The Evaluation of Several Corrosion Mitigation Strategies for Oil Coolers Used by the Strategic Petroleum Reserve

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Abstract

The goal of this study was to first establish the fitness for service of the carbon steel based oil coolers presently located at the Bryan Mound and West Hackberry sites, and second, to compare quantitatively the performance of two proposed corrosion mitigation strategies. To address these goals, a series of flow loops were constructed to simulate the conditions present within the oil coolers allowing the performance of each corrosion mitigation strategy, as well as the baseline performance of the existing systems, to be assessed. As prior experimentation had indicated that the corrosion and fouling was relatively uniform within the oil coolers, the hot and cold side of the system were simulated, representing the extremes of temperature observed within a typical oil cooler. Upon completion of the experiment, the depth of localized attack observed on carbon steel was such that perforation of the tube walls would likely result within a 180 day drawdown procedure at West Hackberry. Furthermore, considering the average rate of wall recession (from LPR measurements), combined with the extensive localized attack (pitting) which occurred in both environments, the tubing wall thickness remaining after 180 days would be less than that required to contain the operating pressures of the oil coolers for both sites. Finally, the inhibitor package, while it did reduce the measured corrosion rate in the case of the West Hackberry solutions, did not provide a sufficient reduction in the observed attack to justify its use.
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**Introduction and Background**

At each of the SPR sites, oil is stored in massive underground caverns located within natural salt domes. In order to extract the oil, water is pumped into the cavern, displacing the oil and forcing it out of the cavern. Due to the depth of the caverns, over time the oil increases in temperature. This temperature increase causes an increase in the vapor pressure of certain low molecular weight species within the oil to unacceptably high levels. As a result, the oil must be cooled prior to being delivered to its final destination/storage container. The cooling of the oil is accomplished through the use of large tube-sheet heat exchangers known as oil coolers (Figure 1). These heat exchangers are constructed largely of carbon steel which conforms to ASTM A214A or A179. The cooling media used in these exchangers is the same water that is used to extract the oil from the caverns. This cooling water is passed through the tubes in the oil cooler, and the oil is passed through the shell of the oil cooler. The source of the water at most of the SPR sites is drawn from an intercoastal waterway – as such, the water is very high in chloride, sulfate, and calcium, with pHs at or slightly above neutral. This combination of carbon steel and a high chloride water source has resulted in severe corrosion, leading to tube fouling and/or failure within the oil coolers. At the Bryan Mound site, water is taken from the Brazos river. As the water within the Brazos is very high in calcium, significant calcium fouling of the tubes within the oil coolers has been observed. Clearly, failure by either corrosion perforation or fouling will have a negative impact on the effectiveness of the heat exchanger. As the corrosion damage and fouling increases in severity, it can prevent the system from functioning at the level necessary to complete a drawdown operation (i.e., large scale extraction of oil from the caverns).

Several strategies were proposed by DynMcDermott/SPR to address this corrosion and fouling issue. The first of the proposed solutions was the replacement of the carbon steel with a material intrinsically resistant to corrosion and fouling in SPR service environments. The particular material selected was a superferritic stainless steel. The second potential solution was to leave the existing carbon steel tubing in place, and chemically moderate the corrosion and fouling processes via a corrosion inhibitor and deposit control agent. Each of the aforementioned mitigation strategies had its own set of advantages and disadvantages. In the case of material replacement, the clear advantage was the insured performance of the system.
The disadvantage of replacing the carbon steel with a superferritic stainless is the considerable material cost increase associated with such materials when compared to carbon steel. Chemical treatment would be a considerably lower cost alternative – however, due to the once-through, open design of the system, both the concentration and chemical composition of any materials used would be limited. In addition, because the water used to cool the oil is also pumped directly into the cavern, potential interactions of the oil with the inhibitor would also need to be considered.

A series of evaluations were performed to first establish the nature of the corrosion product within the oil coolers. The results of these tests indicated that no organic material was present, thus it is unlikely that microbiologically induced corrosion played an important role in the observed attack. Another set of experiments, performed by SWRI, were conducted to assess the impact that the inhibitor and deposit control agent might have on the oil stored in the cavern. These tests established that it was very unlikely that any undesirable interactions between the oil and the corrosion inhibitor/anti-foulant chemistry would occur. Once it was established that both of the proposed solutions were in fact viable as a potential candidate for evaluation as a corrosion mitigation strategy, a test program to evaluate both systems was assembled. This proposed test program had two goals – the first being to establish if the proposed chemical treatment could be used to effectively control the scaling and corrosion of carbon steel pipes, and the second being to establish if a particular variety of superferritic stainless steel (SeaCure) tubing would be a viable solution to the problem as well. In both cases, the tendency for calcium scale to form as well as the degree of corrosion observed was to be quantitatively assessed.

In the initially proposed test program, tube bundles were to be assembled at the West Hackberry site and evaluated for a period of 90 days. During the test period, each tube bundle would be exposed to flowing water with a chemistry which represented both the West Hackberry and Bryan Mound sites. In the case of the carbon steel tubing, bundles were to be evaluated both with and without the presence of the inhibitor. In order to accomplish this, source water from West Hackberry would be modified on site such that it simulated the Bryan Mound water. Inhibitor would be added to the appropriate flow streams as well. This proposed test program had a number of aspects which were cause for concern. First, testing was to occur from November through March. During the program, the tubing would be exposed to ambient conditions (i.e., the tube bundles would be outside, exposed to the elements, rather than within an operating oil cooler). As a result, the tubing would see operating temperatures that are on average close to 60 degree’s cooler than those in actual service, in addition to lacking the temperature differential between the tube and shell side of the exchangers. This raised a concern as both the corrosion rate and calcium scale formation rate are a strong function of temperature, both becoming elevated as the temperature increases. For this reason, if the test is to accurately simulate the conditions within an actual heat exchanger, it is imperative that the thermal aspects of the heat exchangers be simulated as well as the chemical ones. The second concern was the ability to accurately simulate the solutions required for this test – more specifically, the ability to create a water chemistry similar to Bryan Mound at the West Hackberry site, as well as maintain appropriate inhibitor levels in all of the water chemistries evaluated. Due to the large volume of solution required, in addition to the considerable alterations in solution chemistry which would need to be accomplished, this would be a difficult process to assemble and control. Due to these issues, it was proposed that a series of laboratory scale flow loops be constructed that would
allow more precise control of the thermal and chemical aspects of each heat exchanger. The following report details the results of this laboratory based study.

The goal of the study detailed below was twofold – first, this study sought to establish the fitness for service of the oil coolers presently in service at the Bryan Mound and West Hackberry sites. More specifically, to demonstrate their ability to function properly for a full drawdown procedure (approximately 180 days of continuous operation) Presently, the oil coolers at both sites (as well as the other sites not directly assessed in this study) are experiencing extensive corrosion and fouling which hinders their ability to function properly. Second, this study also sought to compare the performance of a number of proposed corrosion mitigation strategies to address issues with the carbon steel piping presently in place. Several approaches have been presented to address these issues, including the use of an inhibitor and deposit control system as well as the application of materials that are intrinsically more resistant to attack in the environments of interest. To address these goals, a series of flow loops were constructed at Sandia National Laboratories (SNL) to simulate the conditions present within the oil coolers in use at the Bryan Mound and West Hackberry SPR sites, allowing the performance of each corrosion mitigation strategy, as well as the baseline performance of the existing systems, to be assessed.

The Bryan Mound and West Hackberry sites were selected (by DM/SPR) as they represent the extremes in terms of calcium fouling and general corrosion within the SPR complex. While other locations are not directly addressed by this study, the knowledge gained here can be used to gauge the appropriateness of the corrosion mitigation strategies for those sites as well.

It should be noted that the experiments performed in this study were done on new tubing, whereas the existing oil coolers have contained solution, and in some cases, been operated. As such, in the existing oil coolers, corrosion will have already taken place, the wall thicknesses reduced, thermal and flow performance degraded, etc. The impact that is predicted from this study would be superimposed upon the initial condition of the existing systems. In other words, the extent of attack observed in this study will likely be less severe than that which would be present in a field system operated for a similar time period due to the presence of pre-existing corrosion damage within the actual oil coolers.

Experimental Approach/Methods

Materials

Three different materials were evaluated in this study, along with a single inhibitor chemistry. They were

- ASTM A214A Electric-resistance-welded (ERW) carbon steel tube
  - Initial material used in heat exchanger tube bundles
- ASTM A179 Seamless cold-drawn low carbon steel tube
Carbon steel which has been used to replace/repair damaged ERW carbon steel tube bundles

- SeaCure® superferritic stainless steel (Trent Tube)
  - Material currently being utilized to replace existing carbon steel tube bundles

- Inhibitor Chemistry (GE Betz) – 6ppm Flogard MS6201 (phosphate inhibitor), 3ppm Depositrol PY5203 (anionic polymer deposit control agent)
  - Proposed low-cost alternative to material replacement for carbon steel tube bundles

Rotating Cylinder Electrode Experiments

The rotating cylinder electrode (RCE) technique is frequently used to assess the extent of flow-assisted/influenced corrosion in systems where turbulent flow is expected.\(^5\)\(^-\)\(^7\) Due to the high nominal fluid velocity in the SPR oil coolers (264 cm/s), the flow within them is turbulent in nature, and as such, readily simulated by a rotating cylinder electrode. Appropriate rotation rates corresponding to fluid velocities of 150, 250, and 350 cm/s were calculated. Calculations were conducted to determine the cylinder rotation rates required to simulate the mass transport observed at the interior surface of a tube within the heat exchanger, the details of which are presented elsewhere in the literature.\(^5\) Rotation rates of 1500, 3500, and 5000 rpm were selected based upon these calculations.

An organo-phosphate based inhibitor, Flogard MS6201 (GE Betz), was selected for evaluation by the SPR and was included in this study. The manufacturer recommended a concentration of 6ppm (corresponding to approximately 3ppm of phosphate) for the SPR once-through system, based upon their knowledge of the inhibitors corrosion inhibition abilities. In this portion of the study, inhibitor concentrations ranging from 3 to 12ppm were evaluated to assess the validity of the manufacturer’s recommendation, as well as establish the implications of a higher and lower concentration (the latter to assess the impact of inhibitor depletion).

The solution chemistry used for all of the RCE experiments was based upon recent analyses of the water chemistry at the Bryan Mound and West Hackberry sites. The compositions of the two environments and their corresponding laboratory made simulation are listed in the table below.

<table>
<thead>
<tr>
<th></th>
<th>Bryan Mound</th>
<th>West Hackberry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Recent Actual Conc.</td>
<td>Simulant Conc.</td>
</tr>
<tr>
<td><strong>Chloride</strong></td>
<td>14.8 – 16.6 g/L</td>
<td>15.5 g/L</td>
</tr>
<tr>
<td><strong>Bicarbonate</strong></td>
<td>125 – 129 mg/L</td>
<td>127 mg/L</td>
</tr>
<tr>
<td><strong>Sulfate</strong></td>
<td>1.9 – 2.01 g/L</td>
<td>1.95 g/L</td>
</tr>
<tr>
<td><strong>Calcium</strong></td>
<td>311 – 521 mg/L</td>
<td>400 mg/L</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>8.06</td>
<td>8.06</td>
</tr>
</tbody>
</table>

The laboratory solutions were formulated using calcium chloride dihydrate, sodium chloride, sodium sulfate decahydrate sulfate, and sodium bicarbonate. Once each solution was mixed, the pH was adjusted as needed using NaOH. Appropriate concentrations of the inhibitor
were added to this base chemistry. The inhibitor concentrations selected ranged from 0 to 12ppm of inhibitor, bracketing the 6ppm recommended by GE Betz.

Electrochemical testing was conducted utilizing a Gamry PC4/750 potentiostat and associated control software. Each sample was allowed to stabilize for 1 hour in solution prior to electrochemical testing. Anodic polarization was performed by starting 30mV cathodic of the open circuit potential at a scan rate of 0.1667mV/s. Cathodic experiments were performed with the same scan rate, initiating from a potential 30mV anodic of the open circuit potential. Samples were 12mm diameter, 7.95mm height, 1018 carbon steel (total exposed area of 3 cm²). Each sample was polished to a dry 600 grit finish on a lathe prior to performing a test. Anodic and cathodic experiments were performed for each inhibitor concentration (0, 3, 6, 9, and 12ppm) and each rotation rate (1500, 3500, and 5000rpm) at two temperatures (70°F and 90°F). A freshly polished sample was used for each experiment.

Flow Loops – Design and Operating Conditions

A flow system was designed and constructed to allow for simulation of the conditions present within an actual oil cooler. The flow rates, internal (tube side) and external (shell side) temperatures were selected based upon the typical operating conditions within an actual system. The flow rate within the tubes was provided by DM (an HTRI report), and were maintained at 6gpm for each tube segment. Initially, the temperatures which we planned to select were ones which represented the worst case in terms of corrosion and fouling – as such, we attempted to identify the location within the oil coolers that was most heavily attacked. However, analyses performed by DM/SPR indicated that the corrosion/fouling was relatively uniform within the tubing (i.e., no region is worse than any other). As such, test conditions were selected to bracket those which exist at various positions within the actual oil coolers. Temperatures were selected (combination of tube and shell side temperatures) which captured the conditions at the hot side (oil inlet, water outlet) and cool side (water inlet, oil outlet) of the heat exchanger during the summer (since temperatures would be higher at that time, exacerbating any corrosion processes taking place). The temperatures corresponding to the hot and cold side of the oil coolers were a tube side temperature of 95°F and shell side temperature of 120°F for the former, and a tube side temperature of 85°F and shell side temperature of 95°F for the latter.

As mentioned previously, the oil coolers at each of the SPR sites are once through systems – in other words, the water which passes through the heat exchangers only passes through once – it is not a loop. This creates a challenge for a laboratory scale system, as in order to operate in the same manner, a prohibitively large quantity of water would need to be kept on hand. As an example, at a flow rate of 6gpm, the system would require 8640 gallons per tube segment per day – corresponding to 777600 gallons per tube for the total 90 day operating time of the system – clearly this was not feasible. As such, a closed loop, recirculating system was designed and constructed. In this system, the initial solution chemistry was identical to that present within an actual heat exchanger (i.e., source water taken from the SPR site). As time progressed, the solution chemistry was periodically monitored and adjustments made to maintain this similarity (e.g., chemical additions, filtering corrosion product particulates, etc.).
An overall schematic of the system is presented in Figure 2 (a pictoral walk-around of the system is presented in Appendix 1). The system is a closed loop, recirculating system which allowed the temperature, water chemistry, and flow rate to be controlled as a function of time. Instrumentation to monitor the corrosion performance of each tubing material was also incorporated into the system. The overall system consisted of twelve tube side loops (where a chemistry similar to the source water at the Bryan Mound and West Hackberry sites was maintained), and two shell side loops (which maintained a shell side temperature equivalent to the that of a typical oil temperature in the actual oil coolers). Each shell side loop controlled the temperature of six tube side loops.

Each shell side loop (Figure 3) consisted of three primary components – the main exposure tank, a heat exchanger, and a circulation pump. Water was pumped through the heat exchanger, where its temperature was adjusted appropriately. The heat exchanger utilized processed hot water from the building, and the degree of flow (and hence heating) was regulated via a three way valve associated PID controller. After passing through the heat exchanger, the water passed through the main exposure tank, across the tube side loops, and was then pumped back through the heat exchanger. Each shell side loop contained approximately 48 gallons of deionized water with 200ppm of a phosphate corrosion inhibitor (to minimize external attack of the tube segments).
The tube side loops (Figure 4) contained the SPR source water chemistry (from the West Hackberry or Bryan Mound site). Each tube side loop consisted of a stabilization tank, a pump, a heat exchanger, and a manifold which contained the metal tubing being evaluated by each loop. The stabilization tank was used to maintain a large volume of solution, and was where all solution sampling and augmentation took place. In addition, a gas dispersion tube was present in each tank, and air was continuously bubbled through the tank to ensure that the oxygen concentration was not depleted over time. Water was pumped from the stabilization tank, through a heat exchanger to set the desired tube side temperature. The heat exchanger utilized processed chilled water from the building along with a three way valve and associated PID controller. Once brought to temperature, the water was pumped through a manifold containing tubes of the desired metallurgy, then returned to the stabilization tank. Each manifold contained, in addition to the tube segments being evaluated, a corrosion sensor and ports for thermocouples. The water temperature and flow rate were monitored and maintained throughout the test. Each tube side loop contained approximately 32 gallons of solution which was either used as is, or with the addition of the previously described inhibitor and anti-foulant chemistry.

Flow Loops - Solution Chemistry

To ensure that the water used in this study was as close as possible in composition to that present at both the West Hackberry and Bryan Mound sites, actual site water was used. 600 gallons were obtained from each site prior to initiation of the test. The water was taken at a single time then shipped to Sandia. It should be noted that the water chemistry utilized in this test represents a snapshot in time – in other words, it is representative for the site at the time it was taken. It does not account for temporal variations in the solution chemistry due, as an example, to action of the tides at the Bryan Mound site. Speaking specifically to the Bryan Mound water, the sample used for this experiment was indicative of river water, and as such had
Figure 4: Schematic of a single tube side loop containing the water chemistry relevant to each SPR site

A lower chloride level than during times where the tides have reversed flow in the channel. As a result, some components, such as calcium, will be higher than average, while others, such as chloride will be lower – the resulting solution is less corrosive (potentially significantly so), but with a larger potential to cause calcium fouling within the oil coolers.

A follow-up test to examine the potential for calcium fouling in the Bryan Mound water at peak calcium levels was also performed. In this case, the as-received Bryan Mound water was increased to the historical maximum calcium (400ppm), sulfate (1900ppm), and bicarbonate (125ppm) levels using calcium chloride, sodium sulfate, and sodium bicarbonate.

Flow Loop - Testing/Data analysis methods

A variety of techniques were utilized to assess the corrosion performance of each material during and upon completion of the test. They include:

1. CorrPro corrosion sensors in each flow loop allowed real time assessment of the corrosion rate as a function of time

2. Measurement of temperature and flow performance of each flow loop as a function of time

3. Post test dissection of each tube to establish the nature, and determine the extent of the observed corrosion
4. Mathematical assessment of thermal performance degradation as a function of time (i.e., impact of corrosion product on both flow rate and overall thermal performance of the system)

Results/Discussion

Rotating Cylinder Electrode Inhibitor Study

The anodic and cathodic kinetics of 1018 carbon steel, similar in composition to the steel presently within the SPR oil coolers, was evaluated utilizing rotating cylinder electrodes in a series of environment/temperature combinations which simulated the conditions present within an actual oil cooler. Corrosion inhibitor levels which bracket those recommended by the manufacturer were selected in an effort to verify their specification, and ensure that higher or lower concentrations would not result in increased performance of the inhibitor package. Initial experiments performed with the corrosion inhibitor both with and without the anti-fouling agent established that the anti-fouling agent did not have a statistically significant impact on the electrochemical behavior of carbon steel in the inhibited solution. The anti-fouling agent was therefore excluded from the remainder of the RCE tests to simplify the experiment.

Potentiodynamic polarization experiments were performed on electrodes at rotation rates of 1500, 3500, and 5000 rpm, corresponding to fluid velocities of 150, 250, and 350 cm/s, respectively – bracketing the nominal operating velocity of 264 cm/s for an actual oil cooler. Inhibitor concentrations of 0 (baseline), 3, 6, 9, and 12ppm were evaluated at temperatures of 70°F and 90°F as detailed above. The polarization curves are presented in Appendix 2. Below is a summary of the pertinent results from each experiment. Note that only a single experiment was performed at each condition – as such, the data should be considered to be a more qualitative assessment of the relative performance of each inhibitor solution, rather than the definitive result.

West Hackberry, 70°F

1500 rpm
While insufficient data is available above and below the open circuit potential to allow for direct measurement of the corrosion current density, it can be assessed qualitatively. In this case, the corrosion current density was observed to decrease as the inhibitor concentration increased. The open circuit potential was driven in the anodic (less negative) direction as the inhibitor was increased in concentration to 9 ppm, then shifted in the cathodic direction. The general shape of the anodic curve was changed as the inhibitor concentration increased, with the slope increasing as the concentration did. The oxygen reduction kinetics were increasingly suppressed as the inhibitor concentration increased from 3 to 6 ppm, then began to recover at 9 and 12 ppm (which were comparable to one another). The kinetics of water reduction appeared to be unchanged by the inhibitor for all concentrations.
3500 rpm
Qualitatively, as with the 1500 rpm experiments, the corrosion current density decreased with increasing inhibitor concentration. The open circuit potential was also impacted by the inhibitor, but the limited data set presented here did not reveal any trends with concentration. The impact of increasing inhibitor concentration on both the anodic and cathodic kinetics was similar to that observed at 1500 rpm. Again, suppression of the oxygen reduction kinetics was maximized at 6 ppm, then dropped off as the concentration was increased.

5000 rpm
Qualitatively, as with the 1500 and 3500 rpm experiments, the corrosion current density decreased with increasing inhibitor concentration. The open circuit potential was also impacted by the inhibitor, but the limited data set presented here did not reveal any trends with concentration. The impact of increasing inhibitor concentration on both the anodic and cathodic kinetics was similar to that observed at 1500 rpm. The magnitude of the difference between the 6ppm and the 3, 9, or 12 ppm concentrations on the oxygen reduction reaction kinetics was more dramatic than at other concentrations.

West Hackberry, 90°F

1500 rpm
Qualitatively, the corrosion current density appeared to be largely unchanged by the inhibitor. The open circuit potential for samples in inhibited solutions was shifted, but the limited data set presented here did not reveal any clear trends. The overall shape of the anodic polarization curve was unchanged by the inhibitor (just shifted in potential). The oxygen reduction kinetics were increased at low concentrations of inhibitors (at 3 and 6 ppm for low overpotentials), and decreased at higher concentrations (9 and 12 ppm). The water reduction kinetics were unchanged by the inhibitor.

3500 rpm
As with the 1500 rpm experiments, qualitatively the corrosion current density appeared to be largely unchanged by the inhibitor. The open circuit potential for samples in inhibited solutions was shifted, but the limited data set presented here did not reveal any clear trends. The overall shape of the anodic polarization curve was unchanged by the inhibitor (just shifted in potential). The oxygen reduction kinetics were suppressed at higher concentrations (9 and 12 ppm). The water reduction kinetics were unchanged by the inhibitor.

5000 rpm
Qualitatively the corrosion current density was reduced with increasing inhibitor concentration. The open circuit potential was driven in the anodic (less negative) direction as the inhibitor was increased in concentration to 9 ppm, then shifted in the cathodic direction. The overall shape of the anodic polarization curve was unchanged by the inhibitor (just shifted in potential). The oxygen reduction kinetics were slightly suppressed at 9 ppm then more dramatically suppressed at 12 ppm. The water reduction kinetics were again unchanged by the inhibitor.
Bryan Mound, 70°F

1500 rpm
Qualitatively, the corrosion current density was decreased by the presence of the inhibitor, but the magnitude of the effect did not increase markedly with concentration. The open circuit potential was shifted more anodic by the inhibitor, but as before, the limited data set presented here was insufficient to identify any trends with concentration. The slope of the anodic polarization curve decreased with inhibitor concentrations of 3 and 6 ppm, then began to increase as the concentration increased to 9 and 12 ppm. The oxygen reduction kinetics were suppressed at 9 and 12 ppm concentrations of inhibitor. The water reduction kinetics did not appear to be impacted by the presence of the inhibitor.

3500 rpm
Qualitatively, the corrosion current density was decreased by the presence of the inhibitor, but the magnitude of the effect did not increase markedly with concentration. The open circuit potential was shifted more anodic by the inhibitor, with the effect being largest at 3 and 6 ppm, then becoming increasingly cathodic at 9 and 12 ppm. The shape of the anodic polarization curve was largely unchanged by the inhibitor. The oxygen reduction kinetics were increased for low overpotentials at 3 ppm of inhibitor, unchanged (relative to the baseline) for 6 ppm, then suppressed slightly at 9 and 12 ppm of inhibitor. The water reduction kinetics appeared to be decreased as the concentration of inhibitor increased.

5000 rpm
Qualitatively, the corrosion current density was decreased by the presence of the inhibitor, but the magnitude of the effect did not increase markedly with concentration. The open circuit potential was shifted more anodic by the inhibitor, with the effect being largest at 3 and 6 ppm, then becoming increasingly cathodic at 9 and 12 ppm. The slope of the anodic polarization curve was increased by the presence of the inhibitor, but the magnitude of the increase was independent of concentration. The oxygen reduction kinetics were unchanged at 3 ppm and 6 ppm of inhibitor, then increasingly suppressed for 9 and 12 ppm of inhibitor. The water reduction kinetics appeared to be unchanged.

Bryan Mound, 90°F

1500 rpm
Qualitatively, the corrosion current density appeared to increase with increased concentration of inhibitor. The open circuit potential was shifted anodically by the presence of the inhibitor, but no trends were revealed by the limited data set presented here. The shape of the anodic polarization curve was unchanged by the presence of the inhibitor. Oxygen reduction kinetics were increased by the presence of the inhibitor, but the magnitude of the change appeared to be independent of concentration. The water reduction kinetics were unaltered by the presence of the inhibitor.
3500 rpm
Qualitatively, the corrosion current density appeared to decrease as the inhibitor concentration increased. The slope of the anodic polarization curve was unchanged for all concentrations save 12 ppm, at which point it was decreased significantly. The oxygen reduction kinetics were increased for 3 and 6 ppm, then decreased slightly at 9 ppm and significantly at 12 ppm of inhibitor. The water reduction kinetics were unaltered by the presence of the inhibitor.

5000 rpm
Qualitatively, the corrosion current density appeared to decrease as the inhibitor concentration increased. The slope of the anodic polarization curve was unchanged for all concentrations save 12 ppm, at which point it was decreased significantly. The oxygen reduction kinetics were increased for 3 and 6 ppm, then decreased slightly at 9 ppm and significantly at 12 ppm of inhibitor. The water reduction kinetics were unaltered by the presence of the inhibitor.

Although the dataset presented above was limited in size (with a single experiment performed at each combination of base water chemistry, inhibitor concentration, and temperature), it can be used to qualitatively assess the performance of the inhibitor package recommended by G.E. Betz. The results have demonstrated that deviating markedly from 6 ppm (either above or below) can result in increased electrochemical activity under a variety of different environmental conditions. As such, it appears that the recommendation of 6 ppm is a sound one.

Corrosion Sensors

Corrosion sensors made of a carbon steel similar in composition to the carbon steel tubing were placed into the exit manifold for each of the 12 flow loops. The corrosion rate was monitored using a commercially available LPR (linear polarization resistance) probe. The standard probe design was used for carbon steel, while custom sensors were fabricated (by the

Figure 5: Corrosion sensor data for carbon steel in each solution chemistry.
manufacturer) for the superferritic stainless steel. The results are presented in Figure 5.

As can be seen in the figure, in the case of the low temperature loops, the corrosion rate for all of the carbon steel samples (independent of the presence of inhibitor) initiated at 30 mpy, and then gradually changed with time. For West Hackberry, the corrosion rate gradually increased, stabilizing at a rate of 80 mpy for untreated water, and 50 to 60 mpy for the treated water. The samples in Bryan mound water decreased to approximately 15 mpy (both inhibited and uninhibited). The corrosion rate of the SeaCure material was effectively zero in both Bryan Mound and West Hackberry water.

In the high temperature loops, the samples exposed to West Hackberry had an initial corrosion rate of 30 mpy, then gradually increased to 150 mpy in the raw water and 60 mpy in the treated water. The Bryan mound samples behaved similarly to the low temperature case, with the corrosion rate again stabilizing at approximately 15 mpy (both with and without the presence of the inhibitor). Once again, the corrosion rate of the SeaCure material was effectively zero in both Bryan Mound and West Hackberry water.

Of primary concern in the operation of the heat exchangers is the remaining wall thickness in each tube section. While the corrosion rate data does not in and of itself provide this information, the average reduction in wall thickness as a function of time can be estimated based upon those results. In Figure 6, the average depth of corrosion as a function of time is presented. In each case, the depth was calculated assuming that the corrosion rate was constant and equal to the previous measurement for the time periods between measurements. Considering the nature of the corrosion rates as presented above, this is a reasonable assumption to make, and the resulting calculation should thus be reasonably accurate. As can be seen in the figure, the average depth of corrosion increases linearly with time. If the data for each flow loop is extrapolated to 180 days (the time of a single drawdown procedure), the following average corrosion depths and percent metal losses (based on calculated original and post measured weights of the corroded carbon steel tube samples) are achieved.

Figure 6: Average depth of corrosion as a function of time (calculated from corrosion sensor data)
<table>
<thead>
<tr>
<th>Water Chemistry</th>
<th>Corrosion Depth (mils)</th>
<th>% Mass Loss (60 days)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60 Days</td>
<td>180 Days (Estimate)</td>
<td>ERW</td>
</tr>
<tr>
<td>West Hackberry, Low temperature, untreated</td>
<td>10.8</td>
<td>32.4</td>
<td>11.4</td>
</tr>
<tr>
<td>West Hackberry, Low temperature, inhibited</td>
<td>9.6</td>
<td>28.8</td>
<td>5.8</td>
</tr>
<tr>
<td>Bryan Mound, Low temperature, untreated</td>
<td>3.1</td>
<td>6.3</td>
<td>3.2</td>
</tr>
<tr>
<td>Bryan Mound, Low temperature, inhibited</td>
<td>2.5</td>
<td>7.6</td>
<td>2.3</td>
</tr>
<tr>
<td>West Hackberry, High temperature, untreated</td>
<td>19.2</td>
<td>57.6</td>
<td>14.5</td>
</tr>
<tr>
<td>West Hackberry, High temperature, inhibited</td>
<td>11.4</td>
<td>34.2</td>
<td>10.6</td>
</tr>
<tr>
<td>Bryan Mound, High temperature, untreated</td>
<td>2.6</td>
<td>7.9</td>
<td>6.0</td>
</tr>
<tr>
<td>Bryan Mound, High temperature, inhibited</td>
<td>2.4</td>
<td>7.2</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Upon completion of the first 60 days of testing, each of the corrosion sensors were removed and photo documented, the results of which are presented in Appendix 3. The extent of the attack observed was in agreement with the LPR data taken throughout the test. It should be stressed, however, that the attack was not completely uniform in nature – as such, measures of the average reduction in cross section or overall weight-loss may be a poor representation of the true depth/severity of corrosion. Furthermore, as the corrosion progressed, the effective surface area of the probes themselves was changed due to thinning of the probes coupled with the non-uniformity of the corroded surface. As such, the exactness of the reported data will decrease as the electrodes are attacked (i.e., the calculation of corrosion rate from the Corrater instrument assumes a certain sample geometry and surface finish – deviations from that can result in inaccuracies in the reported corrosion rate).

Though not pictured in the appendix, the SeaCure samples appeared the same as they had when they were inserted into the system – no visual attack or discoloration had occurred.

Flow loop corrosion

While the information obtained from the corrosion sensors is very useful, it can not simply be assumed that the measured value is in fact representative of the actual tube segments without performing a physical inspection of the tube walls themselves. As such, tube samples were extracted for each of the carbon steel materials in all of the environments evaluated in this study. Once removed from the test system, a 2 inch segment was cut from the center of each tube and then split longitudinally. The exposed surfaces were then photo documented, after which the copious corrosion product deposits were removed, and the base metal surface again photo documented. The results are presented in Appendices 4 and 5 for the 60 and 90 day data, respectively. As can be seen in the figures, corrosion in the West Hackberry solution was highly localized in nature, with numerous pits visible across the surface. The resulting corrosion product deposit was similarly rough and non-uniform (the surface was locally rough, but the roughness was uniform throughout the tube) the high and low temperature samples were similar in appearance, though the number of sites was reduced somewhat by the presence of inhibitor. In the Bryan Mound solutions, the surface appeared similar in both the treated and untreated solutions at both low and high temperature. The resulting corrosion product was smoother and more uniform in appearance than that observed on samples exposed to West Hackberry water.

Once the corrosion product was removed, a cross sectional analysis was performed on several of the more severely attacked loops, the results of which are presented in Appendix 6.
As can be seen in the figures, the depth of attack in the deepest pits (captured in the appendix) approaches 40% of the remaining wall thickness. In the case of the seamless (i.e., unwelded) tubing, the attack is in the form of a uniform, hemispherical–type pitting. However, in the case of the ERW tubing, this attack is more knife-line like in nature, along the entire length of the weld region. Based upon the results observed at 60 days, it is not unreasonable to expect perforation to occur before the 180 days of a complete drawdown in the case of the West Hackberry water. The Bryan Mound solutions (not pictured here) exhibited a lesser degree of attack, and at this point it appears less likely that perforation would be a risk over the course of a drawdown.

As with the observations made of the corrosion sensors, it should again be stressed that the attack was nonuniform in nature – as such, measures of the average reduction in cross section or overall weight-loss may be a poor representation of the true depth/severity of corrosion. To further illustrate this effect, the depth of localized attack was measured using a digital micrometer equipped with pin anvils. Figure 7 illustrates the results obtained after 60 days of operation. As was seen in the pictures referenced above, the corrosion which occurred at a given point along the tube can be grouped into three general categories – high areas (minimal

![Figure 7: Depth of attack as a function of environmental conditions (60 day data)](image)
attack), low areas (significant, general attack) and pits (significant, local attack). Also indicated on the figure is the maximum depth of attack allowed in order to ensure that the system will be able to contain the operating pressures for the Bryan Mound and West Hackberry sites. As can be seen, there are situations after only 60 days of operation where the depth of attack is sufficient to potentially result in failure of a tube section. Figure 8 shows the maximum pit depth at 60 days (same information as previous figure) as well as the 90 day data. At this point (corresponding to half of a full drawdown cycle) there are numerous material combinations which are at high risk for failure – both with and without the presence of the inhibitor.

Though not pictured in the appendix, the SeaCure samples appeared the same as they had when they were inserted into the system – no visual attack or discoloration had occurred.

**Inhibitor Performance**
As can be seen from the data presented above, the corrosion inhibitor did have a positive effect on both the corrosion rate as measured by the LPR sensors as well as the overall extent of corrosion as demonstrated in the weight loss. The table below presents the % improvement achieved in each case.

<table>
<thead>
<tr>
<th>Water Chemistry</th>
<th>Reduction Achieved by Inhibitor</th>
<th>Overall Weight Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>West Hackberry, Low Temperature</td>
<td>12%</td>
<td>49%</td>
</tr>
<tr>
<td>West Hackberry, High Temperature</td>
<td>19%</td>
<td>29%</td>
</tr>
<tr>
<td>Bryan Mound, Low Temperature</td>
<td>40%</td>
<td>27%</td>
</tr>
<tr>
<td>Bryan Mound, High Temperature</td>
<td>8%</td>
<td>29%</td>
</tr>
</tbody>
</table>

However, as discussed above, the nature of the corrosion that the tubing underwent was not general in nature, but was instead localized (i.e., pitting). Thus it is necessary to evaluate the impact that the inhibitor had on a measure of the degree of localized attack, rather than the overall amount of corrosion that occurred. Looking at the samples themselves (see Appendices 1, 2, and 3), while the number density of pitting/localized attack locations was decreased by the inhibitor, the apparent depth of specific sites was not. Thus the risk of perforation of the tubing, as well as reduction in tubing strength, was not substantially improved by the corrosion inhibitor.

**Heat exchanger thermal and flow performance**

The physical effects of pitting (localized corrosion), wall recession (general corrosion), and iron oxide buildup (fouling with corrosion product) were evaluated for each tube segment in order to estimate the average physical dimensions and composition of the heat exchanger tube walls. This information was used to calculate heat transfer and fluid flow pressure drops for each combination of material and environment. The information from the high and low temperature tube samples were combined to estimate heat transfer and pressure losses at the log mean temperatures that reflect the overall performance of the site oil coolers. A critical consequence due to fouling is the reduction in flow capacity. According to the site systems engineer, the oil coolers can accommodate a factor of four reduction in operating pressure (due to fouling) relative to the initial operating pressure. In the calculations, it was assumed that full flow was maintained for pressure increases up to four times initial conditions. Reduction in flow result in further reduction in heat transfer ability of the oil coolers. This reduction is shown in the table below. The overall heat transfer of the stainless steel tube and the fouled carbon steel tubes are compared to a clean carbon steel tube. If oil temperatures are borderline, continued fouling may not allow sufficient cooling of the delivered oil. Note that full flow can be maintained through the inhibited BM carbon steel samples with flow reductions of 6 to 17 percent for the uninhibited BM samples, whereas flow would be reduced from 28 to 43 percent through the WH carbon steel samples regardless of treatment. As corrosion and fouling was not observed for the SeaCure stainless steel tube samples, there was no corresponding degradation of heat transfer, fluid flow, and pressure loss.
Structural Evaluation

As corrosion progresses and the tube walls thin, their ability to contain the pressures associated with normal operation of the oil coolers will also be diminished. Calculations were made (by Charlie Deluca, DM) to determine the minimum thickness required to contain these operating pressures, and these values were then compared to the minimum wall thickness anticipated based upon the corrosion rates determined by the LPR sensors (summarized in the table below).

<table>
<thead>
<tr>
<th>Water Chemistry</th>
<th>Corrosion Depth 180 day est. (mils)</th>
<th>Minimum Wall Thickness (mils)</th>
<th>Required Wall Thickness (mils)</th>
</tr>
</thead>
<tbody>
<tr>
<td>West Hackberry, Low temperature, untreated</td>
<td>32.4</td>
<td>38.7</td>
<td>55.5</td>
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<tr>
<td>West Hackberry, Low temperature, inhibited</td>
<td>28.8</td>
<td>42.3</td>
<td>55.5</td>
</tr>
<tr>
<td>Bryan Mound, Low temperature, untreated</td>
<td>6.3</td>
<td>64.8</td>
<td>48</td>
</tr>
<tr>
<td>Bryan Mound, Low temperature, inhibited</td>
<td>7.6</td>
<td>63.5</td>
<td>48</td>
</tr>
<tr>
<td>West Hackberry, High temperature, untreated</td>
<td>57.6</td>
<td>13.5</td>
<td>55.5</td>
</tr>
<tr>
<td>West Hackberry, High temperature, inhibited</td>
<td>34.2</td>
<td>36.9</td>
<td>55.5</td>
</tr>
<tr>
<td>Bryan Mound, High temperature, untreated</td>
<td>7.9</td>
<td>63.2</td>
<td>48</td>
</tr>
<tr>
<td>Bryan Mound, High temperature, inhibited</td>
<td>7.2</td>
<td>63.9</td>
<td>48</td>
</tr>
</tbody>
</table>

As can be seen in the table, the resulting wall thicknesses for the loops containing West Hackberry water are below the minimum thickness required. As such, stress induced rupture of these pipes is likely. In the case of the Bryan mound containing loops, the resulting wall thicknesses are 15 to 16 mils thicker than the minimum required, indicating that they should be able to contain normal operating pressures. However, considering the localized nature of the attack observed in this study, particularly for the ERW tubing, it is possible that there will be regions where the depth of attack is 15 mils or more deeper than the average depth of attack. As such, the potential does exist for stress-induced rupture of the tubing exposed to Bryan Mound water, even though the degree of general attack suggests that all is well.

Calcium Fouling

A follow-up test to examine the potential for calcium fouling in the Bryan Mound water at peak calcium levels was also performed. In this case, the as-received Bryan Mound water was increased to a higher than average calcium (400ppm), sulfate (1900ppm), and bicarbonate (125ppm) levels using reagent grade calcium chloride dihydrate, sodium sulfate heptahydrate, and sodium bicarbonate. The solutions in tanks 8 (SeaCure), 11 (carbon steel – untreated) and 12 (carbon steel – inhibited) were augmented, and 3 new segments of carbon steel (seamless) were placed in tanks 11 and 12. The SeaCure samples were unchanged. In addition to augmenting the solution chemistry, the tube side water temperature was reduced to 70°F to
obtain a 50 degree temperature differential with the tube walls. Samples were exposed to solution for approximately 40 days. The solution chemistry was maintained throughout the test, with significant additions being required for the carbon steel containing solutions (both inhibited and uninhibited required similar additions). The SeaCure bath, on the other hand, required very little additional solution adjustment.

Upon completion of the test, the samples were removed, and the deposits analyzed using the same procedures defined previously. In the case of the carbon steel samples, a thin, smooth deposit formed on all of the tubes. This deposit was light brown in color, and considerably more uniform than that observed in the unaugmented Bryan Mound samples. The uninhibited solution had a somewhat courser appearance than samples from the inhibited bath, owing to the localized attack which occurred in some locations along the tube surface. The SeaCure sample also had a very thin, white deposit on the tube wall. This coating was reasonably uniform and was visible both on the tube walls as well as the corrosion sensors.

**Summary of Results**

1. Rotating cylinder experiments illustrated that the 6ppm concentration of inhibitor recommended by the material supplier was a valid choice. Deviating from this concentration in either direction resulted in increased attack under certain specific conditions.

2. Water from the Bryan Mound and West Hackberry sites was obtained, and all testing was performed using this water. In the case of the Bryan Mound water, the measured chloride level suggests that the sample was not taken during high tide. As such, the resulting solution is less corrosive than it would be during high tide when the chloride concentration would be considerably higher.

3. No corrosion was observed on the SeaCure material in any of the environments evaluated in this study, and as such no reduction in either thermal or flow performance would be anticipated.

4. Considerable corrosion of both the ERW and seamless carbon steel was observed in West Hackberry water. The corrosion was both general and localized (pitting) in nature. The ERW tubing was selectively attacked along the entire weld line, the depth of attack approaching the depth of the deepest pits. Though the inhibitor did reduce the attack, the overall extent was still very significant.

5. The estimated wall thickness at 180 days for the carbon steel tubes in West Hackberry water is thinner than what is required to contain the maximum operating pressure of the oil coolers.

6. In Bryan Mound water, attack was predominantly general in nature (though some localized attack was observed), and overall much less severe than was observed in the West Hackberry water. Some localized attack (pitting) was observed, as well as selective
corrosion of the weld line in the ERW tubes. The inhibitor had a negligible impact on the overall degree of corrosion.

7. The estimated wall thickness at 180 days for the carbon steel tubes in Bryan Mound water is only 10 mils greater than what is required to contain the maximum operating pressure of the oil coolers. Given the localized nature of the attack, it is likely that the wall will be thinner than this limit in some locations, introducing a substantial potential for pressure-induced failure.

8. The corrosion resulting from a 60 day exposure to untreated West Hackberry water would result in an 11 to 61% decrease* in thermal efficiency and a 40% reduction in flow rate of the heat exchanger for ERW carbon steel tubing, and an 8 to 55% reduction* in thermal performance and a 28% reduction in flow performance for seamless carbon steel tubing.

9. The corrosion resulting from a 60 day exposure to treated West Hackberry water would result in a 12 to 61% decrease* in thermal efficiency and a 43% reduction in flow rate for ERW carbon steel tubing, and a 10 to 58% reduction* in thermal performance and a 34% reduction in flow rate for seamless carbon steel tubing.

10. The corrosion resulting from a 60 day exposure to untreated Bryan Mound water would result in a 6 to 47% decrease* in the thermal efficiency and a 17% reduction in flow of the heat exchanger for ERW carbon steel tubing, and a 4 to 41% reduction* in thermal performance and a 6% reduction in flow for seamless carbon steel tubing.

11. The corrosion resulting from a 60 day exposure to treated Bryan Mound water would result in a 2 to 28% decrease* in thermal efficiency, with no reduction in flow rate for ERW carbon steel tubing, and a 1 to 23% reduction* in thermal performance and no reduction in flow rate for seamless carbon steel tubing.

12. In all conditions, the SeaCure superferritic stainless steel dramatically outperformed both the seamless and ERW carbon steel (both with and without the inhibitor and anti-foulant present) in terms of corrosion performance and the long term preservation of thermal efficiency.

* The thermal degradation is anticipated to be near the lower percent value based upon the measured 5 to 10% decreases in oil cooler heat transfer capacity during operation of the systems at Bryan Mound and West Hackberry respectively per the site systems engineer.

**Conclusions**

From the data acquired thus far, a number of conclusions can be made in terms of the corrosion performance of the system.

1. The inhibitor package, while it did reduce the measured corrosion rate in the case of the West Hackberry solutions, did not provide a sufficient reduction to justify its use.
While the overall extent of corrosion was reduced, the resulting magnitude and depth of localized attack that was observed still presented the potential for tubing perforation and substantial reductions in tubing strength. In addition, use of an inhibitor would be logistically difficult as it would have to be stockpiled and monitored (to ensure activity) over time.

2. The corrosion rate in West Hackberry, both at low and high temperatures, is sufficiently high that it is reasonable to expect the carbon steel tubes to perforate in a single drawdown procedure. Furthermore, based upon the estimated degree of corrosion at 180 days, the tubing will not be capable of containing the required pressures without bursting.

   The depth of localized attack which was observed was such that perforation of the tube walls would likely result within a 180 day drawdown procedure. In addition, considering the average rate of wall recession (from LPR measurements), the tubing wall thickness remaining after 180 days would be less than that required to contain the operating pressures of the oil coolers.

3. The corrosion rate, as well as the nature of the observed attack in Bryan Mound indicated that there was a smaller risk of corrosion perforation during a drawdown procedure.

   Overall rate of general corrosion, as well as localized attack, suggest that the depth of attack will not be sufficient to result in corrosion perforation (i.e., a pit completely through the tube wall) in the oil coolers, or thinning of the average tube wall thickness to below what is required to contain normal operating pressures. However, it should be noted that the localized attack (esp. attack along a weld line in an ERW tube) combined with the internal operating pressures which the system can see may result in stress-induced failure of the structure - the localized attack would be acting as a stress riser, resulting in crack initiation.

4. Based upon the results obtained to date, it appears unlikely that the carbon steel based oil coolers presently in service are capable of effective operation in the event of a full-scale drawdown.

   The extent of attack observed in this study will likely be less severe than that which would be present in a field system operated for a similar time period due to the presence of pre-existing corrosion damage within the actual oil coolers. As such, because the data obtained here suggests a new system would run the risk of corrosion perforation, as well as the inability to contain the normal operating pressures of the oil cooler, a pre-corroded system would be even less likely to be able to do so.

Recommendations – Application of Project Results

1. Due to the corrosion rate observed for carbon steel in both West Hackberry and Bryan Mound source water, it is clear that carbon steel (both ERW and seamless) is inappropriate for application in the oil coolers in both environments, and should be replaced with a more suitable alternative such as SeaCure.
2. The inhibitor chemistry evaluated in this study is not suitable for use in this application. While there are other chemistries available which may prove to be more effective (note, however, that the chemistry evaluated here was recommended by individuals skilled in inhibitor selection, and as such may have been the best potential choice), due to issues associated with the use of an inhibitor (the need to stockpile inhibitor and ensure it maintains its viability in storage, etc.) it is recommended that inhibitors not be used in the SPR oil coolers.

Project Impact and Future Direction

Throughout the course of this study, the results were provided to DM and SPR to assist in the decision making process. The results of this study, as indicated above, clearly indicated that the currently applied carbon steel was inappropriate for long term use within the oil coolers. DM concurred with this conclusion, and made the recommendation that the replacement of the carbon steel tube bundles with SeaCure was the most appropriate action to take, and furthermore, that the inhibitor chemistry proposed was not able to enhance the performance of the carbon steel to an acceptable level. Their recommendation is presented in Appendix 7.

Once the test program reported here was complete, an effort was made to establish how the newly constructed facility could be applied to address other SPR corrosion concerns. Discussions with SPR resulted in the memo presented in Appendix 8. Although a number of potential future applications were identified, the decision was made not to pursue these avenues, and the system was dismantled.

Acknowledgements

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References


4. SWRI “Determining Decomposition Products of Water Treatment Chemical”, Proj. 01.05093.01.006 (12/28/2001)


Appendix 1

Overview of SNL Flow Loop System
HEAT EXCHANGER TUBE
CORROSION/FOULING EXPERIMENT
LAYOUT PLAN – BUILDING 701 BASEMENT
Overall System view from northwest corner. The stabilization tanks can be seen on the left of the picture, and the low temperature flow loops on the right.

Overall system view from the northeast corner. The high temperature loops can be seen on the left side of the picture, the stabilization tanks and the power panel on the right side.
Overall system view from southwest corner. The stabilization tanks can just be seen on the left side of the picture. The high and low temperature flow loops can be seen on the right side of the picture, along with the equipment utilized to monitor the shell side temperature for each loop as a function of time.

Pump used to control solution flow for the shell side loop – one such pump was used for both the hot side and cold side heat exchangers. The fuse boxes used to protect the equipment in the flow loops are visible at the top of the picture.
Heat exchanger and three-way valve used to control the shell side temperature on the hot side flow loop system. A similar heat exchanger was present on the low temperature shell side flow loop as well. The heat exchangers utilized processed hot water from the building utilities to heat the water in the flow loop.

Overall view of the stabilization tanks. The water return for each loop was on the top of each stabilization tank, and the outlet on the bottom (right side of picture). Air lines were run through the top of each tank to a dispersion tube located inside on the bottom of each tank to ensure that the water remained aerated. Also shown are the power switches used to control the pumps for six of the tube side loops.
View from the center of the system, showing the pumps and valves used to control the flow rate of solution in the 12 tube side loops.

PID controllers and associated temperature sensors, shown here for the high temperature tube side flow loops, were used to monitor and control (via heat exchangers utilizing processed chilled water) the temperature in each loop.
Heat exchangers used to control the temperature in each tube side loop. Each loop had it’s own exchanger, which utilized processed chilled water from the building (whose flow rate was controlled via a three way valve) to control the temperature for each loop.

In addition to the PID controller, the water temperature was monitored (checked) for each of the tube side loops using thermometers and thermal wells which extended into the flow stream.
Each material/environment combination (corresponding to each of the twelve tube side loops) contained a CorrPro corrosion sensor which was utilized to monitor the corrosion rate of each material as a function of time.

CorrPro corrosion sensors used to monitor the corrosion rate as a function of time. The sensor on the top utilized carbon steel rods, while the sensor on the bottom utilized SeaCure stainless steel taken from an actual tube segment. In both cases, the active portion of the sensor is of a known size and geometry, such that the corrosion rate can be calculated from a linear polarization measurement.
The tube segments which were located within each of the two shell side flow loops. Samples are shown here after the first 60 days of the test (at which point the top layer of tubes were removed and analyzed)
Appendix 2

Rotating Cylinder Electrode Polarization Data
West Hackberry, 70°F, 1500rpm

Current Density (A/cm²)

Applied Potential (V_{sce})

Baseline
3 ppm Inhibitor
6 ppm Inhibitor
9 ppm Inhibitor
12 ppm Inhibitor
West Hackberry, 70°F, 1500rpm

![Graph showing Current Density vs. Applied Potential for different Inhibitor concentrations.](Image)

- Current Density (A/cm²)
- Applied Potential (V SCE)

- Baseline
- 3 ppm Inhibitor
- 6 ppm Inhibitor
- 9 ppm Inhibitor
- 12 ppm Inhibitor
West Hackberry, 70°F, 5000rpm

Current Density (A/cm²)

Baseline
3 ppm Inhibitor
6 ppm Inhibitor
9 ppm Inhibitor
12 ppm Inhibitor

Applied Potential (V SCE)

Baseline
3 ppm Inhibitor
6 ppm Inhibitor
9 ppm Inhibitor
12 ppm Inhibitor
West Hackberry, 90°F, 3500rpm

Current Density (A/cm²)

Applied Potential (V_sce)

Baseline
3 ppm Flogard
6 ppm Flogard
9 ppm Flogard
12 ppm Flogard
Bryan Mound, 70°F, 3500rpm

Current Density (A/cm²)

Baseline
3 ppm Flogard
6 ppm Flogard
9 ppm Flogard
12 ppm Flogard

Applied Potential (V_{SCE})

-0.65 to -0.3

Baseline
3 ppm Flogard
6 ppm Flogard
9 ppm Flogard
12 ppm Flogard

Current Density (A/cm²)

1e-9 to 1e-1
Appendix 3

60 Day Corrosion Sensor Photographs
West Hackberry, Low Temperature

Treated

Untreated
Bryan Mound, Low Temperature
West Hackberry, High Temperature
Bryan Mound, High Temperature
Appendix 4

60 Day Tube Wall Photographs
West Hackberry, Low Temperature, Untreated, Seamless
West Hackberry, Untreated, Low Temperature, ERW
West Hackberry, Treated, Low Temperature, Seamless
West Hackberry, Treated, Low Temperature, ERW
Bryan Mound, Untreated, Low Temperature, Seamless
Bryan Mound, Treated, Low Temperature, Seamless
Bryan Mound, Treated, Low Temperature, ERW
West Hackberry, Untreated, High Temperature, Seamless
West Hackberry, Untreated, High Temperature, ERW
West Hackberry, Treated, High Temperature, Seamless
West Hackberry, Treated, High Temperature, ERW
Bryan Mound, Untreated, High Temperature, Seamless
Bryan Mound, Untreated, High Temperature, ERW
Bryan Mound, Treated, High Temperature, Seamless
Appendix 5

90 Day Tube Wall Photographs
<table>
<thead>
<tr>
<th>Material</th>
<th>Solution</th>
<th>Temperature</th>
<th>Inhibitor?</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>SeaCure</td>
<td>Low Temp</td>
<td>---</td>
</tr>
<tr>
<td>1B</td>
<td>SeaCure</td>
<td>Low Temp</td>
<td>---</td>
</tr>
<tr>
<td>1C</td>
<td>SeaCure</td>
<td>Low Temp</td>
<td>---</td>
</tr>
<tr>
<td>2A</td>
<td>SeaCure</td>
<td>Low Temp</td>
<td>---</td>
</tr>
<tr>
<td>2B</td>
<td>SeaCure</td>
<td>Low Temp</td>
<td>---</td>
</tr>
<tr>
<td>2C</td>
<td>SeaCure</td>
<td>Low Temp</td>
<td>---</td>
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<tr>
<td>3A</td>
<td>Seamless</td>
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<td>---</td>
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<tr>
<td>3B</td>
<td>Seamless</td>
<td>Low Temp</td>
<td>---</td>
</tr>
<tr>
<td>3C</td>
<td>ERW</td>
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</tr>
<tr>
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Appendix 6

60 Day Tube Cross Sectional Images
West Hackberry, Low Temperature, Untreated

Seamless, Illustrating depth of attack

ERW, illustrating selective attack at weld line
West Hackberry, High Temperature, Untreated

Seamless, Illustrating depth of attack

![Seamless steel illustrating depth of attack](image1)

ERW, Illustrating selective attack at weld line

![ERW steel illustrating selective attack at weld line](image2)
West Hackberry, High Temperature, Treated

Seamless, Illustrating depth of attack

ERW, illustrating selective attack at weld line
Appendix 7

Memo:
DM Position on HX Tube Replacement
July 29, 2004
60009-PLM-04-0032

Mr. Warren Poarch
United States Department of Energy
Strategic Petroleum Reserve
Project Management Office
900 Commerce Road East
New Orleans, LA 70123

Dear Mr. Poarch:

Subject: Contract No. DE-AE96-03PO92207; DM Position on Replacement of Heat Exchanger Tubes at BM and BC

This letter is written to provide a DM position on whether to keep the replacement of the remaining carbon steel heat exchanger tubes at BM and BC in the 2007-2008 Major Maintenance Budgets. The DM position is that these tube replacements should remain as Major Maintenance Budget items.

Reasons for this recommendation:

1. Significant pitting occurred in carbon steel tubes exposed to Brazos River Water during the Sandia heat exchanger tube test. Localized attack (pitting) occurred on the fresh material utilized in the experiment. The pits observed occurred at a density of 50 to 100 pits per foot after 60 days. For reference, each heat exchanger contains over 50,000 feet of tubing, so that after two months there could potentially be over 5 million points of perforation in each heat exchanger. This pitting density was lowered by the use of water treatment chemicals, but the depth of the pitting was unaffected.

Sandia preliminary test data, as given in their interim report dated November 10, 2003, indicated that on the basis of general corrosion rates the Brazos river water allowed for completion of a drawdown. In calendar year 2004, Sandia further evaluated the tubes from the test for pitting. DM received Figure 1 from Sandia in June 2004 with the results of their analysis which are to be published by September 2004. The pitting represents two months of data. It can be seen from the BM data that for a full six month drawdown.
some pits may extend past the minimal thickness required for the tubes. It is also noted that tubes were new in the Sandia test. The actual tubes in the field are in all likelihood not as pristine as the new tubes used by Sandia. This means that the Sandia test represents a best case scenario. Tubes will only get "less new" with time making pitting more likely over the long run. Quoting from the Sandia draft report: "Due to the corrosion rate observed for carbon steel in both West Hackberry and Bryan Mound source water, it is clear that carbon steel (both ERW and seamless) is inappropriate for application in the oil coolers in both environments, and should be replaced with a more suitable alternative such as SeaCure." Our conclusion is that the long term reliability of carbon steel tubing can be classified as "marginal". Though inhibitors do reduce the risk of developing a pit deep enough to penetrate the tube wall (by reducing the number of pits, not necessarily the pitting depth), it is our position that this risk is not reduced sufficiently to ensure long term performance.

Our earlier assessment of the Sandia test results, briefed in December 2003, was that the BM exchangers would probably be more affected by fouling than by corrosion for a full six month drawdown. Since that time, Sandia has completed their metallurgical examination of the test samples and they have found that pits 0.020 inches deep (approximately 60% of allowable wall losses) were produced within 60-days, despite inhibitor treatment. In fact pitting was more severe with treated than untreated water. One explanation offered by Sandia is that with untreated water general corrosion dominates and pitting is less severe. When the water is treated and general corrosion suppressed, pitting dominates and is far more severe. Sandia's analysis is summarized by Sandia in the following chart.
Nomenclature:
- First letter – tube type (E=ERW, S=Seamless)
- Second Letter – water source (W=West Hackberry, B=Bryan Mound)
- Third letter – loop temperature (L=low temperature, H=high temperature)
- Fourth letter – water treatment (i=inhibited, no letter=untreated)

Figure 1

![Graph showing Depth of Attack (mm) for different material/environment combinations. The graph compares Depth of Attack for 60 Days, Max Depth Bryan Mound, and Max Depth West Hackberry, with different treatments represented by colors.](image-url)
Longer term drawdown risk remains until we correct the deficiency in materials. A planned future change-out to an appropriate material accompanied by continued monitoring of the current carbon steel tubes is a prudent approach to ensure drawdown readiness of the BM and BC exchangers.

2. Sandia also attempted to assess the rate of calcium carbonate deposition in the laboratory test. Sandia was not able to duplicate the deposition visually observed in the field following operation of the exchangers. Calcium was added to the raw water supplied to Sandia from BM in an attempt to enhance deposition. However, deposition did not occur even without the application of deposition prevention chemicals. Our field experience was that, with less than 2 MMB of crude oil processed through the BM Train 2 exchangers, approximately 1500 pounds of iron oxide and 1000 pounds of calcium carbonate had to be chemically removed. Therefore, the lack of calcium deposition experienced during the Sandia test may or may not be representative of an actual drawdown. Chemicals will be added to mitigate the deposition. The planned future change-out to an appropriate material accompanied by continued use of calcium deposition chemicals in the interim is a prudent approach to ensure drawdown readiness of the exchangers.

3. Raw water employed in the Sandia test was relatively low in salt content and biological activity due to the relative freshness of the water in the springtime when the test water was taken from the Brazos River. With salinity and biological activity at other times of the year only likely to be higher, it is not expected that results of an actual drawdown will be better than the test data. Again the current budgeted approach is believed to be most prudent for the long term reliability of these exchanger units.

Patrick Mihalik or Charlie DeLuca can be reached for further details on the Sandia findings.

Sincerely,

G. Brian Tuminello
Director, Operations
& Engineering

Attachments
As stated

cc: W. Gibson FE-44.4
    G. Berndsen FE-4431
    J. Quern FE-4421
    N. Palestina FE-4431
Appendix 8

Memo:
Potential Future Uses of Flow Loop System
date: December 10th, 2003

to: Nick Palestina

from: David Enos and Tom Hinkebein

subject: Potential future applications of the flow loop system at Sandia.

With the completion of the oil cooler simulation experiments, the facility which was designed and assembled to perform that task is now available to be applied towards other SPR issues. This memo serves to outline some of the potential future applications for the flow system. Though many of them will require some modification of the system, these modifications are minor in nature, and would not require much (compared to the investment already made in the system itself) along the lines of resources to complete. These potential applications are discussed below.

Continued evaluation of carbon steel

1. **Calcium fouling study**

   The experimentation conducted to date on calcium fouling using modified water from Bryan Mound failed to reproduce the deposit morphology observed in the field. Furthermore, the single data point which has been obtained does not allow for the assessment of the time dependant growth rate of calcium scale on the tubing surface. To address this, a study using modified water from Bryan Mound (or another site) could be performed, taking care to acquire data on film thickness and composition as a function of time to better understand the fouling process.

2. **Behavior of curved pipe sections**

   To date, all experimentation has been conducted on straight tube segments, two feet in length. While this data is clearly valuable, it may not accurately predict what occurs within a curved section of pipe. There are a number of key differences between the straight and curved sections – namely, increased cold work of the metal itself (resulting in a material more susceptible to corrosion), reduced wall thickness due to the forming process (leading to a lower tolerance of localized attack), and increased potential for flow-assisted corrosion due to the bend. The existing system could be modified to allow for the evaluation of larger, curved segments of tubing.

3. **Provide statistical data for West Hackberry or Bryan Mound water**

   In the initial round of experiments, one loop was used to simulate each pertinent combination of environment and temperature. As such, only a single data point exists for each of the environments evaluated, preventing the effective application of statistical methods to analyze the data. Additional experiments could be performed (using as many as 12 loops for a single environment) to provide the necessary replicate experiments, facilitating the use of statistical methods.
4. Evaluate performance in other water chemistries
   The water samples which were used in the initial experiments were all taken at a single time from each site – as a result, they do not address seasonal variations in water chemistry, variations due to the tides, or any other factors which can significantly alter the aggressiveness of the water. In addition, as the studies performed to date clearly demonstrated the significant differences in corrosivity between two sites waters, it is not unreasonable to assume that similar differences will exist for other site waters. As such, further studies could be conducted in water from other sites. An example is Bayou Choctaw, where the water has been assumed to be benign, but in light of the results from Bryan Mound, may not be.

Evaluation of SeaCure material

1. Calcium fouling study
   Experimentation conducted using the SeaCure material in Bryan Mound water with enhanced calcium, sulfate, and bicarbonate levels has illustrated that calcium scale formation is possible. If this material is to be effectively applied, an understanding of the tendency to form scale, the rate of scale formation, and the ultimate scale thickness which can be achieved on the metal surface would be useful for the determination of maintenance needs (i.e., descaling) of the system itself. Additional experimentation could be performed to establish the kinetics of the scale formation process as well as the nature (composition, adherence, etc.) of the deposit itself, assessing the time-dependant impact which calcium scale would have on the thermal performance of an exchanger composed of SeaCure tubing.

2. Define operating envelope
   The SeaCure material is dramatically more corrosion resistant than carbon steel. However, there are combinations of water chemistry, temperature, and flow rate (or lack thereof) which will result in attack of the SeaCure materials (in the form of pitting). Experimentation could be performed to better understand the electrochemical behavior of the SeaCure material, defining its effective operating window (ensuring that the conditions under which the heat exchangers are used are well within the allowable parameters for the material itself.)

Brine transmission

1. Kinetics of corrosion process for concrete lined steel
   In the past, experimentation aimed at establishing the kinetics of the corrosion reaction occurring at the steel/concrete interface have been less than successful. A potential future use of the flow loop system would be to evaluate hand-toweded concrete lined pipe exposed to flowing brine. This would allow controlled access to the pipe, as well as the application of more sophisticated laboratory techniques than those which have been applied in the past. Experiments could be performed both to determine the kinetics of the corrosion reaction as a function of brine composition and other environmental factors as well as attempt to design sensors which could be placed under the concrete layer to provide information directly related to the electrochemistry occurring at the steel/concrete interface. The results of this potential task would enable both the assessment of the condition of the present pipelines, as well as provide an estimate as to their remaining service life.

2. Kinetics of flow induced corrosion (channeling) in brine pipelines
   Recently, channeling corrosion has been observed during fill of the West Hackberry site. It is unclear why this localized attack is occurring, as Big Hill, which uses nominally the same water chemistry, does not experience this attack. To attempt to determine the factors which control when and to what extent channeling corrosion occurs, the flow loop system could be modified to allow the pipe segments to be exposed to flowing brine containing sediment comparable to that observed at each site. Laboratory based experimental methods could be applied in an effort to determine the nature and kinetics of the corrosion process as a function of environmental parameters, such as solution chemistry and sediment properties.

3. Coating/Lining evaluation for hanging strings
The hanging strings applied at each of the SPR sites, presently constructed using carbon steel, have experienced extensive corrosion within the caverns. The application of protective coatings offers an attractive corrosion mitigation strategy to alleviate the present corrosion issue. The flow loop system could be used to simulate the environment (temperatures and chemistry) of the brine flowing through and surrounding the hanging string, enabling us to assess the corrosion performance of various potential protective coatings.
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