



The CONTACTOR™

Published Monthly by Optimized Gas Treating, Inc.
Volume 10, Issue 1, January, 2016

Effect of Glycol Contamination on Amine Treating

In the December, 2015 issue of The Contactor, space limited us to discussing only the effect of TEG contamination on amine treating. In the present issue, we compare the effects of the three common glycols, MEG, DEG, and TEG. DEG and TEG are most usually used for dehydration. This is often done on offshore platforms to prevent hydrate formation in the pipelines leading to gas processing facilities. Glycol can be carried over in the gas from the dehydration column as mist and entrainment, and it will then enter the amine unit. An alternative to hydrate prevention via dehydration is to add MEG (or methanol) to the gas before it enters the pipeline. Whatever approach is taken, however, any glycol that enters the acid gas removal unit stays there. It becomes part of the solvent in the amine circuit where it can accumulate to occupy a substantial weight (or volume) fraction of the solvent.

In amine treating, the active ingredient in the solvent is the amine so for a fixed volumetric or mass flow rate, a solvent with 10 wt% glycol, for example, has effectively had 10% of the original solution containing the active amine ingredient removed and replaced by relatively inert glycol. So one should expect that a given wt% of one glycol should have much the same effect on acid gas solubility as any other glycol because they all have much the same density. But this is not the end of the story. As Table 1 shows, glycols are quite viscous so adding even small amounts will have a measureable effect on the amine treating solution viscosity.

Table 1 Some Properties of Common Glycols

| | Molec. Weight | NBP (°C) | Density at 20°C (g/mL) | Viscosity (cP) |
|-----|---------------|----------|------------------------|----------------|
| MEG | 62.07 | 197 | 1.115 | 16.9 |
| DEG | 106.12 | 245 | 1.118 | 35.7 |
| TEG | 150.17 | 288 | 1.125 | 49.0 |

In a large part of the CO₂ absorber in an LNG, ammonia, or syngas plant, the rate of absorption of carbon dioxide is controlled by the resistance to mass transfer in the liquid phase. The higher the viscosity, the higher is the liquid-side resistance. Therefore, if there is a substantial glycol concentration, the viscosity of the solvent as a whole will be higher and CO₂ absorption rates will be reduced. This means that a somewhat taller packed column or a few more trays will be needed to produce the same treated gas purity.

Solvent viscosity is only one of the factors needed to understand loss in performance from the presence of glycols in the treating solution. The other is the reduced total solubility of the gas because of the lower concentration and quantity of amine, the reactive ingredient. When glycol gets into an aqueous amine solvent, in effect part of the reactive solvent gets replaced by an equal volume of non-reactive glycol. The capacity for CO₂ is reduced. Quantitatively, all the glycols should have much the same (albeit not identical) effect. In any event, reduced acid gas solubility is likely the dominant cause. Increased mass transfer resistance caused by higher solvent viscosity adds insult to injury, but the main cause of lost performance is reduced total (chemical plus physical) CO₂ (or H₂S) solubility.

Case Study

The conditions for the case study are the same as used in the previous issue of The Contactor. Table 2 shows the gas and solvent compositions. Both columns contain 20 valve-type trays.

Figure 1 shows the effect of the amount and type of glycol on the equilibrium vapor pressure of CO₂ over the solvent of composition shown in Table 2 and having a CO₂ loading of 0.030 mol/mol.

Table 2 Gas and Solvent Conditions

| Gas | | Solvent | |
|-------------------------|------|------------|----|
| H ₂ O | Sat. | MDEA (wt%) | 40 |
| CO ₂ (mol %) | 3.5 | Pip (wt%) | 2 |
| Methane (mol %) | 94.4 | | |
| Ethane (mol %) | 1.8 | | |
| Propane (mol %) | 0.2 | | |
| Butanes (mol %) | 0.1 | | |

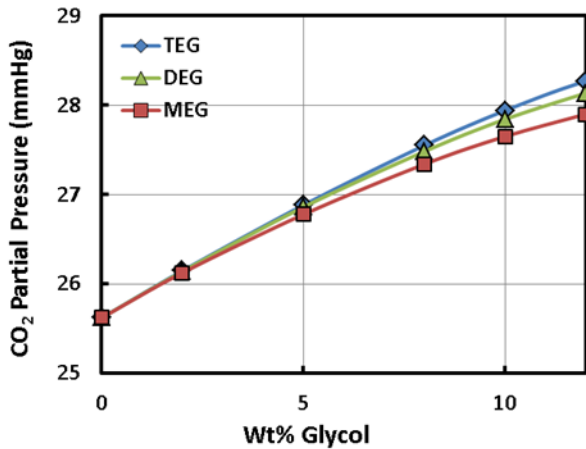


Figure 1 Effect of Glycol on CO₂ Partial Pressure

All three glycols show roughly equivalent effect—increasing contamination results in higher CO₂ partial pressure (equilibrium back pressure) over the solutions. So just on the basis of equilibrium partial pressure, glycol contamination can be expected to result in lower CO₂ absorption rates and, therefore, a loss in treating performance of the solvent.

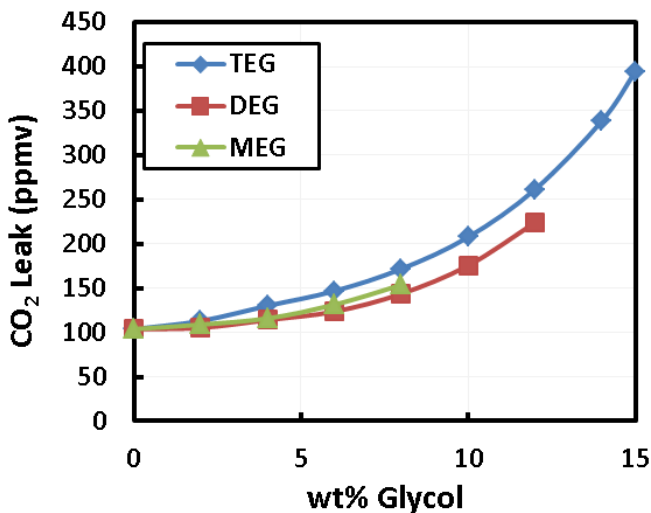


Figure 2 Effect of Glycol on CO₂ Leak

Figure 2 shows the effect of contamination on treating performance. Again, the important parameter is seen to be the contaminant concentration, rather than the identity of the contaminant. In this case, a 12 wt% glycol level can increase the CO₂ leak by a factor of four, far more than is indicated by the 10% increase in CO₂ back pressure. However, the effect is integrated over the entire trayed or packed height of the column, making it additive. The net result is a significant decrease in treating.

Both increased viscosity and higher equilibrium partial pressures affect absorber performance. However, everything isn't necessarily negative. On the positive side, a high concentration of glycol in the treating solution elevates the boiling point. Therefore, the regenerator and reboiler operate at higher temperature and this favors better stripping of CO₂ from the solvent. This is the reason we see MEG performing closer to DEG in terms of CO₂ absorption, despite the fact that MEG is closer to TEG in terms of equilibrium. Bubble point is a *thermodynamic* property that is affected by the *mole fraction* of contaminant (MEG has a relatively low molecular weight) whereas viscosity is a *physical* property affected by *mass fraction* of contaminant.

Amine treating solutions can become contaminated with quite high concentrations of glycols because the glycols have such a low vapor pressure, making them hard to remove, once absorbed into the solvent. They will always affect treating negatively, and their effect can be quite large, to the extent that, in LNG for example, the <50 ppmv carbon dioxide specification on the treated gas may not be met. The reasons for the influence of glycol contamination on treating are several and somewhat complex and, in fact, one effect is actually beneficial. But all can be understood using a comprehensive, mass transfer rate-based approach to process and tower simulation.

ProTreat® provides a way to simulate and quantitatively predict the effect of glycol contamination on gas treating using amine solvents. No other gas treating simulator has this ability.

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