



The CONTACTOR™

Published Quarterly by Optimized Gas Treating, Inc.
Volume 2, Issue 1, 2008

Contamination of a Treating Solution with Caustic Soda Part 2: Simulation

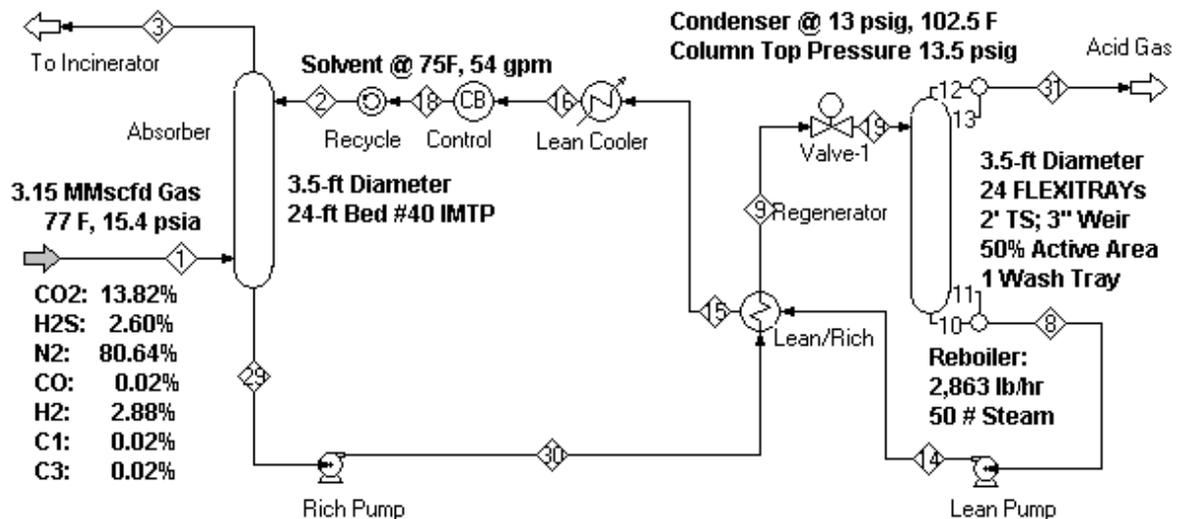


Figure 1 Tail Gas Treating Unit PFD and Operating Conditions

In Part 1, solution analysis and the results of an ion balance were used to show that the slowly deteriorating performance of a refinery, MDEA-based, tail gas treater was caused by leakage of caustic soda from another unit into the treating solution. During the analysis, we also found that the lab value of lean H₂S loading (Table 1) should have resulted in better treating—in fact, a higher lean H₂S loading was masquerading as thiosulfate.

To quantify and understand the role that caustic or alkali carbonate addition plays on treating performance, we will use ProTreat™ simulation under three different sets of assumptions (results are shown in Table 2):

1. Use the plant's onsite amine strength analysis and assume the amine is perfectly clean.
2. Use the January analytical information as-is.
3. Adjust the January analytical information to account for other factors, as discussed later.

Table 1 Analyses and Absorber Performance

Amine (wt%)	Date of Sample		
	Jul	Dec	Jan
Free	37.6	42.6	47.4
Bound	2.5	2.1	0.5
Total	40.1	44.7	47.9
Ions (ppmw)			
Sodium	512	3831	7717
Formate	2,637	2,960	3,812
Acetate	2,270	2,542	3,322
Thiosulfate	4,737	7,394	5,658
Total Anions	9,848	13,043	13,016
DEA (wt%)	2.6	2.0	1.6
H ₂ S load (m/m)	Trace	Trace	0.0055
Meas. Absorber			
H ₂ S (ppmv)	20–30	35–60	160–180
CO ₂ slip, %	NA	NA	84–86

Table 2 Amine System Treating Performance in January as Predicted by ProTreat

	Clean Amine	Amine as Analyzed	Corrected 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	0	1.6	1.6
Equiv. H ₂ S Load from S ₂ O ₃ ⁼		0.0130	
Anion Equiv. w/o S ₂ O ₃ ⁼		0.1424	0.1424
Lean load by charge balance		0.0590	0.0485
Measured Performance			
H ₂ S (ppmv)		160-180	
CO ₂ Slip (%)		84-86	
Simulated 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

Referring to Table 2, the *Clean Amine* case simulates treating performance fairly well *prior to the sodium contamination event* (20–30 ppmv). 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 leak quantitatively.

The main correction was to assign thiosulfate to residual lean H₂S loading for the reasons given in Part 1. For reference, the total thiosulfate (and sulfate) levels in the January analytical results correspond to an equivalent H₂S loading of 0.013 mole/mole, so the total lean loading should be seen to increase from 0.033 to

0.0485 mole/mole. After properly accounting for thiosulfate, the ProTreat model's predicted H₂S leak, CO₂ slip and predicted lean loadings quite accurately matched the observed performance.

Figure 2 shows the treating performance predictions of the ProTreat simulator using the heat stable salt anion content as per the *Corrected-Analysis* case, but with various levels of neutralization with caustic soda. Results obtained under the assumption that the amine was merely inactivated by heat stable salts are also shown.

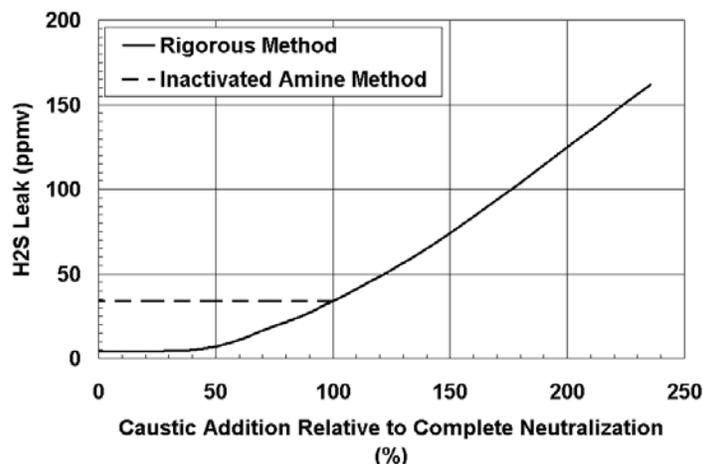


Figure 2 Effect of Partial & Over Neutralization on H₂S Leak from Absorber

Even the partial neutralization of HSSs reduces the benefit of amine protonation on solvent regeneration. 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 only 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.

The main lesson is that 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.

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