Consider new steam system corrosion protection for refineries

For decades, neutralizing and filming amines have been used to protect steam condensate in boiler systems. In refining operations, where steam is utilized to improve fractionation, added attention is needed to the type and amount of amines added to the boiler/steam system to minimize amine chloride salt fouling in the distillation column and crude overhead. New technology in volatile filming corrosion inhibitors and lower-salting neutralizing amines can provide cost-effective solutions for the steam-condensate system and minimize the risk of corrosive amine chloride salt formation. This approach is useful for refinery operations working to maximize distillate production while maintaining protection of “difficult-to-treat” steam condensate systems, e.g., reboilers using flashed steam, and high-alkalinity makeup water sources.

Protecting steam systems. Ensuring the efficiency and reliability of the steam plant is crucial to successful refinery operations. Steam condensate and boiler feedwater (BFW) protection are integral parts of maintaining the total health of the entire steam and boiler system. By mitigating condensate corrosion, the associated equipment and piping are protected. Additionally, by protecting this system, the condensate can be returned to the boiler as high-quality feedwater—thus, recycling valuable water and conserving energy. Finally, minimizing the return of corrosion products greatly improves the efficiency and reliability of steam-generating equipment while minimizing the need for deposit-control chemistry.

Traditionally, refineries have used organic amines to neutralize acidic contaminants, such as carbonic acid, in the steam condensate and raise system pH to prevent corrosion. Refineries may also supplement the neutralizing amine program with a filming corrosion inhibitor. These corrosion inhibitors, including the subset known as filming amines, establish a tenacious barrier film on the metal surface, thus inhibiting contact of the corrosive contaminants (such as carbonic acid, dissolved oxygen and chloride salts) with metal surfaces. A key advantage of effective filming corrosion inhibitors is that they can be fed sub-stoichiometric to the acidic contaminant, thus reducing total treatment costs.

In many cases, an effective filming inhibitor can reduce the requirement for neutralizing amines by providing equivalent corrosion protection at an incrementally lower condensate pH than with the neutralizer alone. This can reduce treatment costs, especially where amine feedrates are high. Historically, traditional filming inhibitors, such as octadecylamine, should be injected into the steam header because of their low volatility and limited ability to enter the steam phase from the boiler when fed to the feedwater.

Consequently, achieving effective system coverage is often difficult with traditional filming inhibitors of limited volatility. For example, many refineries produce and utilize lower-pressure “flash” steam generated from higher-pressure liquid condensate. This flashed steam, often used for critical reboilers, can be heavily laden with carbon dioxide (CO₂), thus increasing the corrosion potential in the affected condensate. A filming inhibitor with limited or no volatility will not readily enter the flash steam from the condensate, which may leave the downstream equipment served by the flash steam vulnerable to severe corrosion. Consequently, satellite feed of traditional neutralizing and/or filming inhibitors to these areas is often required for effective protection, requiring maintenance of the remote feed system, pumps and product inventory.

Polyamine volatile filming inhibitor technology. A new polyamine filming inhibitor technology can allow effective steam-condensate system coverage and protection from one injection location, often the deaerator storage section, as shown in FIG. 1. This is in sharp contrast to the extremely low volatility of traditional filmers discussed earlier.

An additional hurdle for steam treatment is maintaining reliability of the equipment utilizing steam directly within the process. A prime example is the atmospheric crude distillation tower, where stripping steam is used to improve product...
Corrosion Control

A reliable steam-condensate program. As refiners decrease tower top temperatures to increase distillate production, the risk of amine chloride salt formation inside the distillation column increases.

Amine chloride salt fouling depends on a number of factors including: chloride levels, operating temperatures/pressures of the distillation column, other sources of unwanted or tramp ammonia/amines, and even amines used to protect the overhead and associated exchangers, as shown in FIG. 2.

These problems are more directly related to steam-treatment additives in systems where higher levels of neutralizing amine are required to maintain condensate corrosion protection. This is often the case in utilizing high-alkalinity BFW and/or a lower-percentage condensate return. The problem is compounded in fractionation towers operating at lower temperatures where the amine chloride salt point can potentially be driven into the distillation column.

Unless crude oil selection, additives and impurities, and operating parameters are consistently favorable, it is recommended to use steam-condensate protection that will provide minimum impact on refinery operations. There are new steam-condensate corrosion inhibitor technologies now applied to lower-salting neutralizing amines for steam treatment. In combination with the volatile polyamine filming technology, this approach can potentially provide a lower-cost and more-reliable steam-condensate program.

An integrated approach. A collaborative effort between water and process engineering teams discovered a unique solution to ensure maximum reliability of crude unit distillation processes while providing superior condensate protection. Proprietary modeling software was used in the development and application of the new technology. Utilizing low-salt ionic equilibrium modeling in combination with condensate modeling software, many potential steam neutralizing amines were evaluated for their compatibility with the refining process and their effectiveness in managing corrosion in complex condensate systems. This study included a rigorous examination of the potential for forming amine chloride salts under different contaminant loadings and operating conditions in the atmospheric crude unit tower. TABLE 1 lists comparative salt-point temperatures of typical neutralizing amine blends used in refining steam condensate treatments.

Additionally, it was critical to uphold the required critical parameters of neutralizing amines used in steam-condensate treatments, which include the neutralization capacity, basicity, steam-liquid partition coefficient or distribution ratio, and thermal stability at boiler and steam temperatures. A key component, the polyamine volatile filming corrosion inhibitor is typically included with the low-salting amines to further enhance system coverage and reduce the traditional neutralizing amine required for corrosion protection. Consequently, the total “tramp” amine contribution from the stripping steam can be reduced.

Because the modeling program can be used to simulate the potential for ammonia or amine chloride salt formation in crude atmospheric towers and to optimize the model amines and contaminants in complicated steam systems, a more comprehensive approach to refinery system reliability can be taken. The combined modeling approach allows the refiner and specialty chemical supplier to work together to optimize refinery operations while maintaining the required process and water treatment reliability.

For example, by modeling a refinery’s steam condensate system, the refinery operator and process chemical supplier have a better understanding of the amount and type of amines present in the stripping steam. Using that information, combined with an understanding of the other ammonia/amine sources and contaminants (e.g., chlorides), a more accurate model of the atmospheric tower can be derived. This model will then enable the

TABLE 1. Calculated amine blend salt point in crude unit overhead at 8.7 psig (˚F)

<table>
<thead>
<tr>
<th>Chloride, ppm</th>
<th>Original amine blend</th>
<th>Industry standard amine blend</th>
<th>GE Low salt/polyamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>228</td>
<td>212</td>
<td>184</td>
</tr>
<tr>
<td>20</td>
<td>244</td>
<td>224</td>
<td>198</td>
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<td>40</td>
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<td>254</td>
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<td>130</td>
<td>291</td>
<td>259</td>
<td>237</td>
</tr>
<tr>
<td>160</td>
<td>297</td>
<td>263</td>
<td>241</td>
</tr>
</tbody>
</table>

![FIG. 2. Amine sources with a refinery and recycle loops.](image)

![FIG. 3. Nonwettable surface provided by polyamine filmer on corrosion coupons.](image)
refiner to better understand their operating limitations and allow them to maintain optimal reliability and economics.

Low-salt boiler amine and polyamine technologies. Low-salt boiler amine and polyamine technology can provide an opportunity to further optimize refinery boiler and process system reliability and economics. Several refineries have reported encountering limited optimizing economics due to tramp ammonia/amines, often when trying to maximize mid-distillate production and running at lower fractionation tower top temperatures.

In some cases, it is the amine in the stripping steam that can be the limiting factor, and low-salting amines were recommended to reduce/eliminate the bottleneck.3 Two refining cases reported small amounts of traditional amines used in steam-condensate treatment, cyclohexylamine and methoxypropylamine (MOPA), were limitations in maximizing profitability. A compilation of abbreviated case studies are documented in this article.

Case 1: Low-salting boiler amine with no polyamine. One particular refinery was having concern around a particular steam-treatment amine. This refinery had suffered some amine chloride deposits in a crude unit top pumparound circuit. Prior to implementing the polyamine technology, its goal was to use a low-salting boiler amine to achieve the same pH and consequently, the same iron level achievable with industry-standard amines in use. The refinery implemented the low-salting boiler amine blend to replace the higher salting amine from the steam.3 Condensate system modeling was done to predict the required feedrates based on water chemistry and system operating parameters and targets. The low-salting boiler amine achieved the required system pH levels as predicted. As a consequence, the steam-condensate pH and iron levels remained approximately the same, as illustrated in FIG. 4. Although satisfied with the initial change to low-salting boiler amine chemistry, this refinery converted to a low-salt polyamine technical to further optimize performance and economics.

Studies with polyamine and standard amines. Refineries utilizing BFW with high levels of bicarbonate/carbonate alkalinity can generate significant CO2 in the steam and, consequently, elevated levels of corrosive carbonic acid in the condensate. These refineries are often challenged to feed enough neutralizing amine to achieve the required steam-condensate pH levels to protect the condensate piping and equipment. The use of condensate flash tanks to generate low-pressure flashed steam, often for nonvented reboilers carrying liquid levels, can also operate under highly corrosive conditions because of the very high volatility of CO2 to the flashed steam, as illustrated in FIG. 5.

Under these circumstances, it can become very difficult and expensive to maintain corrosion protection by relying only on carbonic acid neutralization and boosting the pH. In addition, the high use of amines can have an adverse impact on the refining operations. In these situations, it is often best to provide a filming technology.

Case 2. A European refinery was experiencing severe corrosion of reboilers/exchangers on a desulfurization unit that used steam with a pH < 6. Due to the corrosion problems, the refiner was replacing unit bundles about every 18 months. Traditional neutralizing amine treatment would require very high feedrates and be deemed uneconomical. As a result, a polyamine-neutralizing amine blend was applied at about 10% of the theoretical “neutralizing amine blend only” feedrate. Almost immediately after initiating the chemistry, the measured total iron levels at the reboiler dropped significantly:

- Reboiler total iron prior to polyamine-amine: > 500 ppb
- Reboiler total iron after polyamine-amine: < 50 ppb

More importantly, during the last scheduled maintenance on one of the reboilers, the refinery was set to replace the bundle per its normal schedule. However, the inspection determined that no bundle replacement was needed because of the improved corrosion control.

Case 3. A similar application at a Southeast US chemical plant showed a tremendous reduction in mild steel condensate corrosion rates with the addition of the polyamine to the BFW. This particular plant had high-alkalinity BFW contributing...
Corrosion Control

over 20 ppm of CO₂ to the steam and no appreciable condensate return. Consequently, the amine requirement for neutralizing the carbonic acid and increasing the pH was significant and uneconomical. A plan was developed to add polyamine and begin reducing the neutralizing amine. FIG. 6 illustrates the results regarding the corrosion rates and mild steel coupon. The plant continues to optimize, and has reduced neutralizing amine by over 70% while improving the mild steel and the copper corrosion rates.

Case 4: Low-salt polyamine blend. A Western US refinery was in the scenario of having high condensate corrosion potential and ammonia/amine chloride salt fouling in the crude and coker operations. To improve operations, key system treat-

ment and corrosion data were evaluated on both the water and process chemistry. Computer modeling of the systems was conducted to predict, select and validate the specific type of low-salt and polyamine chemistry that would be appropriate to improve the reliability and economics for the refinery.

With implementation of the program, the amine salting potential was improved by removing nearly all of the higher salt-point amines from the boiler steam treatment. The steam-condensate pH and iron levels were regularly tested to ensure that corrosion metrics were being met. After several weeks of onsite iron testing and offsite iron corrosion product (ICP) testing, the low-salt polyamine feedrate was decreased further. This change also further reduced the total amine contribution from the stripping steam in the crude tower, while improving economics around chemical spend (TABLE 2). However, as modeling had predicted, this action would lower condensate pH levels in the steam condensate system. It included carrying a lower pH at some critical, nonvented reboilers in the system. Now, more of the corrosion protection responsibility was placed on the polyamine filmer. Chemical usage was minimized, while increasing reliability in steam condensate and refinery process via low-salting amines and filmer protection.

After several more weeks of analysis, the corrosion protection was maintained per on-site data and more accurate ICP off-site iron data indicated an improvement. Four of the five samples in the system, including a nonvented reboiler, showed less-than-detectable iron and copper levels (FIG. 7). Another reboiler had very low iron (< 2 ppb per ICP) at about 0.75–1 pH units lower than initial treatment.

TABLE 2. Steam treatment cost comparison

<table>
<thead>
<tr>
<th></th>
<th>Cost to treat, $/MMlb of steam</th>
<th>Steam pH</th>
<th>Final condensate pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industry-standard amine blend</td>
<td>x</td>
<td>8.38</td>
<td>9.67</td>
</tr>
<tr>
<td>Equivalent steam pH to standard, low-salt/polyamine</td>
<td>0.95x</td>
<td>8.38</td>
<td>9.33</td>
</tr>
<tr>
<td>Lower pH/cost to standard, low-salt/polyamine</td>
<td>0.79x</td>
<td>7.84</td>
<td>9.29</td>
</tr>
</tbody>
</table>

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