The CONTACTOR™

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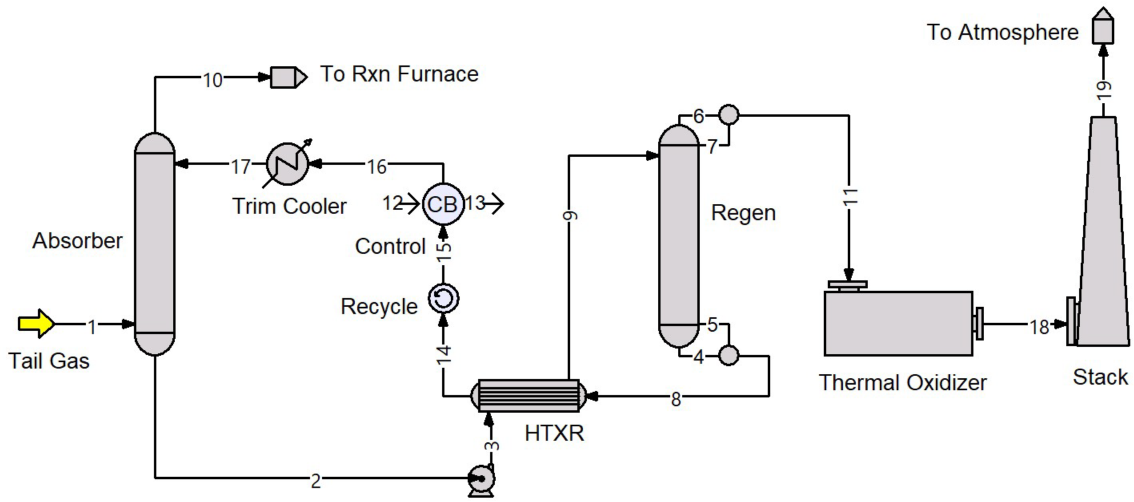
Contaminated Solvents — Effect of Reclaiming on Performance of a Tail Gas Treater



In this writing, we evaluate the impact of heat-stable salts on the performance of a refinery tail gas treating unit (TGTU) and explore how the treatment responds to varying levels of solvent reclaiming†. The TGTU in this refinery employs a conventional approach using 34 wt% MDEA to treat SRU tail gas having 1.7% H_2S and 3.4% CO_2. The contactor has 20 feet of FLEXIPAC® 2Y structured packing to minimize pressure drop and maximize tower capacity.

Typically, TGTUs operate on a separate solvent circuit, but in this case, it was integrated into the refinery MDEA system. Solvent analysis revealed the presence of heat-stable salts (HSSs) at concentrations totaling 0.8115 wt%. Despite this, the unit produced a vent gas containing only 3 ppmv H_2S, prompting the question of the potential impact on treatment performance if the solvent were to undergo HSS removal. To answer this, a reliable simulation capable of modeling the actual equipment and plant solvent was necessary.

ProTreat®, OGT's amine treating simulator, strictly based on mass transfer rates, was used to model the entire plant, including the regenerator with known tray count, HSS level, and reboiler duty. The predicted treatment was 2.3 ppmv H_2S, closely matching the measured level of 3 ppmv H_2S within the instrumentation's accuracy.

Notably, using a model that ignores HSSs would have resulted in a predicted treatment exceeding 44 ppmv, over 10 times the observed value, indicating a potentially significant contribution to the refinery's sulfur emissions. This underscores not only the importance of simulator reliability but also the considerable impact of HSSs on treatment. In a TGTU, a clean solvent may not achieve as low a residual H_2S level as a contaminated solvent.

The table illustrates the influence of different degrees of HSS removal on TGTU performance, specifically on lean solution quality and H_2S treatment. CO_2 slip remains largely unaffected by the reclamation process, whereas the impact on the

† This is a revision of The Contactor, Vol. 1, No. 2, Aug. 2007

unit's H_2S leak is substantial. Notably, the lean loadings of CO_2 and H_2S experience a significant reduction, approximately 10 times for CO_2 and 100 times for H_2S when the solvent contains a full complement of heat-stable salts (HSSs) compared to the virgin solvent. This underscores the profound processing effect of HSSs, particularly in the regenerator, where achieving much lower loadings is feasible when the solvent contains HSSs. This observation aligns with the well-known fact that the addition of small amounts of components such as mineral acids enhances tail gas treating, a fact that is used in some commercial solvents.

Effect of HSS Removal on TGTU Performance

% HSS Removed	Lean CO_2 Load (mol/mol)	Lean H_2S Load (mol/mol)	H_2S 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

Mechanism

The mechanism behind the effect involves intentionally using the parallel between acidified amines and amines contaminated with HSSs. They promote solvent regeneration through the same mechanism by shifting the equilibrium of reactions occurring between acid gases and amines. For instance, in an amine solution like MDEA with H_2S, the molecular gas exists only minimally due to chemical dissociation in the solution, whereby the hydrogen ion produced is neutralized by the amine:

$$\boldsymbol{H_2S = H^+ + HS^-}$$

$$\boldsymbol{R_1R_2R_2N + H^+ = R_1R_2R_2NH^+}$$

The overall reaction is:

$$\boldsymbol{H_2S + R_1R_2R_2N = R_1R_2R_2NH^+ + HS^-}$$

The overall reaction involves methyl and ethanol groups (R_1 and R_2) constituting methyldiethanolamine (MDEA). When part of the amine is neutralized by a small amount of acid (intentionally added) or by HSSs (contaminants), the higher concentration of the protonated amine shifts the reaction equilibrium leftward, favoring decomposition and the formation of free H_2S. Consequently, stripping is favored in the regenerator.

At high loadings, the effect of additional protonation is minimal due to an already high protonated amine concentration. However, in the reboiler, where H_2S loading should be minimal for a low H_2S leak from the TGTU, even a slight increase in protonation is significant. The higher H_2S back-pressure caused by protonation negatively affects absorption, but its beneficial effect on reducing lean loading in the regenerator outweighs the negative impact on back-pressures in the absorber. This can result in a 10 to 20 times lower H_2S leak when HSSs are present in small amounts. Caution is necessary to prevent excessive build-up of HSSs due to their corrosive nature, but an overly aggressive reclamation approach could lead to a loss of treatment effectiveness.

Regarding CO_2, the outlet concentration is controlled by the slow reaction between CO_2 and the amine, specifically the low OH^- ion concentration in the solution, rather than lean loading. Therefore, even a tenfold reduction in lean solvent CO_2 load has a negligible effect on CO_2 slip.

Decisions on reclamation should commence with thorough simulations utilizing a process simulator with high accuracy and reliability. The simulator must be capable of modeling the *actual* system, including detailed solution chemistry and the mass transfer behavior of the real column internals. Accurate regenerator modeling is as crucially important as simulating the absorber.

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To learn more about this and other aspects of gas treating, plan to attend a *ProTreat*® workshop in your region. For details, visit www.protreat.com/seminars.

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