



The CONTACTOR™

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How Reliable Are Measured Values of H₂S Lean Loading?

The H₂S loading of the lean solvent entering an absorber can be critically important to determining the H₂S leak from the absorber. This is especially so in tail gas treating where the absorber is invariably lean end pinched so that the H₂S leak in the treated gas is directly related to the lean solvent H₂S loading and its temperature.

When winning a contract bid for a revamp project depends on having a really tight design, confidently knowing the *actual* lean loading can make the difference between the best possible outcome and a suboptimal design. When the project is greenfield, a good process simulator is the best and most reliable source for this kind of information, as may also be the case in a revamp. But in troubleshooting an absorber it is usually important to know the *real* lean solvent loadings. Solvent loading is almost always obtained by laboratory chemical analysis of solvent samples. The question to be addressed is how reliable the loading values as reported by the laboratory really are. Should one be skeptical?

Chemistry of H₂S Oxidation

Hydrogen sulfide 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 sulfide and bisulfide.

At concentrations of hydrogen sulfide in water below 2 mg/L, aeration is considered to be an ideal process for completely oxidizing it to sulfate. 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.

Luther et al.[†] 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.[‡] 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 sulfide that oxidizes is sulfide 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 an unusual gas treating solvent indeed 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, are shipped to the laboratory in air-filled containers, are prepared for analysis without taking any care to exclude oxygen, and are analyzed in the presence of air. Consequently, the measured solvent loading will invariably be wrong, at least to some degree, and the leaner the original sample, the more erroneous the analysis.

The presence of the heat stable salts sulfate and thiosulfate in a amine samples is often indicative of HS⁻ oxidation already having taken place, quite possibly in the lean amine sample itself. This has been discussed in The Contactor Vol 2, Nos 1 & 2. The oxidation becomes invariably worsened in rich amine samples, where a greater abundance of H₂S reactant is in place.

Incidentally, there is an old wives' tale to the effect that purging regenerator reflux also purges heat stable salts (HSSs). The tale probably originates from reflux water samples sometimes containing small amounts of sulfate and thiosulfate.

[†]George W. Luther, III, Alyssa J. Findlay, Daniel J. MacDon-ald, 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

[‡] Vazquez 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

However, HSSs 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. Salts are ionic components and, as such, they are completely nonvolatile. Perhaps the answer is that they were formed in the reflux water via oxidation of the small concentration of bisulfide there (by oxygen dissolved in the rich amine feed to the regenerator). The only other source is carryover as liquid entrained with the vapor leaving the top of the regenerator. Purging reflux water removes ammonia and trapped H₂S quite effectively. However, any sulfate or thiosulfate it removes was either generated in situ in the reflux water itself, 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 usually is done using carbon steel vessels makes it a certainty that every amine sample from an industrial facility will contain a measurable 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, and given the agitation that always takes place during transportation to the analytical lab, followed by the vigorous agitation imparted by an energetic analytical chemist to ensure the sample is well mixed, it can almost be guaranteed that the analysis results will be wrong to some degree.

Of course, the real lean loading will be whatever the regenerator is producing, but if you are running simulations on the standalone absorber the wrong value of H₂S lean loading will result in a simulation that has very little chance of reproducing the absorber's actual performance. This will make diagnosis of malperformance harder to diagnose.

Unless an absorber *must* be simulated stand-alone, it should always be simulated in a closed circuit with the regenerator and ancillary equipment. 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. Indeed, a ProTreat-simulated value of lean 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 in the task you are performing, 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) be having a negative effect on regenerator performance. ProTreat simulation will allow 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 at all.

To learn more about this and other aspects of gas treating, plan to attend one of our training seminars. Visit www.pro-treat.com/seminars for details.

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