

Are Your Simulation Amines Too Clean?

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ABSTRACT

This paper presents two case studies in which simulation results are compared head-to-head with plant data for amine systems contaminated with sodium and heat stable salt anions (HSSs). Comparisons are with 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 entire system. The outcome is an unequivocal demonstration of the importance of accurate solvent analysis to simulation reliability.

Two sets of plant performance data have been selected for the case studies: (1) an MDEA-based fuel-gas H₂S treating system in which performance suffered when the HSSs level was reduced from 8,000⁺ to 6,000 ppmw (data include measured tray temperatures and detailed GC analysis), and (2) a tail gas unit (TGU) using MDEA contaminated with sodium.

The effect of solvent contaminants on treating plant performance and the importance of basing simulations on actual solvent analyses are shown. In addition to indicating that clean-solvent-based simulations fall well short of the mark when the solvent is in fact contaminated, the need for good analytical data and verification calculations (mass, charge and energy balances) in the simulation is highlighted. The effect of HSSs on solvent stripping is shown to be the primary way in which HSSs influence plant performance, and that it is indeed possible to quantify quite accurately the effect of sodium contamination on amine system performance.

Introduction

Commercial software packages for amine plant simulation use column models that range from simple equilibrium stages, equilibrium stages modified for reaction kinetics, equilibrium stages with computed stage efficiencies, right through to true mass and heat transfer rate models. However, regardless of the underlying principles on which each one is based, simulations of amine plants have traditionally assumed the solvent to be perfectly clean, meaning that it contains only water, amines, and acid gases. In some cases, the solubility of light hydrocarbons and inert gases may be taken into account. Outside the laboratory, clean solvents probably exist in most plants for only a short time immediately following initial system charging and startup.

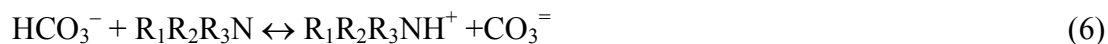
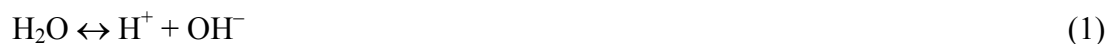
Over time, solvents accumulate contaminants primarily from the gases being treated or through the use of makeup agents (water and amine) that are not completely pure. Contaminants of interest here are frequently the anions of organic and inorganic acids, also called heat stable salts (HSSs). Anions commonly found in amine solutions include thiosulfate, oxalate, sulfite, sulfate, glycolate, propionate, acetate, thiocyanate, formate, and choride, which usually enter the solution as a result of absorption from

the gases or liquids being treated. The use of sulfate or phosphate to enhance H₂S removal in tail gas treating units (TGTUs) is becoming increasingly common. 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, sometimes positive, frequently negative, on amine treating unit performance.

To understand the effect of these anions and cations on performance, we turn first to the chemistry of ionic solutions and show how these ionic species shift reaction equilibria, thereby influencing phase equilibrium and the transfer of species between phases. We then present two case studies that demonstrate various aspects of the importance of using actual solvent analyses in simulations. In addition to showing that clean-solvent-based simulations fall well short of the mark when the solvent is in fact contaminated, the need for good analytical data and verification calculations (mass, charge and energy balances) in the simulation is highlighted. The effect of HSSs on solvent stripping is shown to be the primary way in which HSSs influence plant performance. With an accurate, predictive, regenerator model, it is indeed possible to quantify quite accurately the effect of sodium and HSS contamination on amine system performance.

Chemistry

Clean solvents consist of water solutions of one or more amines together with the acid gases CO₂ and H₂S. A number of reaction equilibria are set up, all involving ionic species, and all depending on the presence of water. For a system containing a single amine together with H₂S and CO₂ in aqueous solution, six equilibrium ionic reactions occur:



If the amine is primary (R₂, R₃ = H) or secondary (R₃ = H), it is also capable of reaction with CO₂ to form the carbamate of the amine; the overall reaction is:

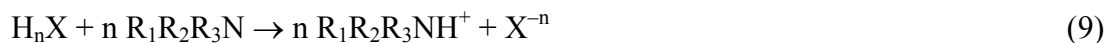


Thus, the four molecular species H₂O, R₁R₂R₃N, CO₂ and H₂S dissociate and react with each other to form seven ions (eight when the amine is primary or secondary). For this perfectly clean amine solvent, reaction equilibria (2) through (7) are shifted towards reactants (i.e., to the left) by increasing the temperature. This thermal reversibility of the reactions is what makes treating with amines economically feasible. But things can go awry when the gas contains certain types of components, even in trace amounts.

After a period of use, especially in treating sour gases generated from refinery cracking operations (Cokers, FCC's), trace amounts of acid anion contaminants can build to significant levels in the solvent. The most commonly found acid anions, formate and thiocyanate, result from the absorption of hydrogen cyanide, with formate being formed by the hydrolysis of the cyanide ion to ammonium formate, and with thiocyanate being formed from dissolved oxygen reacting with H₂S followed by reaction of the oxysulfur anion with cyanide ion. Higher molecular weight organic acid anions come from the hydrolysis of higher molecular weight nitrile compounds. Ammonium ion from the hydrolysis will give up an H⁺ to the amine and is stripped by steam in the regenerator where it will accumulate in the overhead condensing system, leaving the protonated amine/HSS anion pair in the amine solution. Hydrogen from gasoline reformers can contain HCl which will react directly in acid-base neutralization with the amine. Thiosulfates generally result from the reaction of dissolved oxygen with H₂S or from SO₂ reaction with H₂S in Claus tail gas units when no HCN is present. Sulfates can either be formed from absorption of sulfuric acid or from further oxidation of thiosulfates. These are shown in reactions 8a–8f below.



For a strong acid H_nX where X is an n-valent anion (Cl⁻, SO₄⁼, etc.) the reaction with amine is



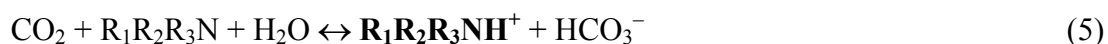
Unlike the acid gas-amine reactions (2–7), reactions (8a-f) and (9) are not *thermally* reversible (thus the term heat stable salt), so the HSSs permanently tie up part of the amine as R₁R₂R₃NH⁺ ion¹. The fact that the amine is gradually converted to HSAS and becomes inactivated is bad enough. But far more worrying is its effect on the ability to regenerate the rich solvent to satisfactory acid gas lean loadings (moles of acid gases per mole of total amine) and to use the regenerated solvent effectively in the absorber². Heat stable salt anions are also known to complex iron ion and accelerate corrosion in the hot, lean section of the amine unit. When the complexed iron contacts higher concentrations of H₂S in the absorber, iron sulfide particles are generated. These particles can foul equipment leading to loss of

¹ We will call the ionic compound R₁R₂R₃NHX 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 (HSS) are actually very effective *regeneration enhancers* but their presence in solution is detrimental to *absorption*.

treating capacity and further exacerbate corrosion by eroding the protective iron sulfide film on carbon steel piping and equipment surfaces.

H₂S absorption takes place primarily via reaction (3), with reaction (4) being of little consequence in the operating pH range of most alkanolamine solutions. With tertiary amines, CO₂ absorption relies mostly on reaction (5), although with primary and secondary amines at normal loadings, reaction (7) dominates. Each reaction has protonated amine, R₁R₂R₃NH⁺, on its right hand side:

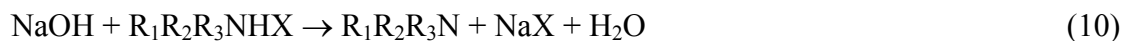


For a lean amine at regenerator temperatures (i.e., towards the bottom of the column and in the reboiler) the acid gas loadings are meant to be quite low so the concentrations of HS⁻, HCO₃⁻ and R₁R₂NCOO⁻ are small. In a clean solvent, the concentration of R₁R₂R₃NH⁺ or R₁R₂NH₂⁺ will be quite small, too. However, when the solvent becomes increasingly contaminated with acid anions that are stronger than HS⁻ and HCO₃⁻, the concentration of protonated amine (R₁R₂R₃NH⁺ or R₁R₂NH₂⁺) at the regenerator's lean end becomes determined by the extent of contamination, as set by reactions (8a–8f, 9). The higher protonated amine concentration drives reactions (3), (5) and (7) strongly to the left which is *beneficial to regeneration* because it produces greater driving force for the reverse or decomposition reaction. Thus, all other conditions being the same, from a mass transfer and phase equilibrium viewpoint, *solvent contaminated with relatively strong-acid is always easier to regenerate than a clean one!*

There is a catch, however. The common ion (R₁R₂R₃NH⁺) also displaces the reactions (3, 5, and 7) towards the left under absorption conditions. Again, all other conditions being the same, a contaminated lean solvent entering an absorber will always exhibit greater acid gas partial pressures than a clean one (at the same temperature, total amine concentration, and acid gas loadings). Acid contamination is *always detrimental to absorption*. It depends very much on the exact conditions of operation as to whether the benefit contributed by the contaminant to regeneration outweighs its penalty to absorption. This is borne out in the case studies that follow.

With increasing time-on-stream, acidic contaminants continue to build until a point is reached where something must be done to recover the permanently neutralized, 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 “neutralize” the amine heat stable salt, that is, remove the proton from the protonated amine and “attach” the anion to the alkali metal ion. This forms the sodium or potassium salt of the HSS, i.e., NaX or KX, and releases R₁R₂R₃NH⁺ or R₁R₂NH₂⁺ back into the free amine forms R₁R₂R₃N or R₁R₂NH. Using NaOH as an example,



However, unless carried out very precisely, neutralization with strong bases can have disastrous, unforeseen consequences. The danger lies in the possibility of *over* neutralization. If the solvent becomes over neutralized, the excess caustic permanently binds H₂S and CO₂:





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 permanent high lean loading. In some cases, an order-of-magnitude increase in lean loading has been observed. The equilibrium of reactions (3), (6), and (7) is driven to the left at conditions in the absorber despite the fact that HS^- and HCO_3^- appear to be bound with sodium³. 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 quantitatively simulate 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 treat is determined. As will become evident from the following case studies, it is equally crucial to account for ionic contaminants and to use a comprehensive solvent analysis.

HSS Contamination of a Refinery Fuel Gas Treater

An MDEA fuel gas treater at Refinery A was experiencing a steady decline in treating performance. Prior to February, 2005, the amine contactor was consistently treating H_2S down to levels of 1–3 ppmv in the vent gas. From February to May of 2005, the H_2S gradually increased to around 17 ppmv in the treated gas. After ruling out foaming as a cause, and that lean/rich exchanger leaks were not present, the plant contacted their corporate Treating/Sulfur Processing Network for troubleshooting and simulation assistance.

Table 1 presents a summary of the absorber feeds and operational data. To facilitate the troubleshooting effort, a bomb sample of the feed gas was caught for analysis by gas chromatography. Lean and rich amine samples were also taken concurrently for strength and loading analysis. Table 2 provides further analytical breakdown of the lean amine solution over time from ion chromatography analysis. In looking at just the data in Tables 1 and 2, a number of explanations could be formulated to explain the deterioration in performance, among them:

1. Absorber was overloaded and was rich-amine-loading pinched,
2. Lean amine feed temperature increased as ambient temperature climbed from February to May,
3. Regenerator performance declined as indicated by the lean loading increase. This could have been caused by tray damage, exchanger fouling, lower reboiler heat input, or decreased heat stable salts.

The picture was complicated further by the results of initial material balance screening calculations around the absorber which showed a nominal 30% inconsistency between the measured rich amine loading and the rich amine loading that would result from a material balance using the inlet gas composition and the metered feed gas and rich amine flows. Consequently, two sets of simulations were developed for the system based upon the assumptions that either flow and GC data, or lean and rich amine lab loadings, were correct. Table 3 presents further operating data around the absorber and principle regenerator on the circuit under these two assumptions outlined above together with a number of simulation results.

³ Although HS^- and HCO_3^- give the appearance of being tied up with sodium, aqueous solutions of their alkali metal salts are completely dissociated; thus, HS^- and HCO_3^- actually exist in free ionic form.

Table 1 Absorber Feed and Treating Performance Summary

Parameter	May 2005 Operations		February 2005 Operations	
	Absorber Feed Gas	Absorber Treated Gas	Absorber Feed Gas	Absorber Treated Gas
Temperature (°F)	100.5	115.3	99–100	108–110
Pressure (psig)	174.3	172.4	176	178
Flowrate (MMscfd)	54.5	Not Available	53.5–55.5	Not Available
Composition (Dry Mole %)	Lab GC	Online GC	Lab GC	Online GC
H ₂ S	17.04	17 ppmv	Not Available	1–3 ppmv
CO ₂	1.21	0.104	Not Available	0.11–0.12
H ₂	11.04	17.7	Not Available	20.4–20.8
N ₂	3.65	3.25	Not Available	2.5–2.7
CH ₄	39.28	49.3	Not Available	46.5–46.9
C ₂ H ₄	3.43	4.1	Not Available	4.8–5.0
C ₂ H ₆	15.02	17.0	Not Available	16.8–17.0
C ₃ H ₆	1.98	2.37	Not Available	2.8–2.9
C ₃ H ₈	3.18	3.94	Not Available	2.8–3.0
C ₄ ⁺	2.47	2.18	Not Available	2.4–2.5
Lean Amine				
Flowrate (gpm)	847–853		766–772	
Lean Loading (mole/mole)				
H ₂ S	0.0046		0.0007–0.0010	
CO ₂	0.0009		Not Available	
Total	0.0055		Not Available	
Temperature (°F)	115		108.6–110.0	

Table 2 Lean Amine Analyses by Ion Chromatography

Date of Sample:	11/10/04	12/8/04	1/12/05	2/9/05	3/9/05	4/13/05
Component						
Free amine (wt%)	40.7	42.5	37.5	40	44.1	42.3
Bound amine (wt%)	2	1.8	1.4	1.1	1.3	0.9
Total amine (wt%)	42.70	44.30	38.90	41.10	45.40	43.20
Ions, ppmw						
Sodium (Na ⁺)	1,573	1,044	1,336	1,401	1,461	1,212
Formate (HCOO ⁻)	7,768	7,935	7,263	6,406	6,159	4,864
Acetate (CH ₃ COO ⁻)	885	672	605	591	370	463
Chloride (Cl ⁻)	46	87	72	54	57	42
Sulfate (SO ₄ ⁻)	0	0	0	0	0	0
Thiosulfate (S ₂ O ₃ ⁻)	38	27	60	0	43	198
Thiocyanate (SCN ⁻)	4,184	1,844	755	638	665	378
Total Anions	12,921	10,566	8,754	7,689	7,293	5,945
Cation Equiv. (meq/g)	0.2365	0.1966	0.1757	0.1533	0.1728	0.1283
Anion Equiv. (meq/g)	0.2617	0.2225	0.1878	0.1649	0.1570	0.1272
Lean Loads by charge bal.	-0.007	-0.007	-0.004	-0.003	0.004	0.000
% amine as HSS	5.4	4.8	4.0	3.0	2.4	2.1
DEA (% of total amine)	0.9	1.3	1.2	1.2	0.9	1.2

Table 3 Simulation Comparison to May 2005 Plant Data

Parameter	May/05 Data	Simulations per GC MB			Simulations per Lab H ₂ S Loads		
		CoP	ProTreat	Other w/o HSS & Na	CoP	ProTreat	Other w/o HSS & Na
Absorber Tray No.		Tray Temperatures (°F)			Tray Temperatures (°F)		
30 (Top)	115.3	115.0	126.3	120.6	115.0	115.1	115.0
25	115.4	115.1	168.2	164.8	115.0	115.3	115.3
20	116.5	115.4	170.1	168.0	115.0	115.6	115.6
11	117.2	124.2	170.3	168.3	116.1	116.6	116.4
7	121.2	138.1	170.2	168.4	120.9	117.9	117.9
3	142.7	150.8	167.5	167.6	136.0	135.4	134.2
1 (Bottom)	144.9	155.4	155.0	155.1	144.0	149.3	147.7
H ₂ S Leak (ppmv)	17	24	17,977	15,897	24	20	29
CO ₂ slip (%)	6.9–7.6*	7.25	63.6	54.2	7.25	8.9	38.4
Lean Mole Loading	Lab						
H ₂ S	0.0046	0.0046	0.0052	0.0459	0.0046	0.0038	0.0132
CO ₂	0.0009	0.0009	0.0000	0.0016	0.0009	0.0000	0.0011
Total	0.0055	0.0055	0.0052	0.0475	0.0055	0.0038	0.0143
Rich Mole Loading	Lab						
H ₂ S	0.446	0.635	0.582	0.640	0.446	0.448	0.465
CO ₂	0.022	0.042	0.016	0.023	0.045	0.029	0.021
Total	0.468	0.678	0.598	0.663	0.491	0.477	0.486
Total per Reg MB [¶]	0.46–0.47						

*per GC analysis; CO₂ slip is 33% per loading measurements

[¶] Indicates total loading obtained via a material balance around the regenerator

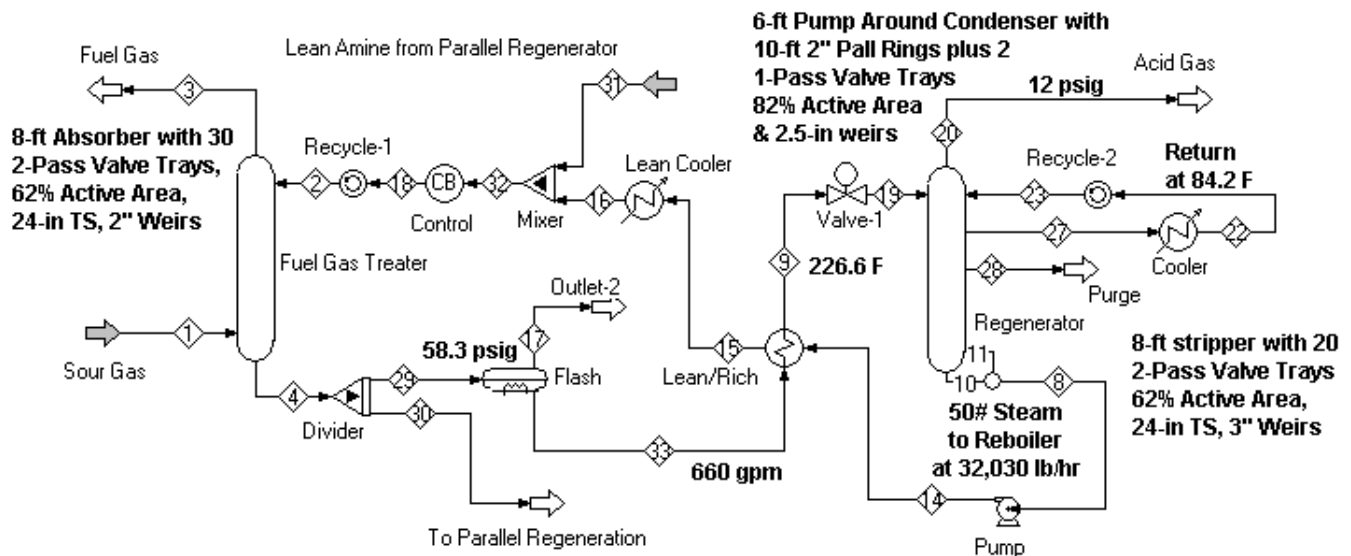


Figure 1 PFD of Fuel Gas Circuit

Figure 1 provides an overview of the amine system together with some data pertinent to the May, 2005 operation (see Table 3). It was fortuitous that this particular unit was well instrumented. A number of the absorber trays contain thermocouples located in the liquid flow path to establish an internal temperature profile (see Table 3). The rich amine temperature is also known allowing the absorber

energy balance to be used to reconcile the plant data. The amine loading change across the regenerator can also be found from the rich amine flow to the regenerator and metered acid gas rate.

Simulations (Table 3) of May operations were run for two sets of conditions using three tools to evaluate the operating data. CoP is an electrolyte-based equilibrium material-balance tool developed in-house by ConocoPhillips that takes into account heat stable salt effects on treating performance. ProTreat™ (Version 3.2) is a commercial mass and heat transfer rate based amine simulator capable of accounting for the effect of HSSs and other ions on treating. It uses rigorous mass-transfer-rate calculations to evaluate absorber and regenerator performance on an actual tray basis. A third simulator, one using tray efficiencies but without HSSs capability, was also available. It was used to demonstrate the effect of not including HSSs in simulations (only the free active amine strength was used). The sets of conditions correspond to operations that result from assuming the feed gas analysis and measured circulation rate are correct, and using:

- (a) The measured feed gas flow rate (i.e., assuming it to be correct), or
- (b) The feed gas flow rate calculated by material balance to give the observed rich solvent loading. (The feed gas flow necessary to achieve a material balance was some 30% lower than measured.)

Table 3 provides a direct comparison between simulation results based on assumptions (a) and (b). It is immediately apparent that using the measured gas flow in both commercial simulation packages produces a highly elevated absorber temperature profile, a hotter than measured rich amine temperature, an H₂S leak a thousand times too high (16,000 to 18,000 ppmv versus 17 ppmv measured), and a CO₂ slip roughly ten times too high (54% to 64%, versus 6.9 to 7.6% measured). On the other hand, when the gas feed rate is derived under assumption (b) above and is used in the simulation, all three simulators show close agreement with the measured absorber temperature profile, and at least order-of-magnitude agreement with the measured H₂S leak. It is noteworthy, however, that not only did the simulations using the actual HSS and sodium contents agree much more closely with the observed H₂S leak, but *the inclusion of HSSs and sodium ion appears to have been essential to reproducing the observed CO₂ slip*. It is mentioned in passing that assuming the gas rate was correct and adjusting the solvent rate by material balance did not produced nearly as good agreement with measured data as adjusting the gas rate. The evidence is fairly convincing that the feed gas flow meter was reading some 30% high. However, we still have not explained why the treating performance deteriorated.

Using ProTreat, a sensitivity analysis was conducted to answer this question. The following variables were changed in cumulative succession from the May, 2005 calibration model to conditions corresponding to February, 2005 operations, and the results are presented in Table 4:

1. Lean amine temperature and to a lesser extent, feed gas temperature were dropped,
2. Amine strength was raised,
3. Regenerator reboiler steam was increased nominally by 10%,
4. Heat stable salt and sodium ion concentrations were increased.

The results suggest that the lean amine temperature increase from February to May played at most a very slight role in hindering treating performance. The higher amine strength in February would have worked in the wrong direction, increasing both the lean loading and the H₂S leak from the absorber, whereas, both were actually lower in February than in May. This suggests that the contactor's treating performance is not limited by a rich end loading pinch. However, in practice the rich loading must be limited to minimize corrosion in the carbon steel equipment. The reboiler steam rate was higher in February than in May, and ProTreat predicts that this would have quite a positive effect on the H₂S leak and the lean loading of H₂S. However, even the increased reboiler duty is insufficient to reduce the H₂S leak to match the measured February performance. Furthermore, tower hydraulic rating indicated that

the regenerator already operated close to jet flood in both February and May (~85% at 0.65 system factor), which constrains the increased steam flow that could be used to reduce emissions. However, when the HSSs and Na levels as per the detailed solution analysis were included in the solvent description, Table 4 shows that *ProTreat predicted very nearly the exact performance observed in February*. The observed H₂S leak was 1–3 ppmv versus a predicted leak of 3 ppmv; predicted 8% CO₂ slip versus 6.9–7.6% measured; predicted 0.0005 H₂S lean mole load versus 0.0007–0.001 observed lean load. The high HSS level in February, combined with a higher reboiler steam flow, allowed the plant to produce 3 ppmv H₂S gas. *The drop in HSS level hurt plant performance!* The third simulation tool (without HSS and Na chemistry capabilities) missed both the reboiler steam benefit and the HSS effect. It also predicted a CO₂ slip some five times greater than observed.

Table 4 H₂S Treat Sensitivity Analysis—ProTreat Predictions

Case	Base May, 2005 Operation	Lower Temp	Higher Amine Strength	Higher Reboiler Steam	Higher HSS	Other Sim w/o HSS & Na
Feed Gas Temperature (°F)	100.5	100	100	100	100	100
Lean Amine Temperature (°F)	115	109.3	109.3	109.3	109.3	109.3
Reboiler Steam (lb/gal)	0.8	0.8	0.8	0.89	0.89	0.89
Total MDEA (wt%)	43.2	43.2	44.2	44.2	44.2	44.8
HSS & Na ⁺ Ions as per	May, 05*	May, 05*	May, 05§	May, 05§	Feb, 05¶	N/A Clean
Calc Lean H ₂ S Mole Loading	0.0038	0.0040	0.0054	0.0017	0.0005	0.0005
Absorber Performance						
H ₂ S (ppmv)	20	18	29	8	3	21
CO ₂ slip (%)	8.9	7.6	7.8	7.8	8.0	40.6

* May, 2005 analysis; § May, 2005 analysis increased proportional to strength; ¶ Feb, 2005 analysis

Lessons Learned

1. A simulation can only be as accurate as the data on which it is built. In this particular case study, alternative material and energy balance verification had to be performed to develop a realistic picture of the problem to be constructed.
2. Complete solution ion chemistry must be taken into account for accurate modeling of treating down to low H₂S levels at low lean loadings. If the solvent contains contaminants, the simulation must account for them.
3. It is insufficient just to have an accurate absorber model. Rigorous rate-based regenerator simulation is absolutely critical to predict plant performance accurately.

Contamination of a Treating Solution with Caustic Soda

Over a period of several months, an MDEA-based tail gas treater at Refinery B experienced deterioration in H₂S treating performance that could not be explained. The basic flowsheet with operating data from 15-Jan-2004 is summarized in Figure 2. 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.

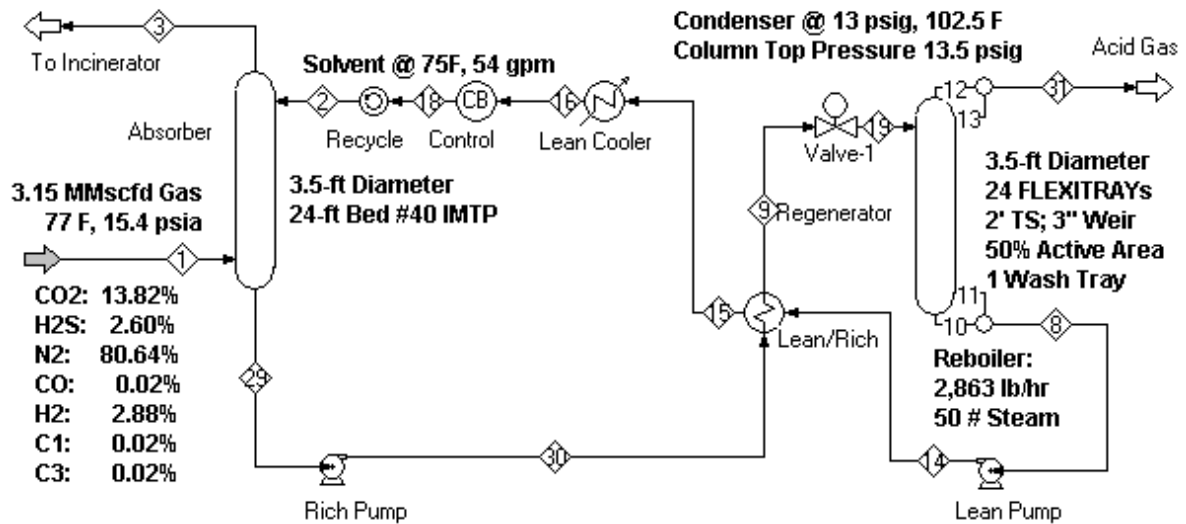


Figure 2 Tail Gas Treating Unit PFD and Operating Conditions

Table 5 summarizes the amine analytical information available at the time of the troubleshooting effort, together with measured absorber performance. At first glance, no smoking guns 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 can 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 H₂S removal worsened.

Table 5 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 ⁻)	142	92	160
Thiosulfate (S ₂ O ₃ ⁻)	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

There were some concerns about the rapid increase of sodium because a rapid cycling type of 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 balance⁴ for each data set. The charge balance allows us to calculate the acid gas anion content of the solution *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 6 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.

Table 6 Charge Balancing for Analytical Data in Table 5

	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 ²⁻)	160	0.00016	0.00005	-0.00010	0.0030	0.0019	0.0033
Thiosulfate (S ₂ O ₃ ²⁻)	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
Calc. Total loading (mole/mole)					0.0138	0.0264	0.0326

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

⁴ 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.

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 7 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 is 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-neutralized with caustic soda. We saw earlier that reactions of acid gases with caustic trap H₂S and CO₂ as *permanent* lean loading:



Table 7 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 discovered that sodium hydroxide was leaking into the amine unit from the ion exchange skid whose function was to control HSS. The sodium was removed using cation exchange methods patented by ConocoPhillips.

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:

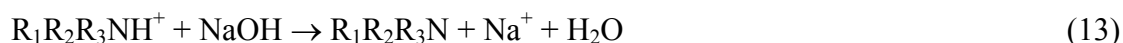
1. Use the plant's onsite amine strength analysis and assume the amine is perfectly clean. The results are tabulated in Table 8 under the heading *Clean Amine*.
2. Use the 15-Jan-04 analytical information as-is. Again, the results are shown in the column headed *Amine as Analyzed*.
3. Adjust the 15-Jan-04 analytical information to account for other factors, as discussed later. Results are listed under *Corrected Amine Analysis*.

Referring to Table 8, the *Clean Amine* case simulates treating performance fairly well *prior to the sodium contamination event*. However, 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; nevertheless, the simulated lean loading 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 8 under *Corrected Amine Analysis*.

Table 8 Amine System 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			
H ₂ S (ppmv)	160-180		
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

The first correction to the amine analytical data centered around 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-neutralized solution because all the bound amine would have disappeared from the circulating solution by exactly the same reaction as the lab titration⁵. 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:



⁵ In conductometric titration, the conductivity change is monitored as NaOH titrant is added. Solution conductivity increases as sodium ions replace the protonated amine.

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 oxidized when the sample was contacted with air:



Typically, we observe an order-of-magnitude difference in the thiosulfate levels between rich- and lean-amine samples from the same contactor. Because this amine system treats Claus tail gas, it could have been subjected to SO₂ breakthrough, which makes it difficult to distinguish between this mechanism and oxidation. However, referring to Table 5, 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 oxidized lean loading⁶. 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 depicted 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 3 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

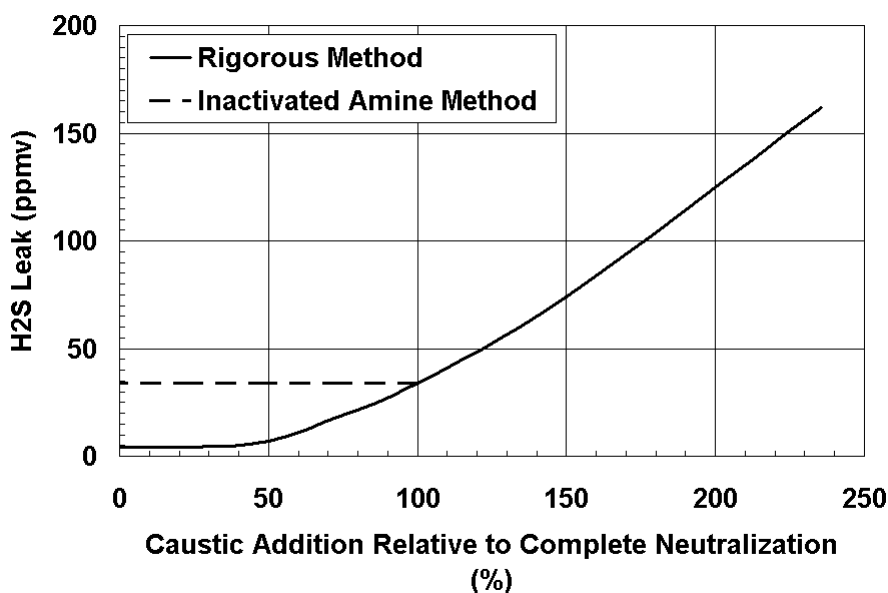


Figure 3 Effect of Partial and Over Neutralization on H₂S Leak from Absorber

⁶ 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 load 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.

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.

The results in Figure 3 suggest that for an under neutralized system, even the partial (less than 100 on the abscissa in Figure 3) removal of amine protonation by sodium hydroxide addition reduces the benefit amine protonation has on solvent regeneration. Reduction of HSS levels translates directly into increasing H₂S leak. However, when the solution becomes *over* neutralized, 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 amine protonation is exactly 100% neutralized with caustic.* For neutralization levels below 100%, this assumption becomes increasingly poor because it entirely misses the huge benefit HSSs have on stripping—in essence, we are back to Case Study 1.

The other, more subtle performance variable that is completely missed by the assumption that HSSs merely inactivates an equivalent amount of amine is the absorber CO₂ slip. 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 lower CO₂ slip predictions than really occur (84.2% versus 86.5%).

Lessons Learned

1. 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.
2. Neutralizing HSSs with NaOH or KOH must be carried out with extreme care, lest the solution becomes over neutralized 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.
3. 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 law of electroneutrality.
4. 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.
5. 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.

In this paper, we have shown how careful analysis of plant and laboratory measurements can be complemented very effectively by a simulation model capable of accounting for all the details and applied to the solution of treating plant operating problems. In both case studies, it quickly became evident that the complete solution ion chemistry had to be taken into account to model treating accurately down to low H_2S levels at low lean loadings. Any solvent contaminants must be included in simulations if these are to predict successfully and accurately the operation of amine plants. In the first study, the contaminants were principally heat stable salts, although performance was altered to some extent by the presence of sodium in the treating solution. In the second case, the heat stable salt problem was overshadowed by such a high sodium level that not only was the protonated amine itself neutralized, but there was enough additional, residual sodium to fix permanently rather high HS^- and HCO_3^- residual lean loadings. *In both cases, removing the HSSs resulted in higher H_2S leak, i.e., poorer treating.* In both case studies, material end energy balances were needed to determine the real status of the lean amine, and in the second study, it was also necessary to do a charge balance before coming to an understanding of the real solution chemistry. All along the way, every piece of plant and laboratory information had first to be doubted, then scrutinized—virtually nothing could be taken for granted at face value. However, by applying sound chemical, physical, and engineering principles, the data were reconciled and the sources of poor performance were identified and corrected.

Simulation formed an important part of these exercises. 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. In the final analysis, 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 the cases studied involved 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.