The CONTACTOR™

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Heat Stable Salts III — Management

In this issue of *The Contactor,* we will look at sources of HSSs and ways to mitigate their effect. Part IV will present some case studies that demonstrate process performance effects.

Sources of HSSs

Most HSSs enter the amine system as contaminants in either the inlet hydrocarbons being treated or by way of impurities in the makeup water. In some cases, mis-lineups of piping are responsible, or even their deliberate introduction into the solvent to adjust the solvent characteristics. Table 1 is provided as a guide to the major sources of HSSs.

Table 1: Common Heat Stable Salt Sources

Source and Relevant Reactions	Reaction Products
Cyanides (Cokers, FCC) $RCN + 2H_2O \rightarrow NH_4^+ + RCOO^-$ $NH_4^+\ Am \leftrightarrow AmH^+ + NH_3$	Formate ($HCOO^-$), Acetate (CH_3COO^-), Glycolate, Propionate, etc. Ammonia (NH_3)
Oxygen Ingress $2HCN + O_2 + H_2S + 2Am \rightarrow 2AmH^+ + 2SCN^- + 2H_2O$ $2H_2S + 2O_2 + 2Am \rightarrow 2AmH^+ + S_2O_3^= + H_2O$ $2H_2S + 4SO_2 + H_2O + 6\ Am \rightarrow 6\ AmH^+ + 3S_2O_3^=$ $S_2O_3^= + 5/2\ O_2 \rightarrow 2SO_4^=$	Thiocyanate (SCN^-), Thiosulfate (S_2O_3=), Sulfate ($SO_4^=$)
Poor Quality Makeup Water Piping mis-lineups Brine carryover Deliberate addition of caustic for neutralization	Chloride (Cl_-) Sodium (Na^+) Potassium (K^+) Calcium (Ca^{2+}) Magnesium (Mg^{2+}) Phosphate (PO_4^{3-})

The effects of heat stable salts can be either acute or prolonged. They are felt in proportion to the rate at which HSSs accumulate in a given system. HSS accumulation can be written as a material balance based on incursion rate, system inventory, and removal rate.

Accumulation = (Incursion – Removal) / Inventory

Systems experiencing high amine losses have a high removal rate of HSSs. But, after amine losses are stopped, the rate of HSS accumulation suddenly increases. This has the unintended consequence that correcting amine loss problems leads to heat stable salt problems, and one of the longer-term consequences of elevated HSS accumulation is higher amine loss due to foam stabilization or increased filter element changeouts.

Corrosion Acceleration

Corrosion acceleration is one of the major long-term problems encountered with HSSs, especially in the hot lean portion of the amine unit. HSS anions are known to chelate iron. An iron sulfide layer normally passivates the surface of carbon steel pipe against corrosion of iron by H_2S. By chelating iron, HSS anions increase the concentration of dissolved ionic iron that can be held in solution. To make matters worse, because of the HSS stripping effect, there is less H_2S in the lean solvent to aid in keeping the passivating layer on the steel. Chelation is chemically equivalent to running high velocities in the piping, which mechanically removes the iron sulfide layer.

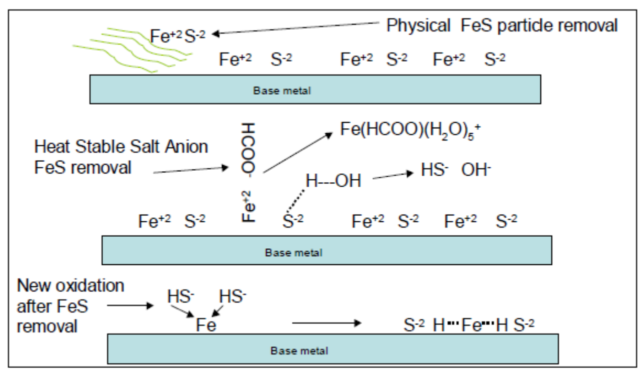

Figure 1: Chelation of Iron by Formate HSS Anion

HSS MANAGEMENT

Prevention

Unfortunately, not much can be done to prevent the incursion of heat stable salts into refinery amine systems. Some HSS precursors can be removed through water wash of the inlet hydrocarbon gas (HCl and SO_2 for instance) with varying success and added cost. The practice of using clean quality makeup water is important (BFW quality or better). Additionally, eliminating oxygen ingress sources should be seriously considered (blanket tanks, eliminate leaks in vacuum gas gathering equipment, etc.). In the case of a sulfur plant tail gas treating unit (TGTU), maintaining good cascade control of the air demand analyser is vital with some benefit for running the Claus plants upstream with the $H_2S:SO_2$ ratio above 2:1 (4:1 to 6:1 is common these days). It should be noted that not all TGTU's, however, were designed to accommodate the additional sulfur load from running excess $H_2S:SO_2$ ratio.

Mitigation

There are a number of methods to mitigate the effects of heat stable salts. Detailed discussion of the practices and technologies available is beyond our scope but in summary:

- Do nothing
- Bleed & Feed
- Caustic Neutralization
- Thermal and Vacuum Reclaiming (Onsite or Offsite)
- Electrodialysis (Mobile and Permanent available)
- Ion Exchange (Mobile and Permanent available)

The cost of HSS management is a trade-off against the operational and maintenance cost of *not* controlling the HSS. A recent case illustrating this was discussed at the 2019 Brimstone Sulfur Symposium by ExxonMobil. A MEA system operating at their Baytown, Texas refinery with 2 wt% HSS in solution for 6 years required replacement of a large portion of the amine regenerator carbon steel shell and trays 1-11. The entire treating plant was down for a month and a half. Just the estimated cost of repairs was USD 1.5MM.

The economics for HSS control is site-dependent and influenced by a number of factors:

<u>HSS Incursion Rate</u>:

Incursion is difficult to predict, but can be correlated from historic data for a given site and basic reaction kinetics.

<u>System Inventory</u>:

Larger inventory means that the system will be able to deal better with a higher HSS incursion rate. This is a big factor in setting the economics for how to deal with HSS. In the case of a Claus TGTU, a common practice is to downgrade the TGTU amine into the primary amine system and make up fresh MDEA into the TGTU. The larger system inventory in the primary amine circuit can provide some "inertia" to absorb the HSS anion increase and be helpful in delaying the need for cleaning. In the event that mobile cleaning is wanted, only one system needs to have clean-up connections.

<u>Amine Losses</u>:

Losses of amine, especially those that are uncontrollable, affect the "apparent" HSS incursion rate. Most large amine losses are controllable, so there is a trade-off between the cost of sloppy amine inventory control and the management of HSS.

<u>Amine Type and Makeup Cost</u>:

Access to supply and local area variability play a role in setting the economics of HSS management. If the amine supply is low cost and inventory is small, some systems may be more economical to manage by bleed-and-feed.

<u>Redundancy</u>:

Although for most sites, this would be a dream come true, there are units that have the flexibility of having an installed "spare" that can be swapped into. In this case, periodic mobile clean-up becomes more economically attractive.

<u>Wastewater Treatment Plant</u>:

The size and health of the onsite WWT plant for digesting amine losses can make or break the bleed and feed option.

<u>Site Access</u>:

Physical access to mobile reclaiming services is an important consideration.

The effectiveness of caustic neutralization has been repeatedly debated by industry. Caustic frees the amine to react once again with the acid gas. In this respect, it restores acid gas handling capacity on the rich side. However, adding caustic does nothing to remove the heat stable salt anions from solution that are still floating around as potential corrosion accelerators. Whether caustic addition reduces the corrosion potential of amine solutions is still debated.

Design Guidelines

Noting all of the preceding factors that interplay and the conflicting guidelines on HSS maintenance levels, the following guidelines are suggested to be considered in the design of new primary amine and MDEA-based TGTU services based upon experience. These guidelines only apply to systems operating at the "normal expected amine strength".

- Run a simulation for clean amine service (no HSSs). For systems that are lean amine pinched, the presence of some HSS will be beneficial to treating. Unless a specialty MDEA solvent is being used, the condition of the unit upon startup or after cleaning) will be clean and free of heat stable salts.
- Use simulation for sensitivity studies on the treating performance at the upper-end of the accepted limits for total heat stable salt anions using the HSSs mixture expected for the amine treating unit's service.
- For units that show differing treating performance under the HSS-laden upper limit, a minimum of two additional sensitivity runs should be done at intermediate HSS conditions equally spaced between the clean and upper-end dirty condition. This determines whether there will be benefit in controlling the HSS to less than the upper corrosion limit.
- For systems where makeup water quality is an issue or caustic neutralization is practiced, a second sensitivity simulation should be run.
- In selective MDEA treating applications that can experience SO_2 breakthroughs or significant oxygen contamination while treating H_2S feeds, sensitivity of the design to MMEA and DEA degradation products should be considered.
- Perform an economic analysis to determine whether periodic batch HSS clean-up should be conducted or if a permanent HSS removal skid should be installed.

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