Testing a Low Temperature Application Corrosion Inhibitor in the Upper Mahiao Power Plant Condensates

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ABSTRACT

The power plant condensates coming from the Upper Mahiao Power Plant is highly saturated with dissolved CO$_2$ and H$_2$S gases, making the condensates acidic with and corrosive to the carbon steel pipeline that is used to transport these condensates from a spray tower to the injection wells. Currently, the power plant condensates are treated with caustic soda (NaOH) to raise the fluid pH. At elevated pH level, corrosion is controlled since the corrosive species present are buffered. However, the caustic soda solution is difficult to handle due to its highly corrosive nature. Also, its present cost in the market is escalating. Thus, a low temperature application corrosion inhibitor was tested and dosed at the carbon steel condensate pipeline downstream of the spray tower, to possibly find an alternative corrosion inhibition treatment that is both effective and cost competitive to the current corrosion inhibitor, Upper Mahiao, Upper Mahiao condensates.

Although most of the NCG have been extracted, the power plant steam condensate is gas-saturated with high dissolved gas levels of CO$_2$ and H$_2$S (Villa, 1999). The acidity of the power plant condensate is attributed to these dissolved gases. At this condition, the corrosion rate along the carbon steel condensate pipeline is high and beyond the acceptable limit of 0.12 mm/yr.

2. PREVIOUS WORKS ON UMPP CONDENSATE CORROSION

2.1 Material Testing (1998)

One of the operational problems encountered by the UM FCRS was the long-term disposal of the high amount of acidic steam condensates generated from the power plant. The carbon steel condensate pipeline experienced cracks and leakages after its utilization in 1997. Radiographic and ultrasonic testing (UT) revealed that significant thinning was observed at that section of the pipeline (Villa, 1997). To preclude recurrence of the same problem during condensate injection, a materials test was conducted. Two series of material testing were conducted at static condition, one in high-CO$_2$ environment (steamline) and in low-CO$_2$ environment (condensate line). Results of the material testing validated that the carbon steel is not suitable as it is susceptible to uniform corrosion, pitting and stress corrosion cracking, and that stainless steel is the most resistant materials for acidic condensate such as from UM power plant. It was therefore recommended that the condensate pipeline material must be made-up of stainless steel.

2.2 Corrosion Process Experiment (2003)

After the field material testing, polarization experiments for UM low and high temperature application were conducted to expound the corrosion process on different materials. The polarization curve on the carbon steel revealed that it could not support an adherent protective film that will shield the material from further corrosion. Potential-pH diagram (Pourbaix) also illustrated that the condensate fluid favors the formation of free corrosion products that will promote uniform corrosion along the line. SEM, EPMA, XRD and X-ray Fluorescence analyses of the corrosion samples showed two layers of corrosion products. The bottom layer was identified as pyrite while the upper layer as hydrated ferrous sulfate. The latter corrosion product was believed to form from the H$_2$S dissolved in the condensate that reacted with the steel, aided by atmospheric oxygen thereby initially forming SO$_4^-$ (Villa, 1999). This testing recommended the use of stainless steel with higher amount of Cr and alloyed with a little amount of Ni and/or Mo to make it more resilient for UM application.
Since the degassed condensate after spraying was still corrosive with pitting, this was initially dosed with sodium hydroxide (NaOH) to elevate the pH. At elevated pH, the resulting condensate did not give acceptable corrosion rates and pitting was still observed. Thus, the pH was further elevated achieved by increased NaOH dosing. Corrosion rate was monitored for 30 days in a pilot test at degassed and dosed conditions to elevate pH. Corrosometer probes and coupons were used to measure corrosion rates using four common construction materials: carbon steel, forged steel wellhead material, and two casing materials. Corrosion rates on the degassed condition still gave high corrosion rate with minimal passive film indicated. At the caustic soda dosed condition, corrosion rates rapidly dropped to below the acceptable limit of 0.12 mm/yr. The corrosion coupons also showed formation of tight, adherent and less porous corrosion products which were identified as magnetite and goethite.

2.3 Corrosion Rate Monitoring at On-Line Condition of UM ZEDS Line (2005)

The UM Zero Effluent Disposal System (ZEDS) was commissioned last December 2002. The evaluation of the ZEDS by Sarabia, et al. (2005) was conducted after the installation of new spray nozzles at the spray tower. Improvement in degassing was observed since the basin fluid pH at the spray tower increased after the nozzles replacement with lower corrosion rate measured. The test had the objective of evaluating the corrosion rate of the return condensate at on-line condition of UM ZEDS line. At the treated section, NaOH was dosed to achieve an elevated pH. The corrosion rate obtained was within the acceptable limit. It was also observed that substantial dissolved oxygen (DO) was present in the condensate, but it did not have a significant influence in the corrosion process. Also, passivation occurred faster in the treated section than in the untreated section.

3. THE LOW-TEMPERATURE APPLICATION CORROSION INHIBITOR TESTING

3.1 Test Objectives

Sodium hydroxide (NaOH) dosing was used to further elevate the condensate pH after degassing at the spray tower. Acceptable corrosion rate was achieved at elevated pH. With the escalating price of NaOH and the risk of transporting and handling such corrosive chemical, it was considered to test a corrosion inhibitor for low temperature application. The inhibitor was tested in November 2008 with the main objective of testing the inhibitor’s effectiveness in controlling the corrosion rate to acceptable level, using the aerated condensate from the spray tower where condensate has dissolved oxygen and with the NaOH dosing system on shutdown condition.

3.2 Low-Temperature Corrosion Inhibitor

The corrosion inhibitor is composed of proprietary fatty amines (<30 weight percent) and isopropyl alcohol (<9 weight percent) based on the composition data from the Material Safety Data Sheet (MSDS). Its product name is GeoGard 8822. The corrosion inhibitor’s physical and chemical properties (Table 1) show that it is a basic liquid inhibitor which is completely soluble in water. Its inhibiting action is made by creating a protective amide film on the pipe wall thereby corrosion attack is prevented which can be done by injecting the inhibitor at high concentration and later optimizing the dosage. This corrosion inhibitor was previously tested at 10 ppm
concentration for acid-treated brine in the Nasuji Sector, Southern Negros Geothermal Production Field. Said experiment was different as such application was in acid-treated brine and at higher temperature of ~120°C.

Table 1. Physical and Chemical Properties of the Corrosion Inhibitor (Source: Material Safety Data Sheet).

<table>
<thead>
<tr>
<th>Physical and Chemical Properties</th>
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</thead>
<tbody>
<tr>
<td>Physical State</td>
</tr>
<tr>
<td>Appearance &amp; Odor</td>
</tr>
<tr>
<td>Solubility in Water</td>
</tr>
<tr>
<td>Specific Gravity</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Vapor Density (lb/gal)</td>
</tr>
</tbody>
</table>

3.3 Test Design

The test was conducted on November 2 to 12, 2008. The large volume power plant condensate was treated during this period with three GCCU’s in-service. Just before terminating the test, the fourth GCCU was synchronized to the grid which increased the condensate flow. The caustic soda dosing was shut during the entire test period.

The dosing program that was implemented in the test was followed from the supplier’s recommendations. The low dosage concentration was considered to be more closely competitive economically with the caustic soda consumption. In cases when the passivating stage exceeded three days of the high dosage period of the test, the program was to proceed at this high dosage level until up to a maximum of 7 days. However, if within 3 days the high dosage sufficiently reduced the corrosion rate to acceptable level, the dosing would then be reduced to low dosage level. If at this concentration the corrosion rate will be maintained or will still improve, then the low dosage is taken as the optimum dosage. Otherwise, if the corrosion rate will increase at the low dosage regime, the optimum dosing will be at an intermediate concentration.

The test dosing system consisted of a metering pump that delivers the corrosion inhibitor through the injection probe installed in the return condensate line. It was equipped with a calibration column for the monitoring of the delivery rate (Fig. 2). A water tank was also provided for the initial calibration of the pump and for flushing the system whenever necessary. The corrosion monitoring focused on the corrosion rate of the power plant return condensates which have undergone spraying or degassing but have been aerated or introduced with dissolved oxygen in the process before being injected to the cold injection wells. Downstream of the inhibitor dosing point, a corrosometer probe and a pair of coupons were inserted for the corrosion monitoring (Fig. 3). The corrosion inhibitor supply limited the test duration. Thus, the use of coupons for the corrosion monitoring were mainly for purposes of checking whether a protective film will be formed during the 10-day testing, and also to characterize the film formed from petrologic analysis of the sample.

3.4 Test Results

A baseline (without corrosion inhibitor dosing) corrosion test was conducted after the test of the low temperature application corrosion inhibitor to compare the results of the treated test with a more recent baseline test (previous baseline test was conducted in March 2008). The updated baseline test was conducted on January 12-15, 2009 using aerated condensate at the Spray Tower basin. The condensate at this point contains dissolved oxygen that could increase the fluid’s corrosive property. Figure 4 shows the recent baseline corrosion rates to be higher than the acceptable limit. These corrosion rates would require a treatment prior to transport in the carbon steel condensate pipelines and injection into the cold injection wells.

Figure 2: Test set-up consisting of a dosing pump, calibration column and a tank for the corrosion inhibitor (left photo). Corrosion monitoring from an LPR test probe was inserted along the condensate line (right photo).
The corrosion rates and corrosion products or passive films formed were evaluated using three different tools: (1) an LPR corrosometer probe which gives real-time corrosion rate readings, (2) corrosion coupons for the adhering passive films, and (3) ultrasonic testing (UT) thickness measurements in selected locations in the condensate pipeline. The measurements were separately conducted to determine the corrosion (thinning) rate of the condensate pipeline downstream of the dosing system. Corrosion inhibitor injection was started at a high dosage rate to induce the formation of a protective film during the early stage of the testing. This encompasses the passivating stage of the inhibition process preventing further corrosion on the inner surface of the pipeline. Passivation was noted in a short period of time as indicated by the reduced corrosion rates.

After the corrosion rate significantly dropped and stabilized at acceptable levels, the dosing rate was reduced and optimized at a lower dosage rate. Figure 5 suggests that significant reduction in corrosion rate was achieved with the corrosion inhibitor dosing. The spikes in corrosion rates that were noted in between test (enclosed by the triangle in Fig. 5) are attributed to the disposal of unsprayed condensate through the by-pass dump line due to operational constraints in the power plant. The unsprayed condensate has lower pH than the sprayed condensate due to the un-exsolved gases. Intermittent brine pumping from the thermal pond was also done on November 6-8, 2008, as shown by the increase in chloride levels (Table 2) of the basin condensate, due also to operational constraint in the FCRS. No significant changes in fluid chemistry were observed during the test, except the shift in Eh values during the test where the caustic soda dosing was shut (Table 2).

Two corrosion coupons (designated as Coupons A and B) were inserted in the condensate pipeline to estimate the corrosion rate and to evaluate the corrosion products and passive films that will be formed. A good agreement of results was observed between the corrosion coupons and the corrosometer. By weight difference of the newly inserted coupons and the cleaned coupons after harvest (Fig. 6), the resulting corrosion rates were comparable to the rates measured by the corrosometer probe. Passive films scraped from the coupons were identified to be iron oxides corrosion products by petrologic analysis.
On the other hand, the UT results suggest that thinning rates during the testing were high at locations where turbulent flow is experienced, such as elbows, but negligible in other monitored locations. UT results can only be interpreted qualitatively due to the very limited data points and short UT test period of 5 days.

Figure 5: Corrosion rate measurement using an LPR corrosometer probe while dosing with low-temperature corrosion inhibitor. The spikes noted were attributed to the disposal of unsprayed condensate through the by-pass line to the basin which was conducted due to operational constraints in the power plant.

Table 2. Condensate chemistry during the test. Note the high chloride concentrations on Nov. 6-8, 2008 after disposal of brine from the thermal pond due to operational constraint in the FCRS.

<table>
<thead>
<tr>
<th>Date</th>
<th>Cl, mg/L</th>
<th>Eh</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>02-Nov-2008</td>
<td>&lt;5.0</td>
<td>28.5</td>
<td>Baseline; w/o inhibitor dosing</td>
</tr>
<tr>
<td>03-Nov 2008</td>
<td>&lt;5.0</td>
<td>-66.8</td>
<td>w/ inhibitor dosing</td>
</tr>
<tr>
<td>04-Nov 2008</td>
<td>&lt;5.0</td>
<td>-104</td>
<td>w/ inhibitor dosing</td>
</tr>
<tr>
<td>06-Nov 2008</td>
<td>104</td>
<td>-132</td>
<td>w/ inhibitor dosing</td>
</tr>
<tr>
<td>08-Nov 2008</td>
<td>770</td>
<td>-158</td>
<td>w/ inhibitor dosing</td>
</tr>
</tbody>
</table>

Figure 6: Corrosion coupons A and B after retrieval, while scraping the passive film and after cleaning.
The Eh-pH (Pourbaix) diagram (Fig. 7) suggests that the caustic soda treated condensate (red filled circles) plot well within the passivating region with hematite being the stable passive film expected to be formed. Without caustic soda dosing (green filled circles), the pH shifts lower to the left and plots close to the border of the uniform corrosion region as the condition with inhibitor dosing (blue filled circle). It must be noted however that the action of the corrosion inhibitor is to coat the inner surface of the pipeline with a protective coating (inhibitor known as filming amine), which is achieved by initially dosing the inhibitor at high concentration. The filming amine coating will prevent the pipeline from undergoing uniform corrosion from the acidic condensates.

CONCLUSIONS

The testing for a low-temperature application corrosion inhibitor in the Upper Mahiao power plant condensates gave promising results in treating the condensate, and yielded acceptable corrosion rate. Important findings from the test include:

1. The passivating stage took place relatively fast from the time of start of high dosage corrosion inhibitor injection;
2. Significant reduction in corrosion rate was obtained that is within the acceptable limit relative to the untreated condensate;
3. Passive film that was formed was iron oxides, consistent in the scraped products in the corrosion coupons and as plotted in the Pourbaix diagram.

Based on the corrosion test results, the low-temperature corrosion inhibitor is effective in inhibiting corrosion along the Upper Mahiao power plant condensate at aerated condition.

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REFERENCES


