Question 59: What is the contribution to salting in crude fractionators and overhead systems due to steam condensate amines, and what are your mitigation strategies?

DENNIS HAYES (Nalco Champion)

Amines have been used in refinery steam systems for decades. When properly applied, the amount of amine that may make it to the crude fractionator towers should be very small; the partial pressure contribution should be so low that the steam condensate amines should not contribute to salt formation. When there is a concern, analysis for amine quantities in the steam and modeling for system salt points can be performed.

PHILLIP THORNTHWAITE (Nalco Champion)

When samples of crude unit overhead water are analyzed for all amine species, it is possible to find small amounts of amines used in the steam system present in the water. In some cases, the amines used in the steam system can be the same as the ones used in the neutralizing amine product injected into the crude unit overhead; for example, MEA (mono ethanol amine) and MOPA (meth oxy propyl amine). In these cases, it is difficult to differentiate what comes in via the steam system or what has been injected as the neutralizer. However, a fundamental point is that if large number of amines are found to be coming from the steam injected into the tower, the first part of any RCA (root cause analysis) would be to determine why such volumes are being injected into the steam condensate system in the first place. With a well-managed steam system, there is little need to inject copious amounts of neutralizing amine to the point where it would subsequently impact salting in the crude unit overheads.

If you are faced with the problem of a gross overdose of neutralizing amine (for whatever reason) and while an investigation is taking place, looking to reduce the number of overhead chlorides is critical. This may require a temporary increase in caustic injection, coupled with the utilization of available levers to optimize desalting performance. However, if there are restrictions on the levels of Na in the residue, options may be limited. Essentially, if you manage your steam system properly, there is little risk posed.

RALPH WAGNER (Dorf Ketal Chemicals LLC)

Amines are a growing issue for the refining industry. They impact desalter performance, increase the potential for overhead corrosion, decrease neutralizer effectiveness, and increase loadings on the wastewater treatment plant. Levels as low as 1 ppm of certain tramp amines in the crude can have a dramatic impact on salt points and associated corrosion in the atmospheric section. Ammonia finds its source from increased severity of the secondary unit. Ultimately, these ammonia and tramp amine land in the desalter washwater via underperforming sour water strippers. At an alkaline washwater pH greater than 8.5, these basic species partition to the crude phase in desalter, eventually distilling into overhead.

The salting point of the ammonia and tramp amine is governed by the partial pressure of chlorides, ammonia, and tramp amines. If the operating temperatures are close enough to salting points, then one can experience salting inside the column. Understanding the source, pathways, and salting point is the key to mitigating the issue. Dorf Ketal's differentiator approach involves comprehensive electrolyte testing across the crude unit and estimation of salting points with a unique simulation tool.

Standard Neutralizing amine used in steam generations are morpholine, dimethylamine, dodecylamine, dimethylaminoethanol, dimethylisopropanolamine, and cyclohexylamine. On estimating the salting point of the amines using Ionic equilibrium model, it is observed to be in the range of 205 to 221°F (96to 105°C). Hence, depending on the column operating temperatures, one should screen amines in the steam to avoid deposition issues in the column.

The first line of defense against amine contamination, the desalter, has typically not performed well enough on amine removal to deal with the problem. Desalter water acidification has been the standard alternative for improving desaltingto better remove amines from the system. There are considerable operator safety issues with handling acids and challenges in maintaining pH control. Upsets in pH are likely to occur with negative consequences on results and equipment. In addition to safety and control concerns, acids can partition into the crude, increasing neutralizing amine demand in the overhead.

Dorf Ketal offers a new class of reactive adjunct desalter chemistry that is non-acid and reactive with crude contaminants to improve desalting and amine removal. The new solution is easier and safer to use, easier to trial, and more flexible in use than acid alternatives. Without the need for capital investment, the new chemistry delivers reduced amines in the crude and more consistency in amine levels in the crude column overhead, which allows for improved control of salting points and corrosion in the crude column, improved reliability, and flexibility to process amine contaminated crudes.

KATHLEEN WILLS (Athlon Solutions)

Steam treatment amines do contribute to salting in atmospheric and vacuum towers. The extent of their contribution depends on the steam treatment amines used and their concentrations. Proper amine selection and controlled application can mitigate their impact.

<u>Use ionic modeling software to predict impact of chemistries.</u> When selecting a steam treatment program, it is critical that ionic modeling software is used to predict the impact that different chemistries will have on the ionic dew point and salt point. The ionic dew point is the temperature at which the first drops of water begin to condense and containshigh concentrations of the ionic species. This ionic dew point creates a salty and corrosive liquid phase. The salt point is the temperatureat which a solid salt precipitates. Both of these points can be controlled by managing the amines that are used for steam treatment and their concentrations. Further discussion on ionic modeling and calculation of these points is discussed in the 2015 NACE paper titled "Crude Unit Overhead Corrosion Control Successfully Driven by Ionic Modeling."

<u>Optimized steam treatment program reduces amine use.</u> Optimizing the steam treatment program can

allow for reduction in the amount of amine used. One refinery was experiencing high corrosion rates in its pumparound circuit and overhead line. It was determined that cyclohexylamine (CHA) and methoxypropylamine (MOPA), both from the steam treatment, were the main amines present in the overhead water and in the pumparound naphtha extractions. Investigation identified that high quantities of the steam treatment amines were being fed because of an accumulation of acid gases which were driving down the pH. Several corrective actions were taken to raise the pH and lower the demand for amine. First, caustic was injected upstream of the RO (reverse osmosis)system to convert the carbonic acid dissolved gas to carbonate and bicarbonate dissolved salts so that they could be removed in the RO system. Additionally, heaters where the acid gas was accumulating were identified and vented in order to reduce the acid gases. After troubleshooting and implementing these solutions, the steam treatment amine quantities were greatly reduced. Reducing the steam treatment amines lowered the ionic dew point by 10°F, reducing the risk of corrosion and providing the refiner with greater flexibility in his fractionator operation.

Utilizing alternate injection locations can remove steam amines from fractionators. In another case,a refinery was experiencing corrosion and fouling in the LVGO (light vacuum gas oil) section of their vacuum tower, as well as in downstream equipment. Ionic modeling predicted CHAand MOPA salting inside of the vacuum tower. A deposit samplewas collected from a filter on the LVGO draw that routinely plugged with corrosion product. The deposit was dissolved in water and analyzed for ionic components. The three main ionic components identified were chloride, CHA and MOPA, confirming the ionic model prediction of salting in the tower. This refinery was able to utilize alternate satellite feed injection locations for the steam treatment amines into the boiler feedwater. The relocated injections are downstream of where this vacuum tower gets boiler feedwater to generate its own, now untreated, steam in the heaters. Since this change was made, fouling of the filter and downstream equipment with corrosion product and salt deposit was significantly reduced, marking improved reliability of the vacuum tower.

There are several online methods available to remove salt from a tower where salting has already occurred. The first is the practice of slumping and waterwashing the tower to remove the salts in a side-draw. The second method is to heat the tower to achieve sublimation of the salts and cause them to leave with the overhead vapors. With either of these methods, it is recommended to closely monitor for corrosion that may be caused by the cleaning events. Another solution is the application of salt dispersant chemistry. There are several proprietary chemistries that are effective in displacing salts, and which can be applied into the tower or into the overhead system.

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