Benefits of Heat Stable Salts in Tail Gas Treaters

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ABSTRACT

It is well-established technology that adding phosphoric acid to N-methyldiethanolamine (MDEA) solutions in tail gas treating units (TGTUs) enables significantly deeper stripping of hydrogen sulphide in the regenerator and permits tail gas to be treated to as low as 10 ppmv H_2S. Most heat stable salts are the organic acid equivalents to phosphoric acid, and they function in exactly the same way. Just like phosphoric acid, under the right absorption conditions they can greatly enhance hydrogen sulphide removal. This contribution explains the mechanism through which stripping promoters act, it shows that removing HSSs to very low levels can be detrimental to the operation of TGTUs, and it provides guidelines on determining when, and how much, HSSs should be left in the treating solvent.
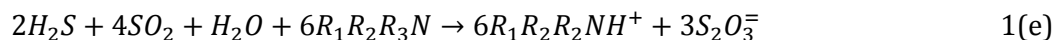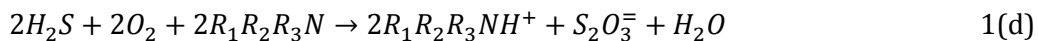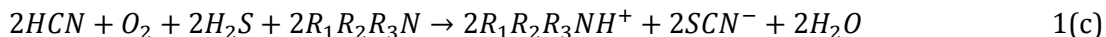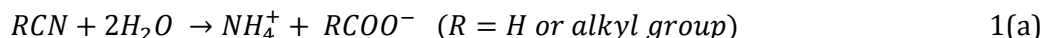
INTRODUCTION

In commercial gas plants, amine treating solvents are invariably contaminated to some degree with a variety of materials, including (1) surface active agents, (2) products formed by the oxidation and thermal degradation of the amines themselves, (3) solids including products of reaction of the acid gases with vessel walls and piping, and (4) contaminants present in or generated by the gas being treated. This article focuses on the effect of contaminants in the last category that either enter the amine system with the gas itself, or are formed by reaction of certain gas components with the solvent. Contaminants in this fourth group are the heat stable salts (HSSs). As a class, they are especially troublesome in refineries because, their precursors such as hydrogen cyanide and ammonia are unavoidably produced in a variety of operations so they are almost always present. The precursors of other HSSs, for example SO_2, are present in the tail gas from sulphur plants. Other HSSs can enter the amine system with the water used to replenish evaporation or other losses.

Heat stable salts are generally the anions of organic and inorganic acids, including formate, acetate, propionate, glycolate, thiocyanate, thiosulphate, oxalate, sulphite, sulphate, and chloride. Common cations are sodium and potassium. Because they are ions they exert no vapour pressure and so are completely nonvolatile. These ionic species remain in solution and cannot be steam or heat stripped; hence, the terms 'heat stable' and 'salt'. Sodium and potassium ions are not sourced in the gas; rather, they usually enter the amine system with poor quality water used to replenish losses from the treating plant. Hydrogen from gasoline reformers can contain hydrogen chloride

which will absorb and react directly in acid-base neutralization with the amine. Phosphate ion is another HSS, but it is one that is purposefully added to the solvent as phosphoric acid. The purpose of adding phosphoric acid is to enhance solvent regeneration by allowing lower solvent lean loadings to be reached with the same regeneration energy. Phosphoric acid is a stripping promoter. This suggests that HSS anions might also act as stripping promoters, something that is borne out in what follows.

It is instructive to trace the formation of HSS anions from their precursors. The most common precursors are hydrogen cyanide which enters with the refinery gas, ammonia which may be in the refinery gas or may be a reaction product of HCN hydrolysis, and sulphur dioxide which enters with sulphur plant tail gas. Oxygen is also required for the formation of certain HSSs. Formate and thiocyanate are products of the reaction of absorbed hydrogen cyanide. Formate forms by the hydrolysis of cyanide ion to ammonium formate (Reaction 1a); thiocyanate forms by the reaction of dissolved oxygen with H_2S followed by reaction of the oxysulphur anion with cyanide ion (Reaction 1c). Higher molecular weight organic acid anions are generated by the hydrolysis of higher molecular weight nitrile compounds (Reaction 1a). Ammonium ion from nitrile hydrolysis will give up an H^+ to the amine (Reaction 1b) and the resulting ammonia is then stripped by steam in the regenerator where it accumulates in the overhead condensing system. This leaves the protonated amine/HSS anion pair in the amine solution. Thiosulphate generally results from the reaction of dissolved oxygen with H_2S (Reaction 1d) or from SO_2 reaction with H_2S (Reaction 1e) in tail gas treaters when no HCN is present. Sulphite can form from absorption of sulphur dioxide, and sulphate can form either from oxidation of sulphite, or from the further oxidation of thiosulphate (Reaction 1f).

$$RCN + 2H_2O \rightarrow NH_4^+ + RCOO^- \quad (R = H \; or \; alkyl \; group) \qquad \text{1(a)}$$

$$NH_4^+ + R_1R_2R_3N \rightleftharpoons R_1R_2R_3NH^+ + NH_3 \qquad \text{1(b)}$$

$$2HCN + O_2 + 2H_2S + 2R_1R_2R_3N \rightarrow 2R_1R_2R_3NH^+ + 2SCN^- + 2H_2O \qquad \text{1(c)}$$

$$2H_2S + 2O_2 + 2R_1R_2R_3N \rightarrow 2R_1R_2R_3NH^+ + S_2O_3^= + H_2O \qquad \text{1(d)}$$

$$2H_2S + 4SO_2 + H_2O + 6R_1R_2R_3N \rightarrow 6R_1R_2R_2NH^+ + 3S_2O_3^= \qquad \text{1(e)}$$

$$S_2O_3^= + \tfrac{5}{2}O_2 \rightarrow 2SO_4^= \qquad \text{1(f)}$$

For a strong acid H_nX where X is an n-valent anion (Cl^-, $SO_4^=$, etc.), the reaction with amine is

$$H_nX + nR_1R_2R_3N \rightarrow nR_1R_2R_3NH^+ + X^{-n} \qquad (2)$$
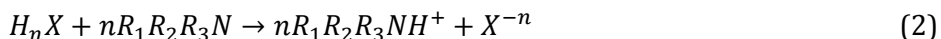
Unlike the acid gas-amine reactions, *none* of these reactions are thermally reversible. HSSs permanently tie up part of the amine as $R_1R_2R_3NH^+$ ion[1] and the amine becomes partially protonated, i.e., neutralized. The amine is gradually converted to HSAS so it becomes inactivated. Heat stable salt anions are also known to complex iron which accelerates corrosion in the hot, lean section of the amine unit. Contact between complexed iron and higher concentrations of H_2S in the absorber generates iron sulphide particles which can foul equipment, lead to loss of treating capacity and further exacerbate corrosion by eroding the protective iron sulphide film on carbon steel piping and equipment surfaces. Although the foregoing description paints a bleak picture of

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[1] The ionic pseudo-compound $R_1R_2R_3NHX$ is called a heat stable _amine_ salt (HSAS) even though it exists only in the fully *dissociated* form, $R_1R_2R_3NH^+ + X^-$, in aqueous solution.

HSSs, they may not always be bad. How and by what mechanism they influence the amine treating process are questions that are addressed quantitatively through a case study, and the results are explained through chemistry.

CASE STUDY

The case study is of the refinery tail gas treating unit (TGTU) shown in Figure 1. This is a conventional system using 33.37 wt% MDEA contaminated with 0.33 wt% DEA to treat tail gas from an SRU. The tail gas has been water quenched so it is saturated with water. Acid gases are 1.7% H_2S and 3.4% CO_2. The contactor contains 20-ft of FLEXIPAK® 2Y structured packing to minimize pressure drop and maximize tower capacity. The regenerator has 20 valve trays with rich amine feed to the 3rd tray from the top.

TGTUs are typically run on a separate solvent circuit; however, this one was being run as part of the refinery MDEA system. An analysis performed by the solvent vendor showed that in addition to being contaminated with DEA, the solvent contained several heat stable salts (HSSs) present at the following concentrations: thiosulfate, 5930 ppmw; Oxalate, 220 ppmw; Acetate, 1150 ppmw; Formate, 815 ppmw. The total HSSs level was 0.8115 wt% (8,115 ppmw). Perhaps surprisingly, the unit nevertheless was producing a vent gas with only a few ppmv H_2S, a very low concentration for a TGTU where 100 ppmv is much more the norm. The solvent is obviously quite contaminated and operations were considering reclaiming. The question was asked: If we reclaim the solvent by removing all the HSSs, will treating performance be affected, and if so, by how much? The right place to start answering this kind of question is a good, reliable simulation capable of modeling the real equipment performance when using the as-analysed, contaminated solvent.

ProTreat® is a completely predictive mass transfer rate based amine treating simulator and was used to model the complete plant, including the details of the actual internals of both the absorber and the regenerator columns. The software accounts for the detailed solution analysis (HSS profile), and uses measured reboiler duty. The predicted hydrogen sulphide treating achieved using the contaminated as-analysed solvent is 6.7 ppmv H_2S, with a CO_2 slip of 77%.

If a model that did not account for HSSs had been used, the predicted H_2S treating would have been more than 100 ppmv, well over 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 H_2S treat. The H_2S leak is plotted as a function of HSS removal in Figure 2. The results suggest that an additional contribution to the refinery's allowable sulphur emissions would almost certainly 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 H_2S level as a contaminated one*. An acceptable level of contamination is determined by the competing factors of very efficient treating and the need to keep corrosion rates within tolerable limits.

CO_2 slip is hardly affected by reclaiming, but reclaiming has a tremendous effect on the unit's H_2S leak. Notice also that when the solvent contains its full complement of HSSs, lean loadings are reduced by a factor of six for CO_2 and a factor of 250 for H_2S compared with the clean solvent. The second lesson is: the processing effect of HSSs really makes itself known 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 phosphoric acid 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. The effect of phosphoric acid in this case study is examined later.
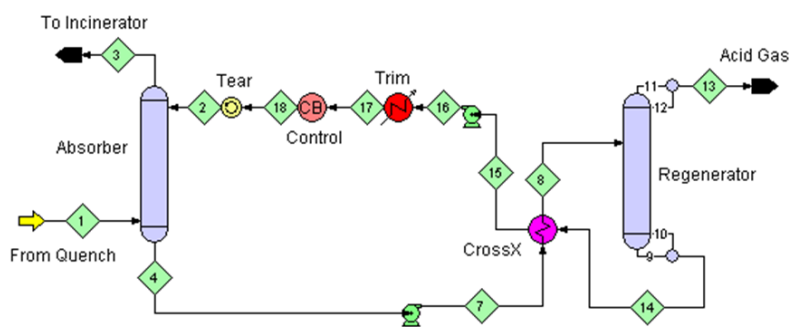
Figure 1   PFD of the TGTU in the Case Study

Table 1   Effect of HSS Level on TGTU Performance

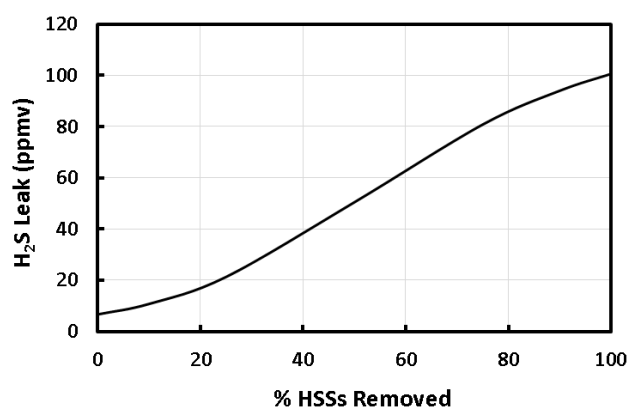| Total HSSs as Percentage of Analysed Level	Lean CO_2 Load (mol/mol)	Lean H_2S Load (mol/mol)	H_2S Leak (ppmv)	CO_2 Slip (%)
0	0.000253	0.0109	100	76.1
10	0.000383	0.00852	94	76.1
25	0.000268	0.00577	89	76.2
50	0.000153	0.00249	51	76.6
75	0.0000920	0.000789	21	77.0
100	0.0000578	0.000194	6.7	77.2
125	0.0000384	0.000045	1.9	77.6

Figure 2   Effect of Heat Stable Salt Removal on H_2S Leak from Absorber

Conclusion 1

   A clean solvent may not treat to nearly as low a residual H_2S level as a contaminated one.

Conclusion 2

Heat stable salts removal has very little effect on the CO2 slipped in MDEA treating.

Conclusion 3

The presence of a substantial concentration of HSSs allows the regenerator to produce a much more cleanly stripped solvent, at least using MDEA.

MECHANISM

Acid anions in MDEA treating solutions promote solvent regeneration by shifting the equilibrium of the acid gas-amine reactions. For example, when H_2S is present in MDEA solvent, very little of it actually exists as the molecule H_2S because when hydrogen sulphide chemically (and instantaneously) dissociates in the solution, the hydrogen ion it produces is immediately neutralized by the amine:

$$H_2S \rightleftharpoons H^+ + HS^- \tag{3}$$

$$R_1R_2R_3N + H^+ \rightleftharpoons R_1R_2R_3NH^+ \tag{4}$$

The overall reaction is

$$H_2S + R_1R_2R_3N \rightleftharpoons R_1R_2R_3NH^+ + HS^- \tag{5}$$

Here R_1 is the methyl group and R_2 and R_3 are the ethanol groups that make up *N*-methyldiethanolamine (MDEA). When part of the amine is neutralized by a small amount of an acid cation, the concentration of the *protonated* form of the amine is higher than it normally would be. This tends to push the reaction equilibrium to the left, towards *free* dissolved hydrogen sulphide. In a regenerator, therefore, 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: in other words, there is only a very small change to an already high concentration. But in the reboiler, for example, the H_2S loading will already be very *small* (if low H_2S 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 there. *In fact, the additional protonation can be 10 to 100 times higher than what would normally be found in well-regenerated, clean, generic MDEA.* The additional amine protonation displaces Reaction (5) strongly to the left, towards the formation of free, molecular H_2S capable of desorbing from the solution. Greater non-acid gas generated protonation enhances solvent regeneration. However, the effect of additional protonation on absorber performance somewhat counteracts its effect on stripping and, depending on circumstances, it may overwhelm the stripping benefit altogether.

The higher H_2S back-pressure caused by the increased protonation arising from HSSs negatively affects absorption. However, it turns out that in TGTUs, its beneficial effect on reducing the lean loading in the regenerator far outweighs its negative effect on back-pressures in the absorber. As shown in the Case Study, the result can easily be a factor of 10 or 20 times lower H_2S 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 what once was superb treating may become very poor treating, unfortunately discovered only post-cleaning. Accurate simulation makes it very easy to predetermine the desired HSS removal level (from a process standpoint) prior to solvent cleaning. Even if the corrosion resulting from high HSS

concentrations is unacceptable and the HSSs *must* be removed, their beneficial effect can still be had by replacing them with a small amount phosphoric acid which supplies the very effective trivalent phosphate cation.

Conclusion 4

Heat stable salts have a highly significant effect on hydrogen sulphide removal in TGTUs and solvent cleaning must be carried out judiciously to avoid nasty surprises. Accurate process simulation is the most effective way to ensure a prudent decision.

CASE STUDY CONTINUED — PHOSPHORIC ACID

Phosphoric acid is a well-establish stripping promoter frequently used in TGTUs. If the MDEA used in a refinery tail gas treating system easily becomes contaminated with HSSs, there seems little point in adding phosphoric acid to the mix because reclaiming will be all too frequent, and whenever the solvent is reclaimed phosphoric acid will also be removed. However, in gas plants HSSs are not usually a problem so the use of phosphoric acid is generally found to be beneficial in gas plant TGTUs.

The details of the case study remain the same but the mixture of HSS contaminants is replaced with various levels of phosphoric acid. Included is one-for-one replacement of the total HSS level with an equal mass concentration of phosphoric acid to get a direct comparison between a mixture of various HSS components and phosphoric acid. Figure 3 shows the effect of phosphoric acid concentration on the H_2S leak from the TGTU.
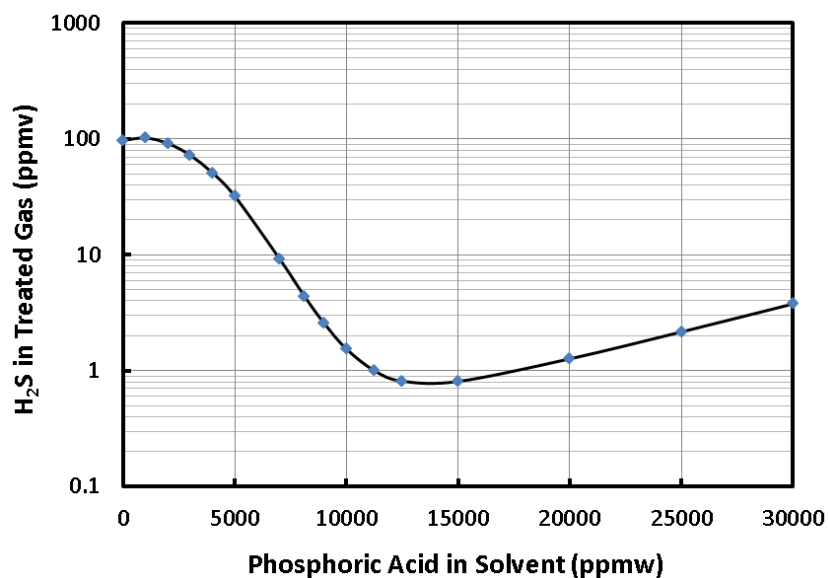

Figure 3   Effect of Phosphoric Acid Concentration on the H_2S Leak from the TGTU Absorber

In this case, there is an optimal concentration of between 1.3 and 1.4 wt% at which the most benefit is realized. A minimum (or maximum) can always be explained by the presence of two competing effects. On the low concentration side of the optimum, increasing phosphoric acid

concentrations drives the equilibrium Reaction (5) to the left. And even as the concentration increases well beyond the optimum level, the loading of both acid gases in the solvent continues to drop. Counteracting this is the increased equilibrium partial pressure of hydrogen sulphide at the top of the absorber which is caused by the higher salt (phosphate ion) concentration, despite the lower H_2S loading of the solvent. Higher backpressure limits the achievable hydrogen sulfide leak.

The optimal concentration is not a uniformly fixed value. Commonly, about 5,000 ppmw is recommended and this usually provides excellent treating down to some 10 ppmv H_2S leak. However, the true optimal concentration depends on the unit and its operating conditions. Note however, that phosphoric acid is a good cleaning agent and, if used *in excess*, it could possibly remove iron sulphide protective films.

Conclusion 5
Just like HSSs, phosphoric acid can be an effective stripping promoter in TGTUs. But there is an optimal level for maximum effectiveness and just what that optimal concentration is depends on the particulars of the operation. One concentration does not 'fit all'.
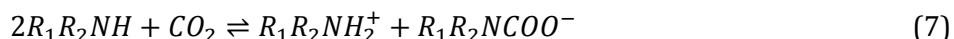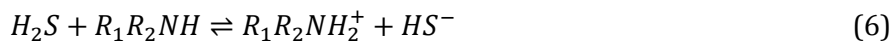
Conclusion 6
High HSS levels are known to be corrosive and this may be the deciding factor dictating when reclaiming should be done. In the same way, phosphoric acid is also corrosive in the sense that it can solubilize iron sulphide protective films. Concentrations greatly in excess of what is necessary to achieve the desired level of treating should not be used. If reclaiming is to be done without benefit of simulation, it might be prudent to set aside a quantity of contaminated solvent to be added back in case the TGTU fails to treat adequately using the cleaned solvent.

CONDITIONS FOR BENEFICIAL RETENTION OF HSSs

The important unaddressed questions are: (a) what are the conditions necessary for HSSs and phosphoric acid to be beneficial, and (b) when they will negatively affect treating. There are two necessary, although not sufficient, conditions for acid anions to be beneficial:

- The main amine constituent in the solvent must not be a carbamate former, although *small* amounts of amines reactive with carbon dioxide and small amounts of CO_2 are permitted.
- Operationally, the absorber must be lean-end pinched.

If the amine forms a carbamate as in Reaction (7), then not only will the hydrogen ion produced by H_2S dissociation neutralise part of the amine according to Reaction (6), but there will also be a substantial amount of protonated amine coproduced with carbamate formation. Carbamate formation is not nearly as easy to thermally reverse as hydrogen sulphide absorption so there will almost invariably be a substantial concentration of protonated amine. Therefore, adding even a few weight percent HSSs will not increase the protonated amine concentration enough to shift materially the equilibrium of Reaction (6) towards the formation of free, dissolvent, volatile hydrogen sulphide.

$$H_2S + R_1R_2NH \rightleftharpoons R_1R_2NH_2^+ + HS^- \tag{6}$$

$$2R_1R_2NH + CO_2 \rightleftharpoons R_1R_2NH_2^+ + R_1R_2NCOO^- \tag{7}$$

The significance of the first condition then is that MDEA and TEA, being tertiary amines, are certainly not carbamate formers, so acid anions may possibly allow stripping of acid gases from these solvents to unprecedented levels. The same is true of hindered secondary amines. Despite not being tertiary, carbamate formation is blocked by stearic hindering so amines in this class may

also respond well to HSSs and the purposeful addition of other acid anions. The solvent must be one that is well suited for slipping carbon dioxide. On the other hand, no amine that reacts with carbon dioxide, releasing hydrogen ion, stands any chance whatever of benefiting from leaving HSSs in the solvent, or from adding a stripping promoter.

The second factor is that the absorber must operate lean-end pinched. In practical terms this means the hydrogen sulphide in the treated gas must be determined directly by lean solvent H_2S loading. But how does one know if an absorber is lean-end pinched? This is another area where a high quality simulation can provide valuable insights. The TGTU absorber gas and liquid temperature profiles, and the profiles of the actual CO_2 concentration in the gas together with the CO_2 concentrations that would be in local equilibrium are shown in Figures 4(a) and (b).

(a) **Gas and Liquid Temperatures**   (b) **Actual and Equilibrium H₂S Levels in Gas**
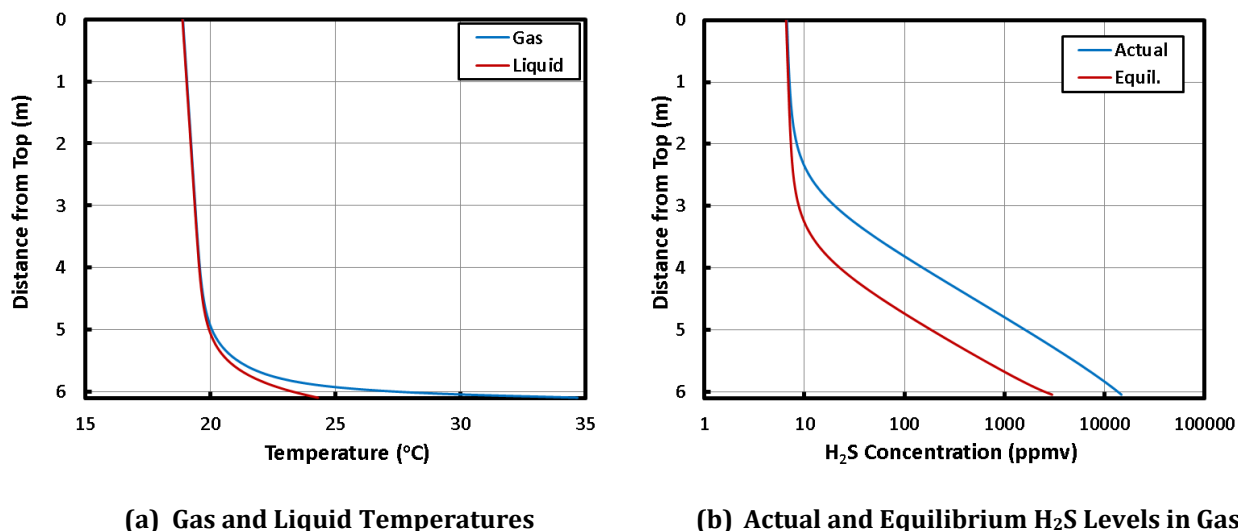
Figure 4   Temperature and CO₂ Composition Profiles in the TGTU Absorber

The temperature profiles in Figure 4(a) are not constant across any section of the absorber at all, so one might be hesitant to call the operation lean-end pinched. However, temperatures continue to change very slowly even across the upper section of the packing because carbon dioxide is absorbed throughout the entire packed bed. However, as Figure 4(b) shows, the hydrogen sulphide concentration in the gas is in almost perfect equilibrium with the liquid over the top 1–1½ metres of packing, i.e., at the lean end of the tower. A column's operation is called pinched when there is no driving force for absorption in some region of the column. Sometimes an absorber is rich-end pinched (typically carbon capture by amine solvents) [1], and in other cases it is bulge pinched [2]. In the present case, the absorber is certainly operating with a lean-end pinch. The hydrogen sulphide leak from this TGTU is determined solely by the lean solvent loading, and the temperature and pressure at the top of the contactor. If the simulated, actual and equilibrium H_2S concentrations did not coincide anywhere in the absorber, it would not be in a pinched state.

Conclusion 7

HSSs and stripping promoters only work in amine solvents that do not react and form carbamates with CO_2. If carbamates are formed, carbon dioxide is next to impossible to reduce to very low levels using heat, a significant protonated amine concentration always remains, and having a few thousands of ppmw HSS or phosphoric acid does not materially shift the equilibrium of H_2S dissociation.

<u>*Conclusion 8*</u>

Any potential benefit from the presence of HSSs or the use of stripping promoters is limited to absorbers that are operating in a lean-end pinch state.

CONCLUDING REMARKS

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 modeling is just as important as simulating the absorber simply because the regenerator sets the acid gas lean loadings and regeneration is where HSSs and stripping promoters exert their primary effect—generating a super lean solvent.

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[2] Weiland, Ralph H., Hatcher, Nathan A., Alvis, R. Scott, *Bulge Pinched CO$_2$ Absorber in an LNG Plant*, LNG Industry, January, 2015 (in press).