



The CONTACTOR™

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Contamination of a Treating Solution with Caustic Soda Part 1: Analyzing the Problem

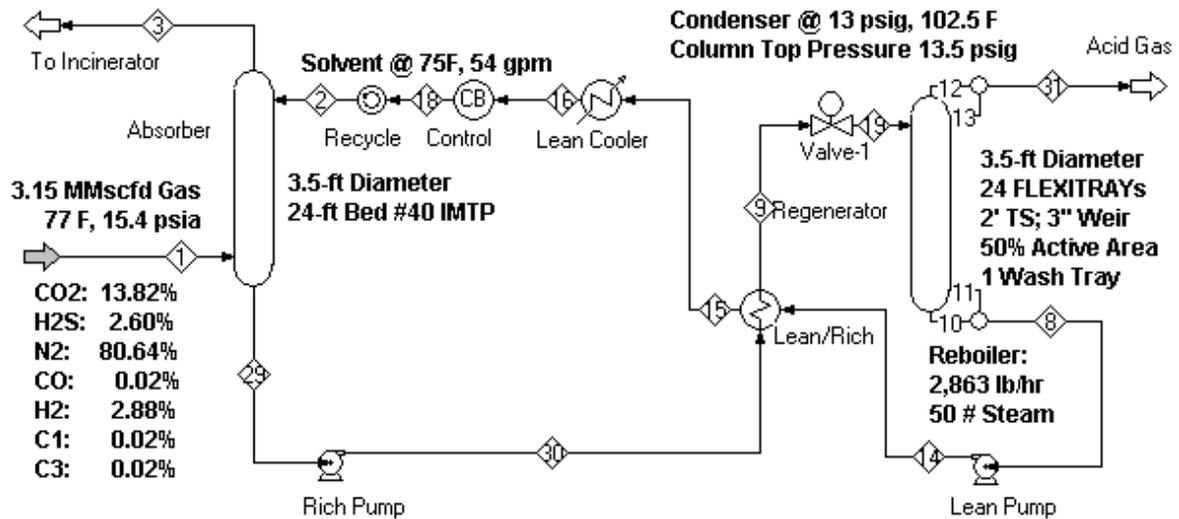


Figure 1 Tail Gas Treating Unit PFD and Operating Conditions

Over a period of several months, an MDEA-based tail gas treater at a refinery 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 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.

Table 1 summarizes the analytical data 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. Although this is a notable increase, 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.

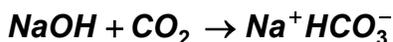
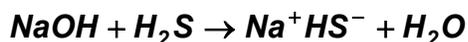
Table 1 Analyses and Absorber Performance

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

There were some concerns about the rapid increase in sodium because an ion exchange system, not caustic addition, was being used for freeing bound amine (continuous reclaiming). The level of all ionic species except thiosulfate increased over the same time period, but the sodium concentration increased quite dramatically, whereas, thiosulfate fluctuated randomly. The ionic chemistry was examined by doing a charge balance for each data set. (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.) The benefits and method of doing a charge balance are planned for the second issue of *The Contactor* in 2008. For now, we just point out that doing a charge balance allows us to determine what electroneutrality says the acid-gas anion content of the solution *has* to be, and this provides a check on the accuracy of lab measurements of acid gas content.

For the January operation, the *total acid gas* loading found by charge balance is 0.0326 mole/mole, a factor of 5–6 times higher than the *H₂S lean loading reported by the plant's onsite analytical lab*. A stand-alone absorber simulation showed that using a 0.006 mole/mole H₂S lean loading fell far short of explaining the poor treating, and it led to the suggestion that perhaps the H₂S lean loading was really quite a bit higher than this.

Table 2 relates the charge-balance-derived loadings to the observed treating performance. Obviously the absorber H₂S leak increases in parallel with increasing charge-balance-based lean loading but there is also a 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 HSS anions. *By January the HSSs had been completely over-neutralized with caustic soda* which traps H₂S and CO₂ as *permanent* lean loading:

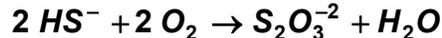


It was found that the sodium was entering the system from a leaking ion exchange skid which was intended to remove HSSs. The sodium was removed using a ConocoPhillips-proprietary cation exchange method.

Table 2 Analysis of Charge Balance Results

Date of Sample:	Jul	Dec	Jan
Charge bal. lean loading (mol/mol)	0.0138	0.0264	0.0326
Sodium Equiv. (meq/g)	0.0223	0.1666	0.3357
HSS Anion Equiv. (meq/g)	0.1856	0.2437	0.2466
Ratio (HSS Anions)/(Sodium)	8.324	1.463	0.7346
Plant meas'd H ₂ S loading (mol/mol)	0.000	0.000	0.005
Measured H ₂ S Leak (ppmv)	20-30	35-60	160-180

It's also interesting to speculate about the source of thiosulfate in the ion chromatography analysis. Was it generated from SO₂ breakthrough or from H₂S lean loading that had oxidized when the sample was contacted with air:



When such detailed measurements are made, 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*. The randomness of the fluctuations in thiosulfate suggest that at least a significant fraction of the thiosulfate is probably oxidized lean loading[†].

In order to quantify and understand the role that caustic or alkali carbonate addition plays on treating performance, it was decided to see whether this system could be simulated with any degree of accuracy. Simulation will form Part 2 of this note and will appear as the next issue of *The Contactor*. The importance of ensuring that a charge balance (electroneutrality) is met, what can be learned from doing this kind of balance, and how actually to carry one out, especially when solvent contamination is of concern, will be discussed in Volume 2, Issue 2 of this series.

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[†] 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 are doubtful