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**REMOVE HEAT STABLE SALTS
FOR BETTER AMINE PLANT PERFORMANCE**

FOLLOW-UP DATA TO AN OCTOBER 1997 ARTICLE PROVES WITH REFINERY EXPERIENCE THAT CAUSTIC NEUTRALIZATION DOES NOT IMPROVE SYSTEM OPERATIONS

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Caustic addition appears to be an inexpensive and easy way to deal with heat stable salt problems in amine systems. However, refinery experience shows that operational problems persist when caustic is used to “neutralize” amine heat stable salts (HSS). In contrast, when caustic addition is replaced by removing HSS and maintaining HSS anions at a low level, the refinery finds greatly improved operation of the amine system, lower maintenance costs and increased refinery throughput. This and other refinery experiences confirm that caustic addition is bad for an amine system.

It is well known in the refining and gas treating industries that accumulation of amine HSS has a very detrimental impact on amine system operations. Amine HSS reduce the effective capacity of the amine solution, contribute to corrosion, and aggravate operational problems such as foaming, amine loss, fouling, etc.

When HSS buildup becomes a problem, operators have a variety of options to manage the problem. The options include replacement of part or all of the solution, HSS removal, or the commonly recommended practice of adding sodium or potassium caustic to “neutralize” the HSS. Many operators chose the “neutralization” over replacement or salt removal as it is perceived to be a more economical way to stop the problem. Unfortunately, “neutralization” addresses only the capacity (available amine strength) issue. When other operational problems (corrosion, foaming,

amine loss, fouling, filter plugging, upsets) persist following neutralization, it may be erroneously assumed that HSS have no relationship to those problems.

However, in Part I¹ we reported corrosion data, collected in a dynamic corrosion test apparatus, that show that caustic additions to amine solutions do little to improve the corrosivity of amine solutions. Thus, the problems aggravated by corrosion products will not go away. In some cases corrosion rates are increased by caustic addition,^{1,2} which may lead to additional operating problems. In this part, we discuss the plant operating problems from plant experience and show how caustic addition has contributed to those problems. In contrast to caustic experience, operating performance improved greatly after HSS and sodium were reduced and maintained at low levels.

PLANT CASE HISTORY

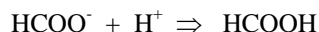
Experience with Neutralization

A Gulf Coast Refiner upgrading heavy sour crudes had a large rate of HSS buildup, sometimes as much as 1000 lb per day (about 20 lb-mole per day) in a "formulated" MDEA solvent system. HSS anion (formate, acetate, thiocyanate, chloride, thiosulfate and sulfate) levels in the range of 3 to 5 wt% (equivalent to 7 to 12% MDEA or up to 25% of the total amine bound with HSS) were quite common. The refiner practiced neutralization as recommended by their amine supplier, usually adding caustic to reduce the amine HSS (bound amine) to less than 2 wt% MDEA. Caustic addition was advertised to significantly reduce corrosion, improve amine performance, and return the bound amine to active amine. Only the last objective was ever achieved, and only to a limited extent.

Corrosion effects. As HSS anion concentrations increased in the system, due to extensive efforts to control amine loss, corrosion rates all over the system increased tremendously. Regenerators corroded so rapidly that weld overlays were required almost yearly. An additional set of lean/rich exchangers was purchased so that fouling and corrosion failures in one set of exchanges would not shut the regenerator down. Reboiler fouling occurred so often that isolation valves had to be installed to clean the exchangers on line. Filter costs reached nearly \$0.4 million per year. Eventually a third regenerator train was installed to allow for one train to be down for repairs. Still, this did not prevent loss of hydrocarbon throughput due to corrosion/fouling problems.

Performance effects. Amine operations at this level of HSS were poor at best. Contactors and regenerators were constantly foaming leading to large losses and sulfur plant upsets. Liquid treaters lost large amounts of amine overhead leading to many water treatment plant permit excursions. Amine system operation was a major bottleneck to hydrocarbon throughput.

Amine restoration effects. Strengths were routinely reported to be in the range of 45% wt% MDEA. Caustic additions did not appear to change the strength. However, the "heat stable amine salts" would go down. It was expected that the strength would go up with caustic addition. It was determined that the major salt anions, formate (HCOO⁻) and acetate (H₃CCOO⁻) built up to levels which actually interfered significantly with the amine strength titration³. These ions would react with acid in the titration as did the actual MDEA in the pH range of the titration end point color indicator as with formate:



Formate, at MW of 45, and acetate at MW of 59, were being counted at 2.6 and 2.0 wt% amine per % salt anion respectively. Since caustic addition did not change the state of these ions, these were still counted in the total strength. Because of this error, the amine was severely undercirculated, rich loadings were excessively high, and this helped aggravate the rate of corrosion over the entire system.

Since caustic addition alone did not solve the problems, an electro dialysis based HSS removal unit was brought in to supplement the neutralization. Caustic additions were continued to control the bound amine at low levels while the electro dialysis unit would try to hold the HSS anion levels in a controlled range of 3 to 5 wt%. This was done

on the basis that the bound amine content was the cause of corrosion acceleration, not the HSS anion interaction with ionic iron in the protective iron sulfide layer.

Maintaining higher salt anion levels was also required to keep the amine level in the electro dialysis unit waste brine (containing the heat stable salts and sodium) low enough for the water treatment system to tolerate. Going to lower salt anion levels increased the power requirement for the separation which made more amine cross the membranes into the brine, eventually rendering the brine untreatable. As with the caustic addition alone, the caustic plus electro dialysis program produced the same poor results in corrosion control, amine system performance, and amine restoration as described above, because the HSS anion levels were not reduced.

Experience with low HSS levels/ ion exchange salt removal

After 3 years of the neutralization/electro dialysis program, a patented ion exchange based HSS removal process was employed to remove HSS and sodium. HSS levels were reduced from 5 wt% to about 1 wt% as anions (2.3 wt% as MDEA) and from 2.5 to about 0.5 wt% sodium. These much lower levels of salt anions can be achieved because the HSS anion removal efficiency and the regenerant waste stream characteristics of the patented ion exchange based removal system are not affected by salt anion concentration in the amine solution.

The ion exchange process frees the amine from the HSS anions, sends the freed amine back to the amine system, and sends the HSS (as innocuous sodium salts) to waste. Amine strength (capacity) is increased, as with caustic neutralization. Unlike caustic neutralization, the ion exchange process removes the undesirable HSS anion from the amine system.

Immediately after the initial cleanup by the patented ion exchange based HSS removal process, heat exchanger fouling problems were eliminated. Filtration costs were cut in half. Antifoam usage dropped by 90%. The system stabilized enough to allow record crude, coker and cat cracker runs simultaneously, while amine consumption was cut in half.

As the HSS anion level rose after the initial cleanup, the problems associated with high anion levels began to resume. Ion exchange cleanup was employed again restoring the system to smooth operations. It was decided at that point to go to continuous removal and maintenance of low salt anion and sodium levels using ion exchange.

As the ion exchange removal process reduced the contaminant levels to about 0.5-0.8 wt% anions (~1-2 wt% as MDEA) and sodium less than 1000 ppm, even greater operational benefits have resulted. Filtration costs have been cut by 80%. All the heat exchangers show little, if any, fouling. Amine losses have been reduced by 90% without detrimental build-up of HSS. Amine purges have obviously been unnecessary as a mode of HSS control.

The operational results of HSS removal by ion exchange are compared to those of caustic addition in Table I.

Miscellaneous experience. A European refiner adds caustic (potassium carbonate) to an MDEA system as HSS concentrations increase, experiencing serious filter plugging in spite of corrosion inhibitor treatment. System instability increases until a major upset occurs and amine loss is so great that makeup with new amine reduces salt and potassium (caustic cation) concentration such that stability returns. Costs of fighting system instability and of new amine are ignored. The cycle repeats itself in the next year.

One US refiner measures increased corrosion rate and finds crevice corrosion initiated by caustic addition to an MDEA system. Subsequent removal of HSS and sodium by a patented ion exchange service immediately reduced the corrosion rate.²

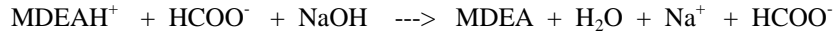
A DEA user adds caustic and sees dissolved iron concentration decrease. At the same time filter change-outs increase. The filters are plugging with iron hydroxide and iron carbonate. Another DEA user reports the solution "clarified" upon caustic addition -- it appeared less black. Here also, the caustic raised the pH and increased the

carbonate concentration in the solution (from the CO₂ loading),⁴ apparently reducing the FeS suspended in the solution. Caustic addition is not a real solution to HSS induced problems in DEA systems.

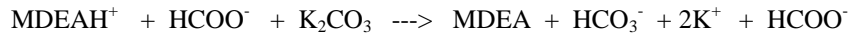
WHY CAUSTIC DOESN'T HELP

Caustic addition only changes the amine bound with HSS anions back to neutral amine, water, and sodium or potassium salts.

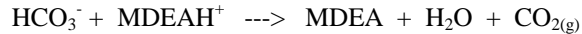
Sodium hydroxide (NaOH) addition:



Potassium carbonate (K_2CO_3) addition:



Later, in the regenerator, if sufficient excess bound amine exists:



In these equations, MDEAH^+ is bound amine, MDEA is free or neutral amine, HCO_3^- is bicarbonate ion, and HCOO^- (formate ion) represents all HSS anions.

The reason caustic doesn't appear to help is that it doesn't affect the concentration of HSS anions which are the cause of the corrosion rate acceleration. The increased corrosion rate destroys equipment faster leading to frequent downtime and repairs. The additional particle buildup from additional corrosion products (iron sulfide) in the system is known to aggravate the foaming/loss problems by helping any hydrocarbon contamination in the amine form foam stabilizing gelatinous layers at the amine/hydrocarbon interfaces⁵. Caustic addition to test solutions in the Mini Amine Plant/ Corrosion Monitoring Cell (MAP/CMC)¹ also freed iron sulfide from the internal surfaces of the MAP adding to the filtration load and removing protection from the metal, helping to maintain accelerated corrosion rates from HSS buildup.

Summary. Caustic addition looks like a cheap and easy way to deal with HSS problems in amine systems. However, plant experience shows that caustic addition does little to improve system performance in the long run. Apparent improvements have counterbalancing negatives which end up making caustic bad for an amine system overall. More effective corrosion control, better overall amine performance, and more complete amine restoration are attained by removing HSS from a contaminated amine system and managing the HSS at low levels thereafter.

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The Authors.

Dr. Arthur L. Cummings, Vice President and Technical Director of MPR Services, Inc., has been involved in research for over 22 years, since receiving the Ph.D. in Analytical-Physical Chemistry from Brigham Young University. His work has led to publications and patents relating to kinetics, thermodynamics, analytical methods, lubricants, sterilants, ion exchange, corrosion, alkanolamines and heat stable salts.

Shade M. Mecum is the President of MPR Services, Inc. He has over 27 years experience in providing services to the oil and gas industry and has held various technical and management positions in Dow Chemical, Dowell Schlumberger, and Schlumberger. Mr. Mecum has a B.Sc. in Chemical Engineering from West Virginia Institute of Technology.

TABLE I

AMINE SYSTEM OPERATIONS IMPROVED BY ION EXCHANGE REMOVAL OF HEAT STABLE SALTS, NOT BY CAUSTIC ADDITION

	DURING CAUSTIC PROGRAM	MAINTAINING LOW HEAT STABLE SALTS BY ION EXCHANGE
CORROSION	Heat Exchanger Fouling and Failure Regenerator Weld Overlay Annually Reboiler Fouling -- Frequent Cleaning Filter Costs High Extra Regenerator Train Installed to Cover Down-time	NO FOULING FILTER COSTS CUT 80%
PERFORMANCE	Foaming continually Amine Losses large Sulfur Plant Upsets Water Treatment Plant Excursions Lean Loading high Bottleneck for hydrocarbon throughput	ANTI-FOAM REDUCED 90% AMINE LOSSES CUT 90% LOWER LEAN LOADING RECORD CRUDE, COKER, and CAT CRACKER RUNS