No matter how small, every refinery has several columns using aqueous amines to remove H₂S and CO₂ from gas streams, and a large refinery can have 20 or more such columns. Almost all natural gas has H₂S, CO₂ or both removed before the gas enters transmission pipelines. For example, synthesis gases used in the ammonia industry must have the CO₂ content reduced to a few hundred parts per million before the catalytic conversion step. Today, post-combustion CO₂ recovery from power plant gases is receiving increased attention. Acid gas removal by aqueous amines is more common than ever. In commercial plants, amine treating solutions are invariably contaminated to some degree with a variety of materials, from surface-active agents to products formed by the oxidation and thermal degradation of the amines themselves, solids including products of reaction of the acid gases with vessel walls and piping or with contaminants present in the gas being treated. This article will focus on the last group of components – contaminants coming in with the gas itself – and in particular the so-called heat-stable salts (HSS). These contaminants are especially vexing in refineries because they are produced unavoidably in a variety of operations and are almost always present. Additionally, some HSS have their source in the tail gas from sulphur plants. Whatever the source, it is interesting to trace their formation.

After a period of time treating sour gases generated by refinery cracking operations (cokers, fluid catalytic cracking [FCC]), trace amounts of acid anion contaminants can build to harmful levels in the solvent. The most commonly found are formate and thiocyanate. They result from the absorption of hydrogen cyanide: formate forms by the hydrolysis of higher-molecular-weight nitrile and cyanide ions to ammonium formate, thiocyanate forms by dissolved absorption of hydrogen cyanide: formate forms by the hydrolysis of the reaction of the acid gases with vessel walls and piping or with contaminants present in the gas being treated. This article will focus on the last group of components – contaminants coming in with the gas itself – and in particular the so-called heat-stable salts (HSS). These contaminants are especially vexing in refineries because they are produced unavoidably in a variety of operations and are almost always present. Additionally, some HSS have their source in the tail gas from sulphur plants. Whatever the source, it is interesting to trace their formation.

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Heat-stable Salts and Amine Unit Performance

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Figure 1

This figure shows the contactor containing 20 feet of FLEXIPAK 2Y structured packing to minimise pressure drop and maximise tower capacity. TGTUs are typically run on a separate solvent circuit; however, this one was being run as part of the refinery MDEA system.
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“America’s Safest Companies”
Occupational Hazards Magazine

“#1 Design Firm – 2000-2007”
Engineering News-Record

“North America’s Top Companies for Leaders”
Hewitt Associates, FORTUNE Magazine, The RBL Group

“Top 10 Most Admired Engineering and Construction Companies”
FORTUNE Magazine
An analysis performed by the solvent vendor showed several HSS present at the concentrations shown in the figure, with total HSS at 0.8115 weight per cent. Perhaps surprisingly, the unit was nevertheless producing a vent gas with only 3ppmv H2S, a very low concentration for a TGTU, where 100ppmv is much more normal. The solvent was obviously quite contaminated and operations were considering reclaiming it. The question was asked: ‘If we reclaim the solvent by removing HSS, what will be the impact be, if any, on treating performance?’ The right place to start answering this kind of question is a good, reliable simulation capable of modelling the real equipment and the real contaminated solvent.

ProTreat™, a mass transfer rate-based amine-treating simulator, was used to model the complete plant, including the regenerator with a known tray count, the detailed solution analysis (HSS profile) and reboiler duty. The predicted treat was 2.3ppmv H2S compared with the measured level of 3ppmv H2S – to within the accuracy of the instrumentation these are identical numbers.

If a model that did not account for HSS had been used, the predicted treat would have been over 44ppmv, more than 10 times the observed value. Table 1 shows the simulated effect of various levels of HSS removal (degrees of reclaiming) on lean solution quality and H2S treat. This suggests that a serious additional contribution to the refinery’s allowable sulphur emissions might result from reclaiming, even if carried out only moderately. Apart from benchmarking the reliability of the simulator, the first lesson is that, at least in a TGTU, a clean solvent may not treat to nearly as low a residual H2S level as a contaminated solvent.

CO2 slip is hardly affected by reclaiming, but reclaiming has a tremendous effect on the unit’s H2S leak. Notice also that when the solvent contains its full complement of HSS, lean loadings are reduced by a factor of 10 for CO2 and a factor of 100 for H2S compared with the virgin solvent. The processing effect of HSS is really felt in the regenerator, where much lower loadings can be achieved when the solvent contains HSS. Perhaps this should not be so surprising. After all, it is well known that the addition of small amounts of phosphoric acid gives superior tail gas-treating, and this is the basis for several speciality solvents offered by vendors. They go by various names such as protonated amines, partially neutralised amines and acidified amines. The rest of this article tries to explain why HSS can have such a profound effect on treating unit performance.

**Mechanism**

Intentionally acidified amines and amines contaminated with HSS all promote solvent regeneration by the same mechanism. They shift the equilibrium of the reactions that occur between the acid gases and the amines. For example, when H2S is present in a solution of amine such as MDEA, very little of it exists as the molecule H2S because when H2S chemically dissociates in the solution, the hydrogen ion it produces is neutralised by the amine:

\[
3. \quad \text{H}_2\text{S} = \text{H}^+ + \text{HS}^-
\]

4. \( \text{R}_1\text{R}_2\text{R}_2\text{N} + \text{H}^+ = \text{R}_1\text{R}_2\text{R}_2\text{NH}^+ \)

The overall reaction is:

5. \( \text{H}_2\text{S} + \text{R}_1\text{R}_2\text{R}_2\text{N} = \text{R}_1\text{R}_2\text{R}_2\text{NH}^+ + \text{HS}^- \)

where \( R_1 \) and \( R_2 \) are the methyl and ethanol groups, respectively, that make up MDEA. When part of the amine is neutralised by a small amount of phosphoric, sulphuric or other acid (purposefully) or by HSS (contaminants), the concentration of the protonated form of the amine is higher than it would normally be. This tends to push the reaction equilibrium to the left. Displacement to the left favours decomposition and the formation of free H2S. Therefore, in a regenerator stripping is favoured.

At high acid gas loadings the impact of a small amount of additional protonation is completely negligible because the protonated amine concentration is already very high (small change to a high concentration). However, in the reboiler, for example, the H2S loading...
will be very small (if low H2S leak is to be achieved from the TGTU), so even a small amount of additional protonation is highly significant relative to the very low concentration of protonated amine normally present. In fact, the additional protonation can be 10–100 times higher than would normally be found in a well-regenerated virgin MDEA solution. The additional amine protonation caused by HSS and purposefully added acids displaces reaction 5 strongly to the left, towards the formation of free molecular H2S capable of desorbing from the solution. Additional (perhaps even artificially introduced) protonation enhances solvent regeneration.

However, the higher H2S back-pressure caused by the increased protonation arising from HSS affects absorption negatively. It turns out that its beneficial effect on reducing the lean loading in the regenerator far outweighs its negative effect on back-pressures in the absorber. The result can easily be a factor of 10 or 20 lower H2S leak when HSS are present in small amounts. Of course, caution is needed not to let HSS build up to too high a level because they are corrosive. Caution is also needed not to reclaim too aggressively, or treat may be lost. Even if the corrosion resulting from high HSS concentrations is unacceptable and the HSS must be removed, their beneficial effect can still be had by replacing them with a small amount of phosphoric acid. Simulation will reveal how much phosphoric acid is enough, how much to reclaim (from a process standpoint) and what the outcome on treating unit performance will be. As for CO2, the outlet CO2 concentration is controlled by the extreme slowness of the reaction between CO2 and the amine (actually the low OH⁻ ion concentration in the solution), and not by lean loading. Thus, the effect on CO2 slip of even a factor of 10 reduction in lean solvent CO2 load is negligible. One factor that does not generally seem to be appreciated is that using stripping promoters such as phosphoric acid to reduce H2S leak is effective only if the contactor is lean-end pinched with respect to H2S. Whether a given column is or is not lean-end pinched is unmistakably shown by mass transfer rate-based simulation of the column. If the column is lean-end pinched, the concentration of H2S will remain small and constant over several metres of packing or several trays at the top (lean end) of the column.

Reclaiming decisions should start with a good set of simulations generated using a process simulator that has high accuracy and reliability. Only mass and heat transfer rate-based simulations meet this criterion. The simulator must also be able to model the actual system under study, especially the detailed solution chemistry and the mass transfer behaviour of the real column internals being used. Accurate regenerator modelling is just as important as simulating the absorber, simply because the regenerator sets the acid gas lean loadings and regeneration is where HSS and stripping promoters have their real effect.

1. The ionic compound R₁R₂R₃NHX is called a heat stable amine salt (HSAS) even though it exists only in the fully dissociated form R₁R₂R₃NH⁺ + X⁻ in aqueous solution.
2. It turns out that these acidic components, heat-stable salts (HSS), are actually very effective regeneration enhancers, but their presence in solution is detrimental to absorption. It is really a question of whether regeneration is helped more than absorption is hurt, and whether the absorber itself is being operated in a region where the effect of much lower lean solvent loadings can be felt at all. Sometimes an HSS is added on purpose – e.g. phosphoric acid – and the effect on solution regeneration is usually dramatic.