

ACCURACY OF MEASURED LEAN AMINE H₂S LOADING¹

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The regenerator in an amine unit for acid gas removal is a huge consumer of energy, accounting for roughly 80% of the unit's OPEX. Yet the regenerator is probably the most neglected and imperfectly understood piece of equipment in the plant. The purpose of the regenerator of course is to strip acid gases from the solvent to prepare it for reuse in the absorber where gas is actually processed to meet some treating specification. Treated gas purity is at least partially, and often completely, determined by the loading of acid gas in the lean solvent produced by the regenerator. Absorbers in this condition are called lean-end pinched, a normal state for TGTUs for example.

The absorber and regenerator operate together in a closed circuit and are obviously mutually dependent, with solvent lean loading being a parameter critically important to the performance of the unit as a whole. Wrong values of solvent lean loading can have enormous consequences in design and troubleshooting. For example, if the lean H₂S loading is wrongly measured to be a lot lower than it really is, the regenerator designed to produce a low measured loading will be specified with the steam flow rate to the reboiler considerably higher than necessary. This translates into a higher anticipated OPEX to produce the falsely low loading value. Consequently, the reboiler will end up being oversized too, and the needlessly high CAPEX and OPEX may collude into a failed revamp bid.

There are a number of methods (mostly wet chemical as well as gas chromatography) to measure lean acid gas loading, but all of them rely on amine solvent samples collected from somewhere within the gas treating unit. How lean amine samples are drawn, how they are transported, and how they are treated during analysis can have a significant effect on the reliability of the analytical results. The issue is one of assuring sample integrity. Should one be skeptical? The question to be addressed then is how reliable the loading values as reported by the laboratory really are and how reliability can be improved by proper and careful sample handling.

Chemistry of H₂S Oxidation

Hydrogen sulphide is produced naturally by the anaerobic breakdown of organic matter, but it is also slowly oxidized in nature to a variety of product species. Air oxidation of H₂S in fresh and seawater is an area of great interest in water treatment and environmental science, as is the oxidation of sulphide and bisulphide.

At concentrations of hydrogen sulphide in water below 2 mg/L, aeration is considered to be an ideal process for completely oxidizing it to sulphate. This level of H₂S is roughly equivalent to a lean loading of 0.000015 in 45 wt% MDEA. The message is that at this loading, H₂S is likely to disappear altogether from a sample exposed to air—the laboratory will probably report zero! At higher loadings it will still tend to disappear in an aerated sample; just perhaps not completely.

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Luther et al.² have shown that the kinetics of H₂S oxidation in seawater follows the kinetic expression:

$$-\frac{d[H_2S]}{dt} = k_2[H_2S][O_2]$$

Vazquez et al.³ have shown that the addition of trace metals, in particular Fe(II), to the reaction vessel they used in their study increased the rate of oxidation such that the half-life of HS⁻ is on the order of minutes in alkaline solutions at room temperature.

The form of hydrogen sulphide that oxidizes is bisulphide ion, not molecular H₂S. But it should also be remembered that when H₂S dissolves into water it immediately dissociates into H⁺ and HS⁻ ions. The dissociation reaction is instantaneous so as soon as an HS⁻ ion is consumed it is immediately replaced, and oxidation proceeds at constant rate until either oxygen or H₂S is completely consumed.

Iron, particularly in the form Fe(II), is a catalyst for HS⁻ oxidation, and it's a very unusual gas treating solvent that is free from iron, and indeed other ionic metal contaminants. The scene is set for H₂S oxidation in amine solvents. Amine solvent samples are usually collected into air filled sample bottles, they are shipped to the laboratory in air-filled containers, the samples are then given a good shaking in their air-filled bottles, they are pipetted for analysis without taking any care to exclude oxygen, and then they are analyzed in the presence of air. Consequently, the measured solvent loading invariably will be wrong, at least to some degree, and the leaner the original sample, the more erroneous the analysis in relative terms.

The presence of the heat stable salts sulphate and thiosulphate in an amine sample is often indicative of HS⁻ oxidation already having taken place, either by oxygen ingress into the treating system, or quite possibly by oxygen introduced into the lean amine sample itself. Oxidation is invariably worse in rich amine samples where a greater abundance of H₂S reactant is present; however, the relative errors are lower, maybe to the point of being unnoticeable.

Incidentally, there is an old wives' tale to the effect that purging regenerator reflux also purges heat stable salts (HSSs). This tale probably originates from reflux water samples sometimes containing small amounts of sulphate and thiosulphate. However, HSSs are ionic species and, therefore, they are completely nonvolatile; after all, they are salts just like their name says they are, so the question should be *how they got into reflux water* in the first place. Perhaps the answer is that they were formed in the reflux water via oxidation of the bisulphide present there (by oxygen dissolved in the rich amine feed to the regenerator), or perhaps they were formed simply by oxidation of H₂S by air introduced in the reflux water sampling and analysis procedure. The only other source is liquid entrained with the vapor leaving the feed tray of the regenerator. Purging reflux water removes ammonia and trapped H₂S quite effectively. However, any sulphate or thiosulphate it removes via blowdown was either generated in situ in the actual reflux water or samples if it, or it arrived via entrainment. Purging via reflux blowdown is certainly not an effective way to remove heat stable salts from the system. Instead, one should either look for the reason HSSs are being generated in the overhead system, or deal with excessive entrainment by proper tray design and demister selection.

The fact that amine treating is carried out in carbon steel vessels makes it a near certainty that every amine sample from an industrial facility will contain a measureable level of dissolved iron in the form Fe(II), a very effective catalyst for HS⁻ oxidation. It's also a fact that there are multiple opportunities for oxygen to find its way into an amine sample. Even taking the sample into an air-filled sample bottle is sufficient to compromise the sample.

²George W. Luther, III, Alyssa J. Findlay, Daniel J. MacDonald, Shannon M. Owings, Thomas E. Hanson, Roxanne A. Beinart, and Peter R. Girguis, *Front Microbiol.* 2011; 2: 62. Downloaded from <http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3153037/> 18 Aug 2016

³Vazquez F. G., Zhang J., Millero F. J. (1989). Effect of metals on the rate of the oxidation of H₂S in seawater. *Geophys. Res. Lett.* 16, 1363–1366

A solid mass transfer rate-based regenerator model is perfectly capable of producing an accurate rendition of the lean loading to be expected in a well-run system. One of the most frequently overlooked and violated physical requirements of a sample analysis is that the measured ionic composition meets a charge balance, i.e., the analysis leaves the solution charge neutral. There is a very useful spreadsheet tool available at <https://www.protreat.com/downloads> that can be used to ensure a given chemical analysis meets the charge neutrality requirement. It also suggests how the charge balance can be enforced by appropriately adjusting the measured H₂S loading of the solvent. Because ProTreat calculations always enforce charge neutrality, the simulator's calculated value of lean H₂S loading is likely to be more accurate than all but the most carefully done measurement. There are three messages:

- If knowing the actual measured lean amine H₂S loading accurately is important to the task in hand, it's paramount that the measurement is made with a sample taken using every precaution to ensure that oxygen is completely excluded from the sample, right from the moment it is drawn from the system into the sample bottle up to the moment its titration or analysis in the laboratory is completed. Aim for zero exposure to oxygen!
- If you are seeing significant levels of HSSs in regenerator reflux water, there is likely a high level of liquid entrainment from the top of the regenerator. This entrainment may (or may not) have a negative effect on regenerator performance. ProTreat simulation allows you to assess how serious the effect of entrainment is.
- Do not try to purge HSSs by blowing down reflux—look for the reason HSSs are present in the first place. There are other reasons to purge reflux; namely to remove ammonia and H₂S for corrosion mitigation and additionally, the purge can remove hydrocarbon in the boiling range that tends to become trapped in the column. But blowdown shouldn't be used to purge HSSs.

The **real** lean loading will be whatever the regenerator is actually producing, and a given treating unit will produce gas using the actual solvent, not a measured or estimated value. However, if the plant is designed using that badly measured value, the design itself will be decidedly non-optimal. The question then is "What are the CAPEX and OPEX penalties from a faultily assessed lean loading?"

Case Study — Revamp of a TGTU

The case study is based on a refinery TGTU being revamped to treat gas from an SRU whose capacity is to be increased from 300 to 450 LTPD. Sulphur recovery is 96%. A 40 wt% MDEA solvent will be used to treat gas containing nominally 2% H₂S and 5% CO₂ at 2 psig, the balance being 1% each of CO and H₂ and the rest nitrogen. The absorber contains 14 two-pass valve type trays. The regenerator contains a total of 24 standard valve trays including 4 reflux trays and a kettle reboiler. The solvent supplier has recently analysed several samples of the lean amine and reported lean H₂S and CO₂ loadings of 0.002 and 0.0002 mol/mol, respectively. The solvent flowrate is scaled up from the known operating case, i.e., scaled from 320 to 475 USgpm on the basis of the SRU's changed sulphur load

Figure 1 shows how solvent lean loadings determined using the ProTreat® simulator respond to regenerator reboiler duty. It shows that reaching a lean H₂S loading value of 0.002 mol/mol will require a regenerator steam flowrate of nearly 2 lb/USgal delivering 51 MMBtu/h of heat. This amounts to about 480 x 10⁶ lb/year of 50 psig steam. At \$4 per 1,000 lb this consumption will cost about \$1.9 million annually. Of course, the heat load also determines the area required for the reboiler tube bundle, i.e., the size and cost of the reboiler, so this may have to be increased, too.

As Figure 2 shows, ProTreat's absorber simulation indicates that 0.002 mol/mol lean H₂S loading will produce a gas with a 23 ppmv H₂S leak. However, the original design made only 100 ppmv, and that is all that was required. It can be easily met with an H₂S lean loading of only 0.005 mol/mol, using only half the reboiler duty needed to achieve 0.002 loading. The annual reboiler steam cost will be about \$950,000 lower.

The amine samples analysed by the solvent supplier were found to contain several heat stable salts including significant amounts of sulphate and thiosulphate, indicators that oxygen had been present somewhere in the amine system or, more likely, in the sample bottles used to collect the lean amine samples. The effect of HSSs and the ability of the charge balance to suggest what the lean H₂S loading actually must be are detailed elsewhere⁴ and shows the real utility of the spreadsheet tool referenced above. Getting the lean loading right either by measurement or by simulation can make a huge difference. When doing a revamp, one of the first steps is to simulate the unit as it is in the pre-revamp condition. Comparison between the simulated and measured lean loading would show an obvious discrepancy. However, there is always a tendency to believe “the data” rather than the simulator. In this case that tendency could result in a million dollar mistake. This is one of the reasons it is so important to use a simulator that can be trusted to produce realistic and accurate predictions of plant performance. Doing so can point to the reason behind large discrepancies between simulation and measurement. Just because something has been measured doesn’t make the measurement right, and just because something has been simulated doesn’t make the simulation correct. However, predictions using a first-rate simulator can often be more reliable than measurement,

Use a reliable, well-tested rate based simulator to model the whole amine unit all at once. When solvent regeneration is done robustly, lean loadings will often be so low that the most accurate assessment is simulation, not measurement. This is especially the case if sampling and analysis are not done with great care and attention to preserving the sample’s integrity. Oxygen isn’t the enemy just of amine treating units—it’s the enemy of solvent sampling and analysis as well. Reported measurements of lean solvent H₂S loading should be treated with skepticism and should always be validated by ensuring the reported sample analysis obeys a charge balance by calculating to a charge neutral solution.

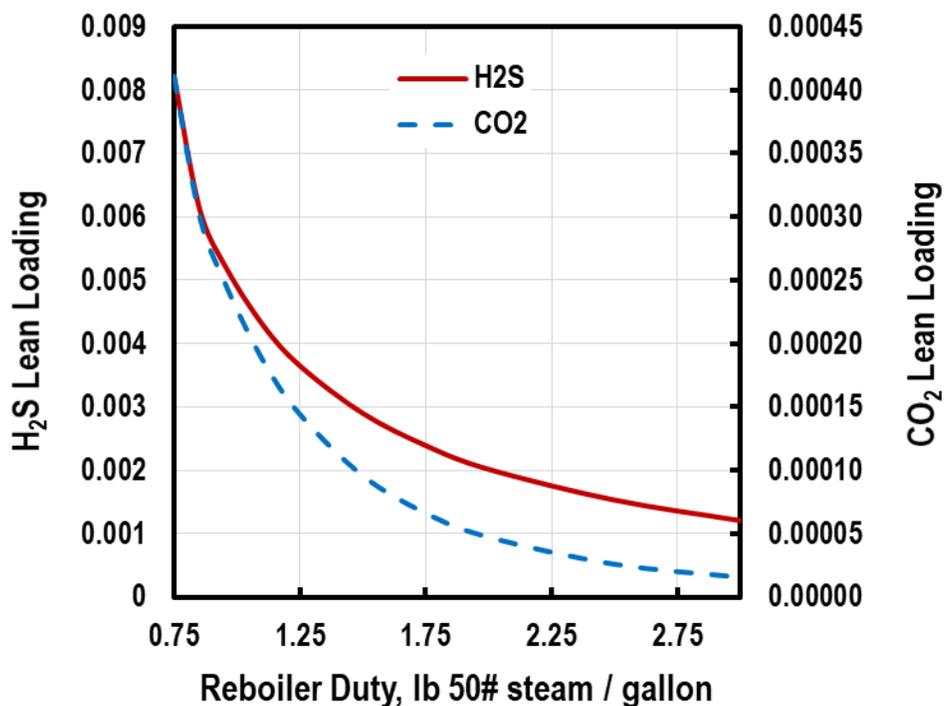


Figure 1 Lean Solvent Acid Gas Loadings Are Highly Dependent on Reboiler Duty

⁴ Nathan A. Hatcher, Alfred E. Keller, Ralph H. Weiland, & M. S. Sivasubramanian, *Are Your Simulation Amines Too Clean?*, Paper presented at the Laurence Reid Gas Conditioning Conference, Norman, OK, February, 2006

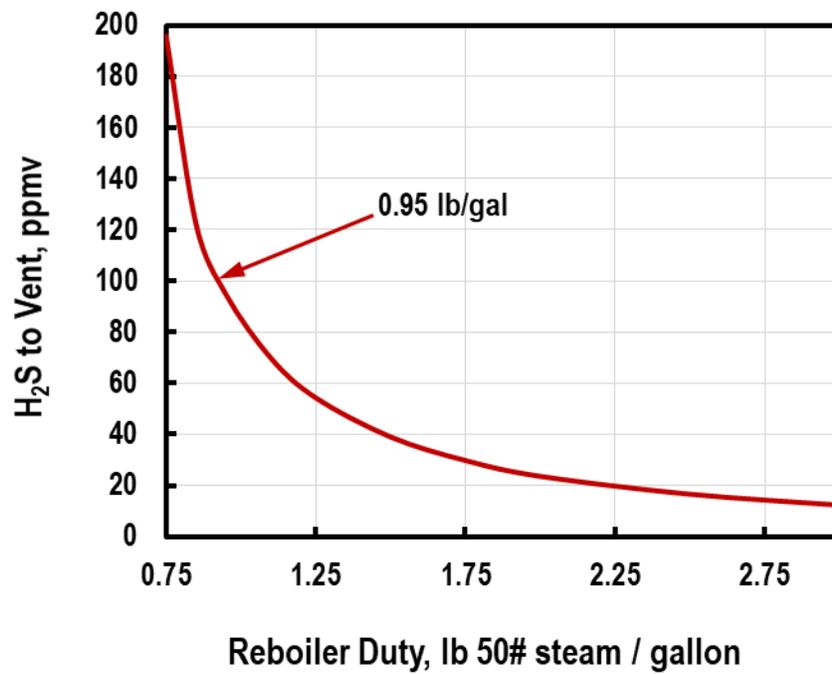


Figure 2 How Treating Is Affected by Reboiler Duty

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