



The CONTACTOR™

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Enhanced Treating Using MDEA with H₃PO₄

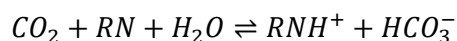
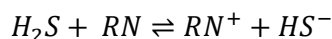
Partially neutralizing an amine, especially MDEA, to improve its regenerability has been practiced since the first patent on the subject was issued to Union Carbide Corp. (*Euro-pean Patent 0134948*, June 29, 1984) some 35 years ago.

In this issue of *The Contactor* we begin with a brief review of the chemistry behind the technology, then look at general guidelines for figuring out what lean solvent acid gas loadings are required to meet specific H₂S treating goals, and finish with a comparison between ProTreat® simulation and performance data from an operating tail gas treating unit (TGTU).

Process Chemistry

The technology finds its greatest application in TGTUs where maximum selectivity for H₂S removal is desired and where absorbers tend almost invariably to be lean-end pinched, i.e., when performance is determined by the solvent's lean loading. This happens when the absorber is overly tall or solvent rate is too high, so equilibrium limits are reached below the top of the absorber, i.e., before the gas leaves the absorber.

Solvent regeneration depends on reversal of the reactions that occurred in the absorber and thus are driven by shifting of reaction equilibria at the elevated temperatures characteristic of a regenerator. At such high temperatures, reactions tend to be at equilibrium everywhere. For H₂S and CO₂ the main reactions are:



If by some manner or means we can increase the protonated amine ($R_1R_2R_3NH^+$) concentration, this will drive both reactions to the left, towards higher concentrations of free H₂S and CO₂. In a regenerator this translates into higher concentration driving forces for stripping. One way to do this is by partially acidifying the solvent by adding a *small* amount of an acid.

Phosphoric acid is the most common additive for acidification. Typically it is used at about the 1,000s of ppmw level in MDEA and, as shown elsewhere (Weiland, R. H. & Subramanian, S., Paper presented at the Fall Meeting of AIChE, Austin, TX, Nov 7, 2004), this appears to be the optimal concentration range when the neat solvent is 50 wt% active ingredients.

Guidelines for Lean Solvent Loading

The whole purpose of acidification is to shift reaction equilibria towards free acid gases, thereby enabling them to be driven more easily from solution. Phosphoric acid is trivalent and dissociates into dihydrogen phosphate ($H_2PO_4^-$), hydrogen phosphate (HPO_4^{2-}), and phosphate (PO_4^{3-}) ions. The formation of each generates 1, 2 and 3 hydrogen ions which attach to MDEA and neutralize it accordingly. At 25°C, pKa values for these species are 2.12, 7.21 and 12.32–12.66 for the formation of the monovalent, divalent, and trivalent species, respectively. Amines are modestly alkaline so HPO_4^{2-} is the main (but not the only) form in a typical solvent stream.

If a TGTU absorber is lean-end pinched in H₂S (as they almost always are), lean loading with respect to H₂S is the controlling parameter and final treated gas composition can be determined fairly closely by a simple vapor-liquid equilibrium calculation at the absorber top temperature and pressure for the nominated H₂S level in the treated gas. Figure 1 shows the maximum possible H₂S loading that thermodynamically can achieve the indicated absorber H₂S leak. This is a *thermodynamic* calculation and, according to thermodynamics, any higher loading simply will be unable to treat to the desired level. Lean loadings of CO₂ as high as 0.001 mol/mol have almost negligible effect on H₂S equilibrium.

Whether an absorber is lean-end pinched can best be determined through simulation. Figures 2(a) and 2(b) show H₂S profiles in pinched and non-pinched absorbers, respectively, using MDEA (note logarithmic scales). If the absorber is lean-end pinched, treating is controlled entirely by lean solvent loading; otherwise, it is controlled by mass transfer rates, hence less affected by lean loading. In non-pinched cases, doing anything to lower the lean loading, either by boiling the solvent harder or by using a stripping promoter such as phosphoric acid, is really not necessary. These actions will *not* result in greatly improved treating, although they may have a minor effect.

Stripping ratio (or reflux ratio) is a poor indicator of stripping in TGTU applications because the total amount of H₂S captured in the absorber is relatively small, leading to a seemingly high value of stripping ratio (moles water per mole acid gas in the stripper overhead). What is needed is sufficiently high solvent flow to force the absorber into a lean-end pinch condition, **and** sufficient reboiler duty to produce treated gas

that meets the treating specification. Under these conditions it will be found that the lean loading corresponds to what is read from Figure 1.

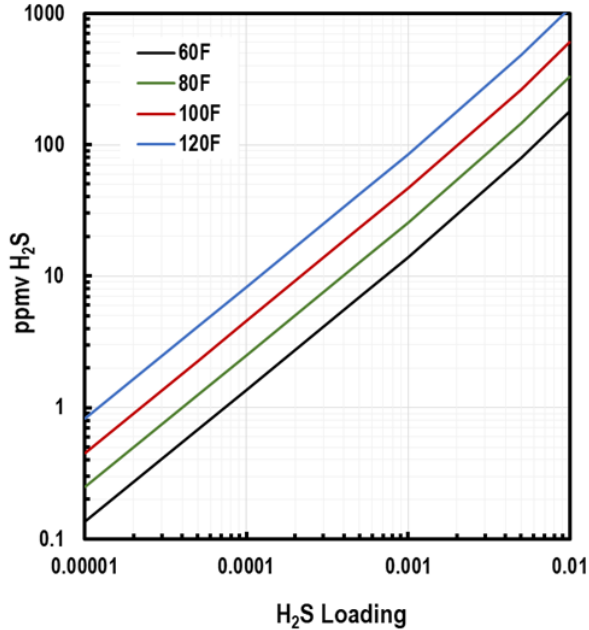
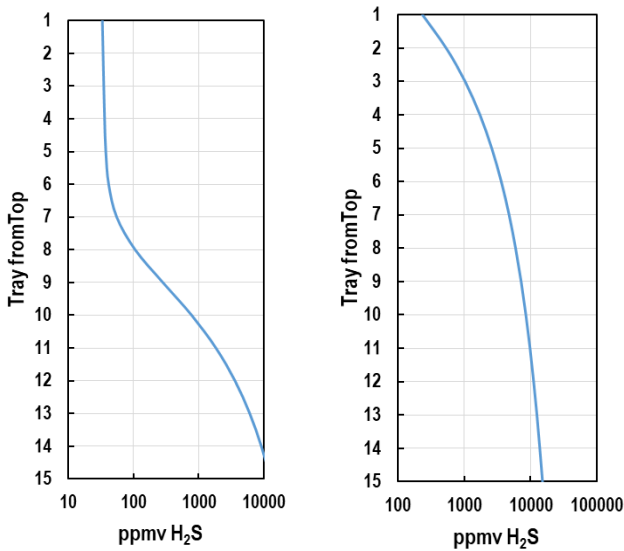


Figure 1 Equilibrium ppmv H₂S vs. Lean Loading in 49.5 wt% MDEA + 0.5 wt% Phosphoric Acid at 1 psig Total Pressure



(a) Pinched (325 gpm) (b) Not Pinched (200 gpm)

Figure 2 Typical H₂S Profiles in a TGTU Absorber; Note Logarithmic Scale

It may be worth noting that phosphoric acid (or any other neutralizing agent, such as high concentrations of even heat stable salts) increases acid gas partial pressures not just in a regenerator which *makes stripping easier*, but they have the same effect in absorbers, and this makes absorption *harder*.

Thus, success of this technology rests on the changing temperature dependence of the reaction equilibria and the equilibrium partial pressures of H₂S. It is imperative that the increase of equilibrium partial pressures at reboiler temperatures is greater than the increase at absorber temperatures.

Stripping Promoter in Practice

The example case is H₂S removal in a refinery TGTU, handling gas with 1.5% CO₂ and 1.75% H₂S. The unit used a H₃PO₄ promoted MDEA solvent, with other contaminants. Data from several plant trials showed treating in the range 2–12 ppmv H₂S. ProTreat® simulation of the unit predicted 6.2 ppmv, right in the middle of the measurements. Incidentally, a simulation with the phosphoric acid additive *removed* showed treating to 36 ppmv. Thus, promotion with phosphoric acid reduced the H₂S leak by a factor of six, and ProTreat correctly predicted the benefit with very high accuracy, without adjustments.

Summary

Effective use of a stripping promoter relies on the absorber being lean end pinched because only in such cases does a reduced lean solvent H₂S loading directly affect the final treating level—there is a one-to-one correspondence between lean solvent H₂S loading and H₂S in the treated gas. If the absorber is not lean-end pinched, a stripping promoter can actually harm treating because the stripping agent elevates H₂S backpressure throughout both absorber and regenerator and, in some cases, the absorber peak temperature can be fairly high. Finally, ProTreat® simulation with generic MDEA should always be performed to indicate just how much benefit, if any, a stripping promoter is likely to bring. In many cases, keeping the stripping promoter up one's sleeve may be a prudent way to extricate oneself from a design that almost works, but not quite.

ProTreat simulation clearly separates situations that can benefit from a stripping promoter from those that cannot. The potential benefits can be quantified and costed against other options such as increased solvent rate, higher reboiler duty, and the use of one stripping promoter over another, e.g., phosphoric acid vs. citric acid. Simulations also quantify the effect of removing heat stable salts (HSSs) from the solvent and let you avoid the shock of learning your unit can no longer treat adequately following solvent cleanup via HSSs removal. Being prepared and knowing what to do can save the cost of many hours and even days of off-spec operation

To learn more about this and other aspects of gas treating, plan to attend one of our training seminars. For details visit www.oqtr.com/seminars.

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