

Troubleshooting a Contaminated Refinery Tail Gas Amine Treater*

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ABSTRACT

This paper presents a study where simulation played a key role in troubleshooting performance of a tail gas treating unit contaminated with sodium and heat stable salt anions (HSSs). Comparisons are made between plant performance data and simulations that (a) assume clean amine, (b) allow HSSs just to inactivate part of the amine, and (c) fully account for the effect of HSSs and alkali metal ions on the chemistry of the system. The outcome demonstrates unequivocally that simulation accuracy is predicated upon accurate solvent analysis.

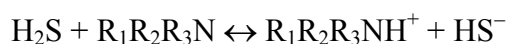
Introduction

Amine plant simulation has traditionally assumed the solvent to be perfectly clean, containing only water, amines, and acid gases, along with light hydrocarbons and fixed gases. However, outside the laboratory, clean solvents probably exist in most plants for only a short time immediately following initial system charging and startup.

Over time, solvents accumulate contaminants from the gases being treated, through the use of makeup agents (water and amine) that are not completely pure, and by the purposeful addition of chemicals (such as certain mineral acids) intended to improve performance. The anions of organic and inorganic acids are referred to as heat stable salts (HSSs) and include thiosulfate, oxalate, sulfate, glycolate, propionate, acetate, thiocyanate, formate, and chloride. Contaminants may also be cationic such as alkali metal ions (sodium, potassium, calcium, and magnesium) that accumulate from the result of makeup water hardness or through deliberate addition in the form of hydroxides or carbonates to deprotonate amine associated with heat stable amine salt anions. All of these ions can have a profound effect on amine treating unit performance.

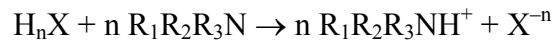
Process and Solvent Chemistry

Clean solvents are water solutions of one or more amines together with the acid gases CO₂ and H₂S. The reactions of H₂S and CO₂ with amines all generate ions, and all involve protonation of the amine. The reactions are reversible and the reactants are all volatile species so the solvent can be stripped thermally, an essential characteristic in treating with amines. As an example, the reversible reaction of H₂S with amine is illustrated here:



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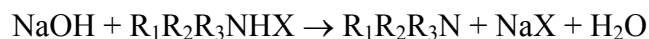
After a period of use, especially in treating sour gases generated from refinery cracking operations (Cokers, FCCs), trace amounts of acid anion contaminants can build to significant levels in the solvent. The commonly found acid anions are formed by oxidation, hydrolysis, and other reactions of contaminants that enter the treating system with the sour gas. These reactions all ultimately produce protonated amine as a reaction product as generically shown below. For a strong acid H_nX where X is an n -valent anion (Cl^- , SO_4^{2-} , etc.) the reaction with amine is



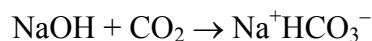
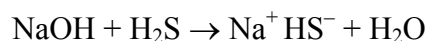
Thus, HSSs are an *additional* source of protonated amine, above and beyond the protonation that results from simple acid gas absorption. HSS anions are generated from much stronger acids than the acid gases being treated and their reactions with amines are irreversible. Thermal regeneration is not possible so they permanently tie up part of the amine as $R_1R_2R_3NH^+$ ion.

In a lean MDEA solution at regenerator temperatures (i.e., towards the bottom of the column and in the reboiler) the total acid gas loading is usually quite low so the concentrations of HS^- , HCO_3^- and protonated amine are also small. However, as the solvent becomes increasingly contaminated with acid anions that are stronger than HS^- and HCO_3^- , the concentration of protonated amine at the regenerator's lean end becomes determined by the extent of contamination rather than the acid gas loading. The higher protonated amine concentration drives the acid gas reactions strongly towards product decomposition. Thus, all other conditions being equal, *solvent contaminated with relatively strong-acid is always easier to regenerate than a clean one!* Of course, this forcing of the reverse reaction also occurs in the absorber; however, the extent of reduction in lean loading usually far outweighs the negative effect on absorption.

With increasing time-on-stream, acidic contaminants continue to build until a point is reached where something must be done to recover the permanently neutralised, bound amine to restore free amine circulation capacity or to prevent the amine unit from self dissolving through corrosion. Some operators employ addition of a stronger base (typically NaOH or KOH) to "neutralise" the amine heat stable salt, that is, remove the proton from the protonated amine and "attach" the anion to the alkali metal cation. This forms the sodium or potassium salt of the HSS, i.e., NaX or KX, and releases $R_1R_2R_3NH^+$ or $R_1R_2NH_2^+$ back into the free amine forms $R_1R_2R_3N$ or R_1R_2NH . Using NaOH as an example,



However, unless carried out very carefully, neutralization with strong bases can have disastrous, unforeseen consequences. The danger lies in the possibility of *over* neutralization. If the solvent becomes over neutralised, the excess caustic irreversibly binds H_2S and CO_2 :



The resulting elevated concentrations of HS^- and HCO_3^- remain in solution no matter how hard the solvent is stripped in the regenerator, i.e. there is a permanently high, heat

stable lean loading. In some cases, an order-of-magnitude increase in lean loading has been observed. The net result is failure to meet treated gas specifications by a wide margin which cannot be overcome using more reboiler energy or increased solvent circulation rate. The excess sodium associates with HS^- and HCO_3^- , and the situation will remain that way until HSSs again build up to a level sufficient to displace these ions fully and consume all the excess caustic.

To understand and simulate quantitatively the effect of HSSs and alkali metal ions on treating performance, one must be able to model the regenerator with just as much confidence and accuracy as the absorber—the regenerator sets lean solution quality, the main controlling factor at the lean end of the absorber where performance is determined. It is equally crucial to account for ionic contaminants and to use a comprehensive solvent analysis.

Contamination of a Treating Solution with Caustic Soda

Over a period of several months, an MDEA-based, refinery tail gas treater experienced deterioration in H_2S treating performance that could not be explained. The basic flowsheet with operating data from 15-Jan-2004 is summarised in Figure 1. Lean amine samples taken on the lean/rich exchanger inlet and outlet did not indicate the presence of a leak. Gamma scans of both the absorber and regenerator towers indicated satisfactory hydraulic performance of the internals. Further troubleshooting was carried out in conjunction with process simulation using ProTreat™ (Version 3.2), a commercial amine treating simulator that uses a true mass and heat transfer rate model for columns, and accounts for heat stable salts and alkali metal ions.

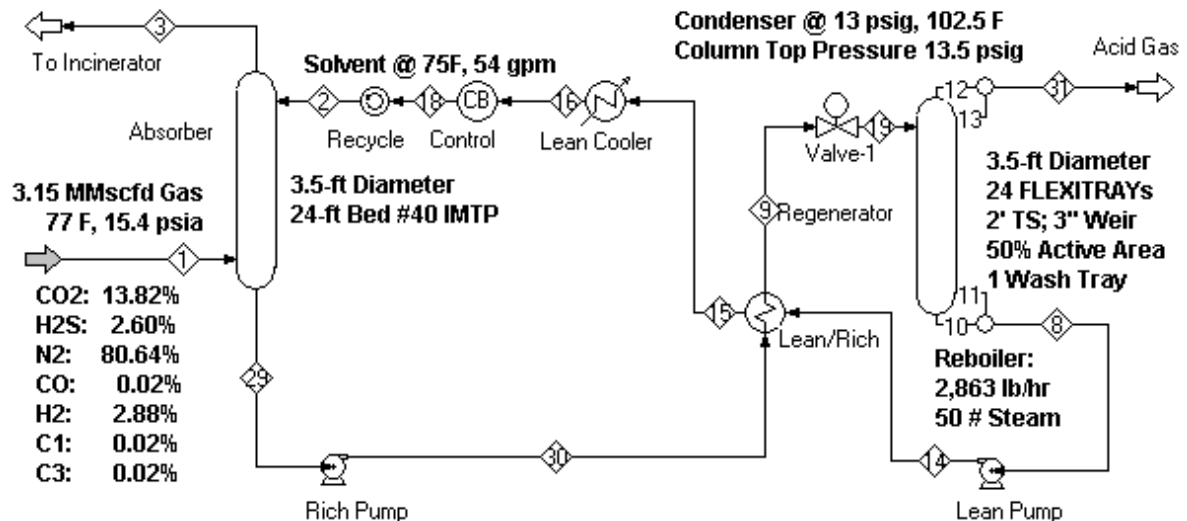


Figure 1 Tail Gas Treating Unit PFD and Operating Conditions

Table 1 summarises the amine analytical information available at the time of the troubleshooting effort, together with measured absorber performance. At first glance, no obvious causes are readily apparent. Lean loading from the plant's onsite analysis increased from undetectable levels to 0.005-0.006 mole/mole in January. This might be considered a notable increase; however, the levels in January are right where most in the industry would feel comfortable targeting a sound design. The increasing amine strength over time might be expected to provide better treating, yet H_2S removal worsened—in fact, it worsened greatly.

There were some concerns about the rapid increase of sodium because an ion exchange system, not caustic addition, was being used for freeing bound amine. The level of all ionic species except sulfate, thiosulfate and thiocyanate increased over the same time period, but the sodium concentration increased quite dramatically. Sulfate and thiosulfate appear to have fluctuated randomly, while thiocyanate decreased slightly. The ionic chemistry bears further examination. The first step was to perform a charge balance¹ for each data set. The charge balance allows the acid gas anion content of the solution to be calculated *indirectly* so that it can be compared with direct measurements. This makes it a useful tool for checking the accuracy of measurements of acid gas content.

Table 1 Raw Amine Analytical Results and Absorber Performance

Amine	Date of Sample		
	27-Aug-03	17-Dec-03	15-Jan-04
Free amine (wt%)	37.6	42.6	47.4
Bound amine (wt%)	2.5	2.1	0.5
Total amine (wt%)	40.1	44.7	47.9
Ions (ppmw)			
Sodium (Na ⁺)	512	3831	7717
Formate (HCOO ⁻)	2,637	2,960	3,812
Acetate (CH ₃ COO ⁻)	2,270	2,542	3,322
Chloride (Cl ⁻)	7	12	27
Sulfate (SO ₄ ²⁻)	142	92	160
Thiosulfate (S ₂ O ₃ ²⁻)	4,737	7,394	5,658
Thiocyanate (SCN ⁻)	54	43	36
Total Anions	9,848	13,043	13,016
DEA (% of total amine on weight basis)	2.6	2.0	1.6
Plant onsite lab titrated H ₂ S loading (mole/mole)	Trace	Trace	0.005–0.006
Measured Absorber Performance			
H ₂ S (ppmv)	20-30	35-60	160-180
CO ₂ slip, %	Not avail.	Not avail.	84-86

Table 2 illustrates the basic calculation methodology for performing a charge balance on the amine analytical data from 15-Jan-04. First, all measured cations and anions must be converted to a consistent set of molar concentrations—mole fractions are used in this example. The mole fractions are multiplied by their respective charges to determine the overall (molar) charge of the solution. The acid gases, which exist in solution as bisulfide and bicarbonate ions, result from weak acid ionization and do not show up with clarity in an ion chromatogram. Therefore, acid gas loading is *calculated* to force the charge balance to close. In this example, the equivalent weight fraction of bisulfide ion required to close the charge balance was calculated. From this weight fraction of bisulfide ion, the acid gas loading is calculated by dividing the equivalent *mole* fraction of bisulfide ion by the mole fraction of either total or free amine, depending upon the definition preferred for acid gas loading. While we used bisulfide ion as an example, the same moles of charge would result from using bicarbonate.

¹ In addition to the requirements that mass and energy balance, it is also necessary in ionic systems that the solution be charge neutral. This condition is met by adjusting the HS⁻ and/or HCO₃⁻ concentrations until positive and negative charges balance.

For the 15-Jan-04 operation, the *total* acid gas loading found by charge balance is 0.0326 mole/mole. This is a factor of 5–6 times higher than the H₂S lean loading reported by the plant’s onsite analytical lab (0.005–0.006 mole/mole). When a stand-alone absorber simulation was run using 0.006 mole/mole H₂S lean loading (as measured by the laboratory), with the remaining additional loading of 0.027 mole/mole assigned to CO₂, it was found that this H₂S lean loading (namely, 0.006 mole/mole) fell far short of explaining the poor treating. This led us to speculate that perhaps the H₂S lean loading was really quite a bit higher than the 0.005–0.006 mole/mole found by titration.

Table 3 shows the charge-balance-derived loadings for the various samples together with the observed treating performance. It is immediately apparent that the absorber H₂S leak increases in parallel with increasing charge-balance-based lean loading. But perhaps of more importance is the large change in the equivalents of sodium relative to the equivalents of non-HS⁻ anions. In fact, in the January sample there are actually more equivalents of Na⁺ than there are equivalents of HSS anions. The significance of this is that by January the HSSs had been over-neutralised with caustic soda. We saw earlier that reactions of acid gases with caustic trap H₂S and CO₂ as *permanent* lean loading:

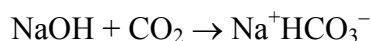
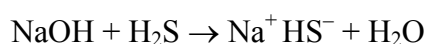


Table 2 Charge Balancing for Analytical Data in Table 1

	15-Jan-04				27-Aug-03	17-Dec-03	15-Jan-04
	wt%	Weight Fraction Species	Mole Fraction Species	Mole Fraction Charge	meq/g	meq/g	meq/g
Amine							
Free	47.4	0.47400	0.12346				
Bound (MDEAH ⁺)	0.5	0.00500	0.00130	0.00130	0.2097	0.1762	0.0419
Total	47.9	0.47900	0.12476				4.0185
Ions	ppmw						
Sodium (Na ⁺)	7717	0.00772	0.01042	0.01042	0.0223	0.1666	0.3357
Formate (HCOO ⁻)	3812	0.00381	0.00263	-0.00263	0.0586	0.0658	0.0847
Acetate (CH ₃ COO ⁻)	3322	0.00332	0.00175	-0.00175	0.0384	0.0431	0.0563
Chloride (Cl ⁻)	27	0.00003	0.00002	-0.00002	0.0002	0.0003	0.0008
Sulfate (SO ₄ ⁼)	160	0.00016	0.00005	-0.00010	0.0030	0.0019	0.0033
Thiosulfate (S ₂ O ₃ ⁼)	5658	0.00566	0.00157	-0.00313	0.0845	0.1319	0.1009
Thiocyanate (SCN ⁻)	36	0.00004	0.00002	-0.00002	0.0009	0.0007	0.0006
Other Components							
Acid gas as HS ⁻		0.00433	0.00407	-0.00407	0.0464	0.0991	0.1310
Water		0.49593	0.85471				0.0000
Total		1.00000	1.00000	0.00000			0.0000
Calculated Total loading (mole/mole)					0.0138	0.0264	0.0326

Table 3 Analysis of Charge Balance Results

Date of Sample:	27-Aug-03	17-Dec-03	15-Jan-04
Total charge balanced lean loading, mole/mole	0.0138	0.0264	0.0326
Sodium Equivalents, meq/g	0.0223	0.1666	0.3357
Non-Acid-Gas Anion Equivalents, meq/g	0.1856	0.2437	0.2466
Ratio (Non-acid-gas Anions) : (Sodium)	8.324	1.463	0.7346
Plant onsite lab titrated H ₂ S loading, mole/mole	0.000	0.000	0.005-0.006
Measured H ₂ S Leak from Absorber, ppmv	20-30	35-60	160-180

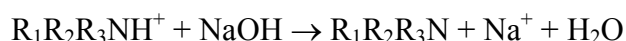
We now had a quite plausible explanation as to why treating performance deteriorated in this system. When informed of these observations, plant personnel found that sodium hydroxide was entering the amine unit from the ion exchange skid, possibly by inadequate washing of the resin after regeneration. The sodium was removed using cation exchange methods patented by ConocoPhillips and treating performance of the system was restored.

In order to quantify and understand the role that caustic or alkali carbonate addition plays on treating performance, we decided to see whether this system could be simulated with any degree of accuracy. The study was carried out using ProTreat under three different sets of assumptions:

- Use the plant's onsite amine strength analysis and assume the amine is perfectly clean. The results are tabulated in Table 4 under the heading *Clean Amine*.
- Use the 15-Jan-04 analytical information as-is. Again, the results are shown in the column headed *Amine as Analyzed*.
- Adjust the 15-Jan-04 analytical information to account for other factors, as discussed later. Results are listed under *Corrected Amine Analysis*.

Referring to Table 4, the *Clean Amine* case appears to simulate treating performance fairly well prior to the sodium contamination event; however, this outcome is probably fortuitous in view of the significant levels of both HSSs and sodium even at that time. Nonetheless, if clean amine had been used as the simulation basis throughout the troubleshooting exercise, the wrong conclusions easily may have been drawn. The *Amine as Analyzed* case trends in the right direction on treating performance; however, the simulated lean loading² does not compare well with either the measured or ion-balance-calculated lean loading. It also misses the H₂S slip quantitatively. When considered together, these observations point either to simulator imperfections or to a faulty assumption or data. This drove further investigation to find out what was at fault and led to two further corrections to the analytical data. Results are shown in Table 4 under *Corrected Amine Analysis*.

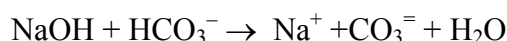
The first correction to the amine analytical data involved the bound amine figure. Bound amine (R₁R₂R₃NH⁺ concentration) was determined in these samples by conductometric titration. The analytical chemists felt that the conductometric titration for bound amine:



should have shown zero concentration for an over-neutralised solution because all the bound amine would have disappeared from the circulating solution by exactly the same reaction as

² The simulation was of the complete flowsheet and the lean loadings shown in the table are ProTreat predictions, not measured values.

the lab titration³. However, past experience with MEA systems had shown an interference with residual CO₂ lean loading through the solution conductivity change (and pH titration, as well) via the reaction:



We also questioned whether the thiosulfate appearing in the ion chromatography analysis was generated either from an SO₂ breakthrough or from H₂S lean loading that had oxidised when the sample was contacted with air:

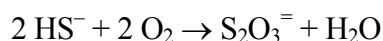


Table 4 Treating Performance on 15-Jan-04 Predicted by ProTreat

	Clean Amine	Amine as Analyzed	Corrected Amine Analysis
Component			
Free amine (wt%)	49.9	47.4	47.4
Bound amine (wt%)	0.0	0.5	0.0
Total amine (wt%)	49.9	47.9	47.4
Ions, ppmw			
Sodium (Na ⁺)	0	7717	7717
Formate (HCOO ⁻)	0	3,812	3,812
Acetate (CH ₃ COO ⁻)	0	3,322	3,322
Chloride (Cl ⁻)	0	27	27
Sulfate (SO ₄ ⁼)	0	160	0
Thiosulfate (S ₂ O ₃ ⁼)	0	5,658	0
Thiocyanate (SCN ⁻)	0	36	36
Total Anions	0	13016	7198
DEA,% of total amine (wt. basis)	0	1.6	1.6
Equiv. H ₂ S Loading from S ₂ O ₃ ⁼ and SO ₄ ⁼		0.0130	
Anion Equiv. w/o S ₂ O ₃ ⁼ and SO ₄ ⁼		0.1424	0.1424
Total lean loading per charge balance		0.0590	0.0485
Measured Absorber Performance	160-180		
H ₂ S (ppmv)	84-86		
CO ₂ Slip (%)	84-86		
Simulated Absorber Performance			
H ₂ S Leak (ppmv)	21	82	162
CO ₂ Slip (%)	88.8	87.4	86.9
Lean loadings (mole/mole)			
H ₂ S	0.0015	0.0096	0.0197
CO ₂	0.0016	0.0094	0.0217
Total	0.0031	0.0190	0.0414

In our experience, *it is not uncommon to observe an order-of-magnitude difference in the thiosulfate levels between rich- and lean-amine samples from the same contactor.*

³ In conductometric titration, the conductivity change is monitored as NaOH titrant is added. Solution conductivity increases as sodium ions replace the protonated amine.

Because this amine system treats Claus tail gas, it could have been subjected to SO₂ breakthrough, which would make it difficult to distinguish between this mechanism and oxidation. However, referring to Table 1, the sulfate and thiosulfate levels appear to be *randomly* varying; whereas, other anions of significance (formates and acetates) are steadily increasing. If an SO₂ breakthrough had occurred, the thiosulfate level ought to have remained high; however, it actually dropped substantially between 17-Dec-03 and 15-Jan-04. Therefore, at least a significant fraction of the thiosulfate is probably oxidised lean loading⁴. For reference, the total thiosulfate and sulfate levels in the 15-Jan-04 analytical results correspond to an equivalent molar H₂S loading of 0.013 mole/mole.

We decided to bracket the treating performance by assuming that the thiosulfate and sulfate were the result of lean loading oxidation in solution for the *Corrected-Amine-Analysis* case. Converting these species back to the equivalent amount of H₂S in the circulating lean amine, the total lean loading should be seen to increase from 0.033 to 0.0485 mole/mole. ProTreat quite accurately reflected the observed performance using the SO₄⁼- and S₂O₃⁼-free solvent in terms of predicted H₂S leak and CO₂ slip as well as the predicted lean loadings.

Once confidence could be placed on simulation to describe accurately the treating performance in a sodium/heat stable salt contaminated amine solution, the effects of caustic neutralization (and over-neutralization) could be assessed. Figure 2 shows the treating performance predictions of the ProTreat simulator using the heat stable salt anion content as per the *Corrected-Amine-Analysis* case, but with various levels of neutralization with caustic soda. The results obtained under the assumption that the amine was merely inactivated by heat stable salts are also shown. In this case, the simulation was run without HSS components present and the amine strength adjusted to the equivalent free amine concentration.

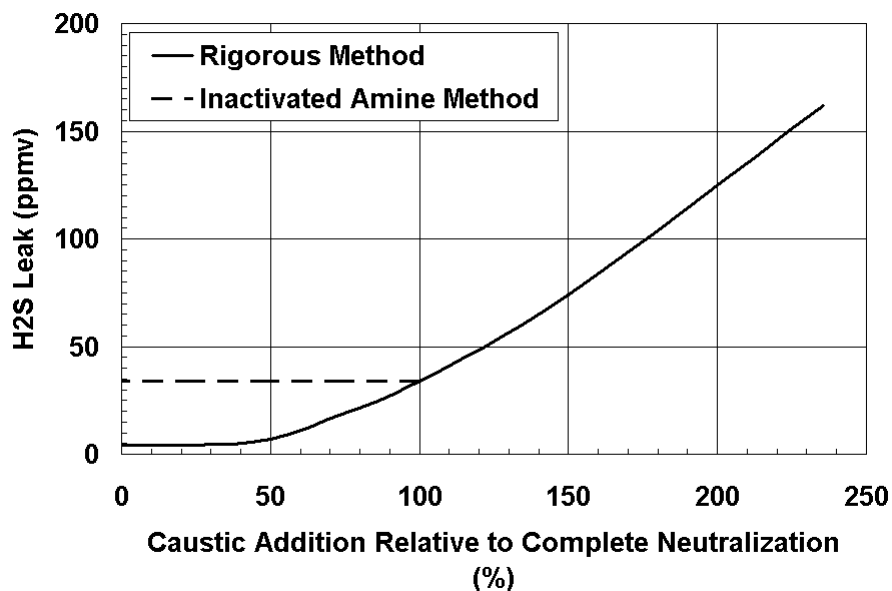


Figure 2 Effect of Partial and Over Neutralization on H₂S Leak from Absorber

⁴ Experience with the collection, transportation, and analysis of lean amine samples has led to the conclusion that unless every precaution is taken to exclude the samples from contact with air, as much as 80 to 90% of the lean H₂S loading will disappear, only to reappear as thiosulfate. When common practice is to sample directly into an empty (air-filled) bottle, leave an air space for expansion at the top, then ship the sample (often with vigorous agitation) for several days and analyze it in an air environment, the validity of most, if not all, lean amine H₂S loading analyses must be viewed with deep suspicion.

The results in Figure 2 suggest that for an under neutralised system, even the partial (less than 100 on the abscissa in Figure 2) removal of amine protonation by sodium hydroxide addition reduces the benefit amine protonation has on solvent regeneration. This translates directly into increasing H₂S leak. However, when the solution becomes *over* neutralised, treating performance declines extremely rapidly simply because the excess caustic results in permanent fixing of H₂S and CO₂ lean loading (i.e., HS⁻ and HCO₃⁻ ions). *The simulation assumption that the sole HSS effect is to remove an equivalent amount of amine from solution is a very poor one unless the protonated amine is exactly 100% neutralised with caustic.* For neutralization levels below 100%, this assumption becomes increasingly poor because it entirely misses the huge benefit HSSs have on stripping.

There is another, more subtle performance variable that is completely missed by the assumption that HSSs merely inactivate an equivalent amount of amine, namely, the absorber CO₂ slip. Assuming that amine inactivation as the only consequence of HSSs results in an artificially low free amine concentration. As a result, the rich amine loading in the absorber simulation is artificially high. This increases the calculated temperature rise across the column and leads to higher CO₂ pickup, thus slightly lower CO₂ slip predictions than really occur (84.2% versus 86.5%).

Lessons Learned

- The presence of HSSs may be responsible for better treating than would be obtained without them so caution should be exercised before HSSs are reduced or removed altogether.
- Neutralizing HSSs with NaOH or KOH must be carried out with extreme care, lest the solution becomes over neutralised and the ability to treat satisfactorily is completely lost. Treating ability is severely and negatively affected by excess sodium (or other alkali metals) in the solvent.
- When treating problems are experienced, a detailed ionic analysis of the solution should be obtained and the results checked via a charge balance for compliance with the requirement of electroneutrality.
- Lean amine samples should be taken into sample bottles filled with nitrogen in such a way as to exclude air. The samples must be kept away from air during collection, shipping, handling, and laboratory analysis; otherwise, a large part of the lean H₂S loading will appear, not as loading, but as oxidation products such as sulfate and thiosulfate.
- Simulations that do not account correctly for all the ionic species may give erroneous results that can lead to unnecessary and expensive changes to plant equipment and solvents.

Conclusions and Summary

Troubleshooting amine treating unit problems involves much more than simply plugging plant data into an amine plant simulation model. In the first place, amine treating chemistry is a rather complex system of ionic reactions, some thermally reversible, others not, with common ion effects and great potential for inconsistencies in plant data. In addition, treating is often done selectively and this requires the treating operation to be analyzed as a mass-transfer-rate process—solely basing it on phase equilibrium is completely inadequate to

understanding the process and the problem. *What is more, all too often an attempt is made to analyze only the operation of the absorber without recognizing that its performance hinges completely on the quality of the lean amine being produced by the regenerator.* Thus, a first rate regenerator model is just as important as a good absorber simulation.

Simulation with a model capable of accounting for all the details very effectively compliments careful analysis of plant and laboratory measurements when it is applied to the solution of treating plant operating problems. The complete solution ion chemistry must be taken into account by including *all* solvent contaminants in simulations before accurate and successful predictions of amine plant operations can be expected. In this study, the heat stable salt problem was overshadowed by such a high sodium level that not only was the protonated amine itself neutralised, but there was also enough additional, residual sodium to permanently fix rather high HS^- and HCO_3^- residual lean loadings. *The ultimate result of neutralizing the HSSs was higher H_2S leak, i.e., poorer treating.* This root cause behind the poor treating could not be readily identified until a charge balance revealed that the lab analyses violated the requirement of solution electroneutrality.

Simulation formed an important part of this study. In particular, using an amine simulator capable of accounting for the effects of all the factors, including detailed solution chemistry, formed an integral part of the analyses and troubleshooting effort. Simulations that do not account correctly for all the ionic species may give erroneous results that can lead to unnecessary and expensive changes to plant equipment and solvents. Because this study involved highly selective treating, the fact that the ProTreat simulator was based on sound mass-transfer-rate principles enabled the modeling to compliment the analyses—without such a true mass-transfer-rate basis, the simulations would have been of little or no help. Furthermore, accurately simulating regeneration was critical to the successful simulation and analysis of each set of plant data.