inhibitor into the oil phase reduces the effective inhibitor concentration in the water phase, where the corrosion reaction is taking place, and, therefore, reduces its effectiveness to reduce corrosion rates. The average reduction in effectiveness for inhibitor concentrations of 50 ppm and greater was 4.5 percent. Increasing the effective inhibitor concentration above 100 ppm resulted in no change to the surface coverage values.

6.2 Recommendations

In general test results for chloride concentrations of 3 and 18 wt% showed little difference in CO₂ corrosion rates. This trend held true expect in cases where pitting occurred. Chloride concentration can change the conductivity of the solution, thereby causing an increased surface pitting. It would be beneficial in simulating field conditions to study the effect of NaCl concentration on pitting corrosion of both carbon steel and corrosion resistance alloys. Pitting corrosion is one of the more aggressive forms of
corrosion damage and often goes undetected until unalterable damage has occurred. Developing a model for the prediction of pitting corrosion and bettering understanding the conditions that cause it is recommended for future work.

This study looked at a low sand erosion concentration of 0.3 weight percent, which results in an erosion rate of about 115 mpy. Sand production in pipeline is typically very small. Therefore, it would be beneficial to investigate additional ranges of sand concentrations. Hassani presented results for erosion rates of 160 mpy and 340 mpy\textsuperscript{5}. Further reducing the sand rate would be more comparable to field conditions. Using weight loss probes for low erosion rates requires a long time to get measurable data. It is instead recommended to use the ER probes in order to get more accurate data in a relatively short amount of time, as compared to the weight loss method. The three-cell configuration is ideal for these types of tests because all three components can be measured simultaneously reducing test time. An example test setup would include a carbon steel ER probe, 316 stainless steel ER probe, and a carbon steel LPR probe.
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APPENDIX A

PROCEDURE FOR OPERATING TEST LOOP

Figure A.1: Schematic of 3-Cell E/C Test Loops

The following procedures will describe test solution preparation, system setup, preparing the test probes, adding sand and inhibitor to tests, and cleaning the system for both Loop #3 and Loop #4. Valve references can be found in Figure A1. Referring to the legend, the circles represent ball valves; triangle I indicates the inhibitor injection port; triangle II is the vacuum port for the test section; the rectangles indicate the three test cells, and the arrows show the direction the fluid is flowing. Not shown, but also included, are the pressure valve and the sand feeder. These two ports are located at the top of the tank and can be seen in Figure 3.5.
A.1 – Preparing the System

1. For baseline testing, prepare a test solution in 5 gallons of distilled water using a clean bucket (test composition shown in Table 3.3). For oil/water tests prepare a test solution in at least 3 gallons of distilled water in one bucket (same test composition), then pour 2-2.5 gallons of oil in a separate bucket.

2. With only valves 1, 2, and 3 open, attach vacuum hose to vacuum port on the top of the tank as shown in Figure 3.5. Start the vacuum pump prior to opening the valve at the top of the tank (remembering to open/close all valves slowly).

3. After five minutes, close the vacuum valve and pull the test solution into valve controlled opening at the bottom of the tank. This valve can be seen on Figure 3.5. Reopen the vacuum valve and continue to vacuum the solution for 2 hours. This procedure results in the dissolved oxygen content to be less than 10 ppb.

4. After two hours of vacuuming, close the vacuum valve then shut off the vacuum pump. Immediately connect the CO₂ gas (N₂ for E tests) to the system and pressurize to 20 psig.

5. Turn on the heater to the appropriate temperature and turn on the system pump. Allow the pump to circulate the solution at least six hours to ensure proper temperature is reached and that the solution appropriately mixes and the correct pH is obtained.

6. During this six hour period, the test probes can be prepared as described A.2.

7. Once the system has circulated for six hours the pH needs to be checked before each test. Calibrate the pH probe according the manufactures instructions. They are as follows: i) Rinse the pH probe with distilled water, ii) Calibrate with the pH
7 buffer solution then rinse again with distilled water, iii) Calibrate with the pH 4.5 solution iv) rinse probe again with distilled water before inserting both the pH and temperature probes into the pH meter section of the test loop shown in Figure 3.5.

8. Open the vacuum valve for the pH section before inserting. After inserting pH and temperature probes, vacuum the pH meter section for about 5 seconds.

9. Open the pH and temperature valves allowing the test solution to impact the probes. Wait for the pH to stabilize. If desired pH is not achieved at this point, either an acid or a base can be added until the desired pH is reached.

10. The test probes can now be inserted into the test section located between valves 4 and 5 on Figure A.1. The probes are inserted until they come into contact with the jet nozzle, then using a tape measure or calipers, the probe should be retracted 0.5”. Be sure to center the test probe with the jet nozzle to ensure the entire probe is impacted.

11. Vacuum the test section using the vacuum port described in Figure A.1 for five minutes.

12. Connect the LPR or ER connection wires to the appropriate probes and make sure the software is working properly.

13. Open valve 5 then 4. Close valve 2 then valve 3 to obtain optimal flow rates.

14. Start LPR or ER software and monitor to make sure proper test results.

A.2 – Preparing and Cleaning Test Probes

1. LPR and WL probes need to be sanded to a new polished finish using first the rough sand paper then the more fine 220 grit sand paper. Because the ER probes have a
limited surface metal thickness, proper measures should be taken to limit pitting in tests and prevent rusting of the carbon steel probes when in storage.

2. LPR, WL, and ER probes should be cleaned with acetone. LPR and WL probes are then weighed before placing in the system (Step A.1-10).

3. After testing is complete the probes need to be removed from the test solution as soon as possible to reduce additional corrosion damage.

4. The probes are rinsed in the sink to remove buildup of corrosion byproduct film and salt

5. LPR and WL probes are dried with an air hose, wiped with acetone to stop corrosion due to air exposure, and then placed in an oven at 150°F for at least 10 minutes to finish drying.

6. Allow to cool to room temperature before again cleaning with acetone before weighing.

7. Store probes in a dry, oxygen free container to prolong probe life.

A.3 – Addition of Sand

1. Make sure the sand feeder at the top of the tank is clean and dry (Figure 3.5). Measure sand into 50 mL beaker and pour into the sand feeder. Make sure pressure valve is shut.


3. Close pressure valve on tank and use that hose to pressurize the sand feeder to 30 psig using same gas used for testing (CO₂ for C and E-C, N₂ for E).
4. Keep pressure valve open and open ball valve at the top of the tank to inject sand directly into the tank. Tap the sand feeder to ensure all sand is injected into tank.

5. Close off tank and release pressure from sand feeder. Turn pressure down to 20 psig and reconnect to the tank pressure valve.

A.4 – Addition of Inhibitor

1. First measure out the desired mL of inhibitor using a syringe.

2. Insert the syringe into the valve labeled triangle I in Figure A.1.

3. If injecting inhibitor before the tests starts, it can be injected during the 2 hour vacuum process and will mix into the solution before impacting the probes. In this case, open the injection valve while vacuuming and allow vacuum to draw in inhibitor. Shut the valve and clean the syringe with acetone before storing. Following steps can be skipped.

4. If injecting during an ongoing test, make sure valves 2 and 3 are closed and that the liquid is drained from this section using the proper drain valve.

5. Vacuum the bypass section using the port shown in Figure A.1 by triangle III for about two minutes.

6. Close the vacuum valve and shut off the vacuum pump. Open the inhibitor port and allow the vacuum to draw in the inhibitor.

7. Open valve 3 then 2 for about ten minutes to allow inhibitor to mix into solution. During this time clean the syringe with acetone to until all inhibitor is removed. Store in dry place.

8. After at least ten minutes close valve 2 then 3.
A.5 – Cleaning the System (no oil)

To ensure consistency from one test to the next, a clean system is required. This section describes the testing procedure to be used for tests where no oil or inhibitor are present. This testing procedure requires only the use of cold tap water.

1. Drain the original test solution. Attach a cold water hose to the tank inlet valve and a drain hose to the drain spout located on the discharge side of the circulation pump.
2. Make sure the heater is off and all valves are open so the entire system is being cleaned.
3. Insert cold tap water into the tank for 2-3 minutes. This should be about 5 gallons.
4. Pressurize system with an air hose to 20 psig and start the circulation pump.
5. Allow to circulate for 15-20 minutes before draining. Repeat as necessary until clean. For tests with sand this process might have to be repeated many times before all sand is removed. To check cleanliness, catch a sample of water in a clear glass beaker while the pump is circulating. Use visual inspection to see if there is still sand in the system.

A.6 – Cleaning the System (oil/water mixture or inhibitor)

This procedure is required when oil or inhibitor are used in a test. Oil and inhibitors are difficult to remove from the test system, therefore a more aggressive cleaning process must be used. This procedure requires use of both hot and cold tap water and a non-foaming detergent.
1. Drain the original test solution. If there was oil in system then the solution must be drained in a bucket so the oil can be separated and disposed of appropriately.

2. Open all valves in the system except for any discharge, vacuum, or pressure valves.

3. In a clean bucket mix a five gallon solution of hot water and detergent. Directions for detergent usage are on the package and vary from one manufacture to the next.

4. Use the vacuum to draw solution into the tank. Pressurize with air to 20 psig and turn on the heater to at least 140°F. This temperature is the activation point of the soap and must be reached for the soap to be effective. Circulate the soap for at least an hour.

5. If no oil is was used in the original test solution then the cleaning solution can be drained using the normal drain hose. If oil was used then the cleaning solution must be drained into a bucket so any remaining oil can be disposed of properly.

6. Draw in clean hot tap water into the tank in the same way. Again, allow to circulate at least an hour to ensure a temperature of 140°F is reached.

7. Use the same draining procedure described in 5. If no oil is present when drained skip the next step and instead use the process described in A.5 to finish cleaning.

8. If oil is still present then repeat steps 3-7 until no oil is found. At this point switch to the cleaning process described in A.5.
APPENDIX B
DETERMINING SAND CONCENTRATION

It is important to be able to measure the sand concentration during an ongoing test. During testing sand can become stuck in fittings, the tank, test cells, or the pump. This causes a reduction in sand concentration and also increases the uncertainty in erosion and erosion-corrosion measurements. Being able to measure sand during an ongoing test allows for the operator to add additional sand as needed, maintaining a consistent erosion rate. The following procedure is used to determine the sand concentration during and at the end of testing for both 1.0 and 0.3 weight percent sand concentrations at an average sand particle size of 150µm.

1. Obtain the following: two clean, dry graduated beakers, a filter with a screen, a heat gun, a ring stand, and a squirt bottle with distilled water.

2. Weigh one the beakers with the filter in it. Record this weight.

3. Use the drain valve located at the discharge of the circulation pump to catch a set volume of test solution (100-200 mL recommended) in the weighed beaker.

4. Pour solution through the filter screen and catch with other beaker.

5. Rinse the sand particles with the squirt bottle until all NaCl is removed.

6. Place filter on ring stand and turn on the heat gun until the sand is dry. Turn off the heat gun and allow to cool to room temperature. During this time dry the weighed beaker.

7. Place the filter in the weighed beaker and reweigh. Record the final weight.
8. The sand concentration can then be determined using Equation B.1

\[
\text{Sand Concentration (wt\%)} = \frac{\text{Final Wt. (mg)} - \text{Initial Wt. (mg)}}{\text{Test Solution Captured (mL)}}
\]

B.1

9. This equation can be compared to the total solution volume to get a measurement of the sand concentration present in the test solution.

10. Additional sand can be added using Procedure A.3 as needed. It is recommended that for a twenty-four hour test, the sand concentration be tested every 4-6 hours.