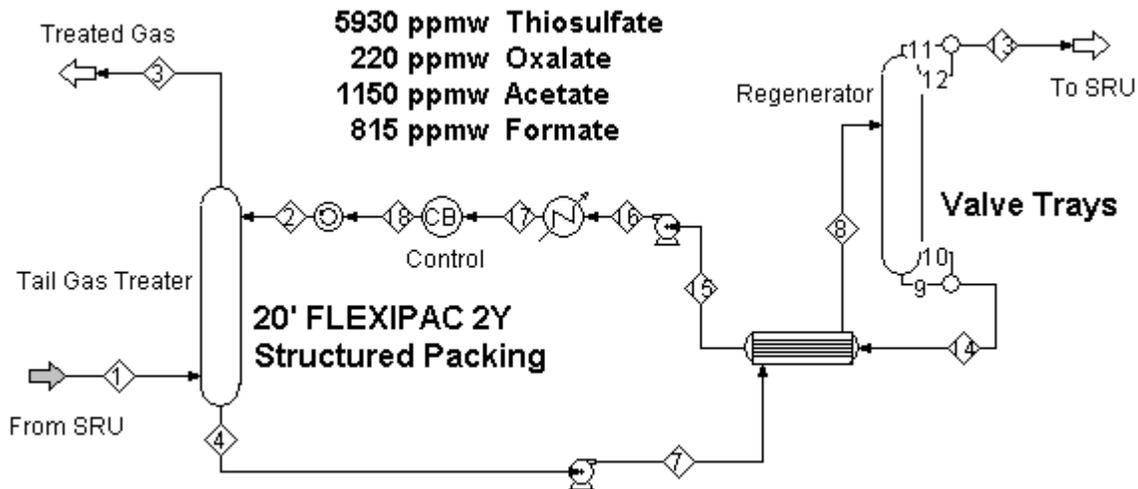




The CONTACTOR™

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Impact of Reclaiming on Performance of a Tail Gas Treater



In this issue, we assess the effect of heat stable salts on the performance of a refinery tail gas treating unit (TGTU) and examine how treating responds to various levels of solvent reclaiming.

The TGTU in this refinery is a fairly conventional unit using 34 wt% MDEA to treat SRU tail gas containing 1.7% H₂S and 3.4% CO₂. As shown in the Figure, the contactor contains 20-ft of FLEXIPAC® 2Y structured packing to minimize pressure drop and maximize tower capacity.

TGTUs are typically run on a separate solvent circuit; however, this one was being run as part of the refinery MDEA system. A solvent analysis showed several heat stable salts (HSSs) present at the concentrations shown in the figure, with total HSSs at 0.8115 wt%. Surprisingly, the unit was producing a vent gas containing only 3 ppmv H₂S. The question is, if we reclaim the solvent by removing HSSs, what will be the impact, if any, on treating performance? The right place to start answering this kind of question is a good,

reliable simulation capable of modeling the real equipment and the real, plant solvent.

ProTreat™, OGT's mass transfer rate based amine treating simulator, was used to model the complete plant, including the regenerator with a known tray count, HSS level, and reboiler duty. The predicted treat was 2.3 ppmv H₂S, compared with the measured level of 3 ppmv H₂S—these are the same to within the accuracy of the instrumentation.

If a model that did not account for HSSs had been used, the predicted treat would have been over 44 ppmv, more than 10 times the observed value, suggesting a serious additional contribution to the refinery's allowable sulfur emissions. The first lesson then, has to do not just with the reliability of various simulators, but with the effect of HSSs on treating. **In a TGTU, a clean solvent probably will not treat to nearly as low a residual H₂S level as a contaminated solvent will.** The rest of this article aims to understand why.

The accompanying Table shows the effect of various levels of HSS removal (degrees of reclaiming) on lean solution quality and H₂S treat.

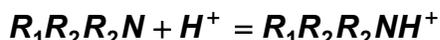
Effect of HSS Removal on TGTU Performance

% HSS Removed	Lean CO ₂ Load (mol/mol)	Lean H ₂ S Load (mol/mol)	H ₂ S Leak (ppmv)	CO ₂ Slip (%)
0	0.000205	0.000071	2.33	66.05
25	0.000320	0.000251	6.45	65.79
50	0.000544	0.000934	17.5	65.55
75	0.001018	0.002790	34.49	65.33
100	0.002044	0.006177	44.32	65.17

CO₂ slip is hardly affected by reclaiming, but reclaiming has a tremendous effect on the unit's H₂S leak. Notice also the lean loadings of CO₂ and H₂S—when the solvent contains its full compliment of HSSs, lean loadings are reduced by a factor of 10 for CO₂ and a factor of 100 for H₂S compared with the virgin solvent. The second lesson is: **the processing effect of HSSs is really felt in the regenerator where much lower loadings can be achieved when the solvent contains HSSs.** Perhaps this should not be so surprising. After all, it is well known that the addition of small amounts of such components as phosphoric and sulfuric acids gives superior tail gas treating—this is the basis for several specialty solvents offered by vendors. They go by various names such as protonated amines, partially-neutralized amines, and acidified amines.

Mechanism

Intentionally acidified amines and amines contaminated with HSSs 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 an amine solution such as MDEA, very little of it exists as the gas H₂S because when H₂S chemically dissociates in the solution, the hydrogen ion it produces is neutralized by the amine:



The overall reaction is



where R₁ and R₂ are the methyl and ethanol groups that make up methyldiethanolamine (MDEA). When part of the amine is neutralized by a small amount of phosphoric, sulfuric, or other acid (purposefully) or by HSSs (contaminants), the concentration of the protonated form of the amine is higher than it normally would be and this tends to push the reaction equilibrium to the left. Displacement to the left favors decomposition and the formation of free H₂S. In a regenerator, therefore, stripping is favored.

At high loadings the impact of a small amount of additional protonation is minimal because the protonated amine concentration is already very high. But in the reboiler, for example, the H₂S loading should be very *small* (if low H₂S leak is to be achieved from the TGTU), so even a small amount of additional protonation is very significant. *In fact, the additional protonation can be factors of 10 higher than what would normally be found in a well-regenerated virgin MDEA solution.*

The higher H₂S back-pressure caused by protonation affects absorption negatively. However, 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 HSSs are present *in small amounts*. Of course, **caution is needed not to let HSSs build up too high because they are corrosive. But caution is also needed not to reclaim too aggressively or treat may be lost.**

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.

Reclaiming decisions should start with a good set of simulations generated using a process simulator that has high accuracy and reliability. The simulator must also be able to model the actual system under study, especially the detailed solution chemistry and the mass transfer behavior of the real column internals being used. Accurate regenerator modeling is just as important as simulating the absorber.

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