

The CONTACTOR™

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Effect of Solvent Temperature on Treating

The effect of temperature on treating is often counter-intuitive. All other things being constant, lower treating temperatures will always result in lowered back-pressures of acid gases over the treating solution. The usual expectation, therefore, is that lower temperatures will mean better treating. The first premise is correct: lower temperatures always result in lower equilibrium partial pressures. But this is not the only factor affected by temperature. Lower temperatures also result in slower rates for the reaction between CO₂ and the amines, as well as higher solvent viscosity. In equilibrium stage models these factors are completely missing. But in a mass and heat transfer rate model such as ProTreat™, both chemical kinetics and resistances to mass transfer in the gas and liquid phases play key roles. Just as heat transfer rates in heat exchangers are controlled by heat transfer resistance films on the hot-side and cold-side of the exchanger, mass transfer rates are controlled by similar mass transfer resistance films on either side of the gas-liquid interface. In a given volume, *V*, of packing, the mass transfer rates through the gas and liquid resistance films are:

$$\text{Rate}_{\text{Gas}} = k_G a V \Delta p$$

$$\text{Rate}_{\text{Liquid}} = E k_L a V \Delta c$$

with these two rates being identical at steady state. The parameters $k_G a$ and $k_L a$ are gas and liquid mass transfer coefficients, Δp and Δc are partial pressure and concentration difference across the films, and E is the enhancement factor, a parameter that accounts for the effect of chemical reaction on the transfer rate through the liquid film. It contains the chemical reaction kinetics, with a faster reaction corresponding to a larger value of E .

Absorption of H₂S is controlled by the gas-side resistance because H₂S *instantaneously* dissociates in the liquid phase, and the bulk of the mass transfer resistance it experiences is thrown

into the gas phase. CO₂ reacts at finite rate with the amines, and sometimes quite slowly, as with MDEA for example. This makes the liquid film the dominant resistance for CO₂ absorption.

Lower temperature increases driving forces for both acid gases, i.e., it increases Δp and Δc because of the reduced equilibrium partial pressures over the solvent, but the viscosity of both phases also increases, thereby lowering the mass transfer coefficients, and incidentally reducing the enhancement factor for CO₂. It's not immediately obvious whether higher driving forces dominate over reduced mass transfer parameters, or vice versa. And there is an additional complication: The backpressure of each acid gas depends not just on the loading[†] of that particular gas but also on the loading of the other gas, too. Thus, if it turns out that temperature causes more (less) CO₂ absorption, it will allow for less (more) H₂S absorption. So the ability to predict even qualitatively the effect of temperature on treating is anything but straightforward. An example may show the temperature effect more clearly.

In this example, a mixture of 37 wt% MDEA and 7 wt% piperazine is used to remove H₂S and CO₂ in a column packed with 40 feet of 2-inch steel Raschig rings. Lean solution H₂S and CO₂ loadings are 0.003 and 0.005 mol/mol respectively. The sour gas is 1.2% H₂S and 4% CO₂ at 60 bar(g). We will look at two cases in which the gas and solvent temperatures are both either 45°C or 65°C. CO₂ hardly reacts at all with MDEA but exhibits fast kinetics with piperazine (1.25x10⁵ L/mol·s at 45°C and 2.52x10⁵ L/mol·s at 65°C). So reducing the temperature by 20°C halves the rate constant but this appears in the enhancement factor as a square root, so the effect is a 30% reduction in the

[†] Solvent loading is the ratio of moles of the particular acid gas per mole of total amine.

enhancement factor. Solvent viscosity doubles and the liquid film coefficient for random packing depends almost inversely on solution viscosity—the effect of temperature on viscosity, hence on mass transfer coefficient, is far more important than its effect on the reaction kinetics.

Figure 1 shows the ProTreat-simulated mole% CO₂ and H₂S in the gas phase at the two temperatures indicated. Figure 2 shows profiles of solvent temperature and solvent viscosity across the tower.

The H₂S composition profile clearly shows the absorber is lean-end pinched with respect to this component because the profile is quite flat at the top of the column and increasing the packing depth will have no significant effect on the H₂S content of the treated gas. In other words, the H₂S leak into the treated gas depends entirely on the solvent lean loading of the acid gases and on the

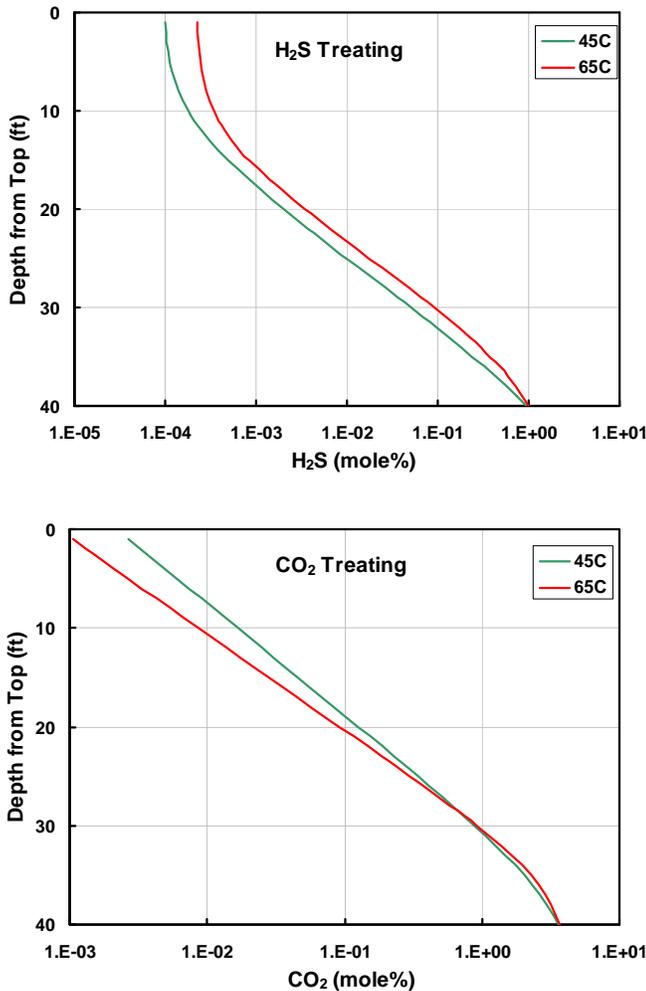


Figure 2 H₂S and CO₂ profiles through absorber — note logarithmic scale

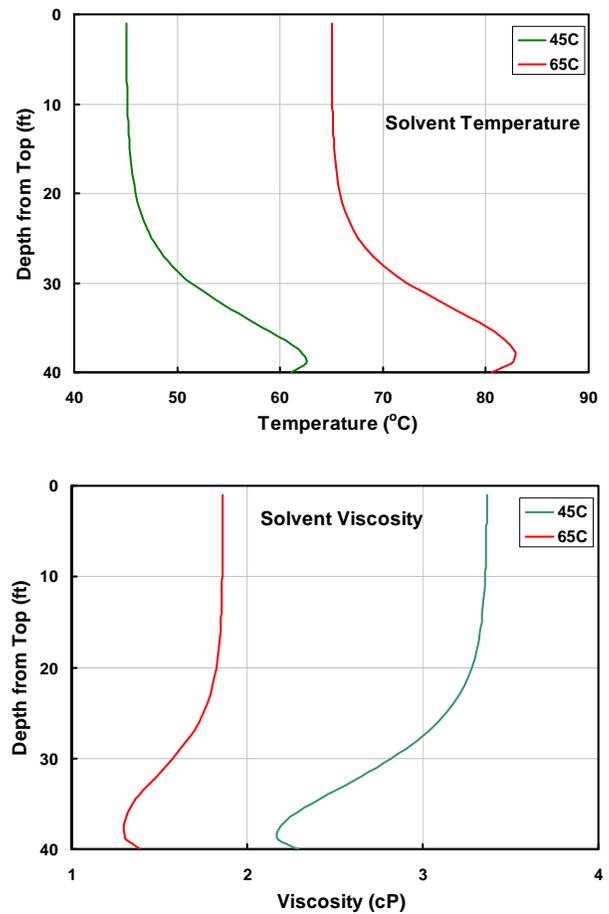


Figure 2 Temperature and solvent viscosity profiles through absorber

temperature. Lower temperature gives a little better H₂S removal because H₂S back pressure is lower.

The CO₂ composition profile is quite different. Here, CO₂ continues to be absorbed all the way up the column and the addition of more packing would improve CO₂ removal. Its absorption rate is *better* at higher temperature because a less viscous solvent offers lower mass transfer resistance to the diffusion of CO₂ through the liquid.

So it's not just a matter of vapor-liquid equilibrium. In the real world where separations are mass transfer rate processes, physical properties affect mass transfer coefficients and their temperature dependence can dominate over the temperature sensitivity of phase equilibrium.

To learn more about this and other aspects of gas treating, plan on attending one of our seminars. Visit www.ogtrt.com/seminars.cfm for details.

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