## TEG-Contaminated Amine Treating Solvents

Natural gas as it comes from wellheads is rarely suitable for direct use. Usually it is predominantly methane, with lesser amounts of heavier hydrocarbons such as ethane, propane, butanes, etc. However, besides hydrocarbons it almost invariably contains the undesirable contaminants hydrogen sulfide and carbon dioxide, and it is always wet. To a greater or lesser degree, the gas must be treated to remove its acidic components, and it also must be dried either to meet pipeline requirements, or the more rigorous demands of liquefaction.

With the exception of some FPSO and FLNG installations, wellhead gas is generally transmitted to a central treating plant through pipelines ranging in length from less than a mile to 1000s of miles. The formation of solid hydrates in wet gases containing carbon dioxide and methane at high pressure is always of concern because of potential plugging. To prevent hydrate formation, gas is sometimes dried using glycols (usually triethylene glycol, TEG) before entering the raw gas pipeline, but most often it is laced with methanol or monoethylene glycol, MEG, as hydrate inhibitors.

The gas, now contaminated with methanol, MEG, or TEG, is then contacted with an amine-based solvent (or in some cases with a physical or even a hybrid solvent) to remove the acid gases to some predetermined level, either < 4ppmv $H_2S$ and <2% $CO_2$ for addition to sales gas transmission lines, or to < 50 ppmv $CO_2$ as feed to an LNG plant.

Methanol and glycols behave radically differently and they end up in different places in a gas plant. Methanol is highly volatile and it tends to slip through to the downstream Claus sulfur recovery unit where it plays havoc with the Claus catalyst. Some also goes out with the treated gas, and if the gas is then fractionated and the ethane and propane fractions are fed to a cracker, the methanol poisons the cracking catalysts. Glycols, on the other hand, have very low (albeit not zero) volatility

and any glycol that arrives at the treating plant can accumulate to remarkably high levels in the amine solvent. In the September, 2015 issue of The Contactor™ we discussed how methanol distributes itself among various process streams and within an amine regenerator. Methanol will be treated in greater detail in a paper to be presented at the 2016 Annual Convention of GPA. In the present issue of The Contactor, we use a case study focusing on TEG contamination and its effect on phase equilibrium, solvent properties, and treating unit performance.

### Case Study: TEG in Piperazine-promoted MDEA

As discussed by Sieder, Katz, and Hearn (*How Glycols Affect the Acid Gas Removal Process*, PTQ, Q4, 2013), a TEG level of a few parts per *billion* in the feed gas can easily build to 10 or 15 wt% in the treating solution. The quantitative effect of such TEG levels depends on many factors, including whether the feed gas is rich or lean in $CO_2$. The case study corresponds to the following gas and solvent compositions:

**Table 1   Gas and Solvent Conditions**

| Gas | | Solvent | |
|---|---|---|---|
| $H_2O$ | 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 | | |

Whether this particular case is LNG or pipeline gas is immaterial: our objective is to show how TEG in the amine can affect treating, and why it is affected that way—first, its effect on the treated gas.

Figure 1 shows that the higher the level of TEG contamination, the worse treating becomes.

What was 100 ppmv $CO_2$ gas with a TEG-free solvent becomes 400 ppmv when the solvent is 15 wt% TEG. There are several possible reasons:

1. TEG replaces several volume (and mole) percentages of the aqueous amine with a *physical* solvent having substantially lower total capacity for $CO_2$ than the reactive amine it replaces. In other words, solvent capacity is necessarily reduced.
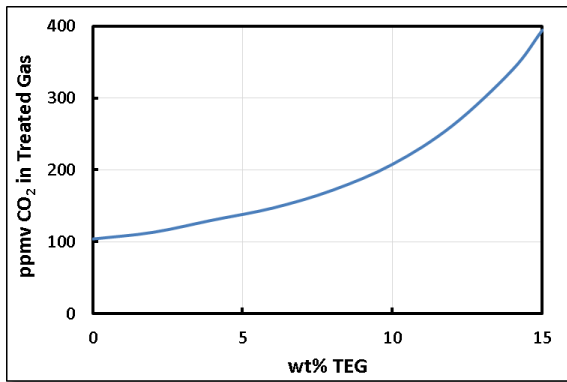


**Figure 1    Effect of TEG Contamination on Treating**

2. This also increases the equilibrium partial pressure of carbon dioxide over the total solvent mixture for a given $CO_2$ loading (defined as moles carbon dioxide per mole of total amine in the solvent).

3. The viscosity of pure TEG at $25^\circ C$ is nearly 50 times that of water and 10 times that of the actual amine solvent at the same temperature. As is the case throughout much of the absorber, $CO_2$ absorption is controlled by the resistance to absorption in the solvent phase. Thus, the increased viscosity that accompanies higher TEG content means lower absorption rates, i.e., worse treating.

Figure 2 shows the effect of TEG level on the viscosity of the lean solvent as it enters the absorber at 120°F. TEG at 15% shows a 50% increase in viscosity; the main cause of poorer treating. Vapor-liquid equilibrium behavior, depending on conditions, can show a 30 to 50% increase in the equilibrium partial pressure of $CO_2$ for this case.
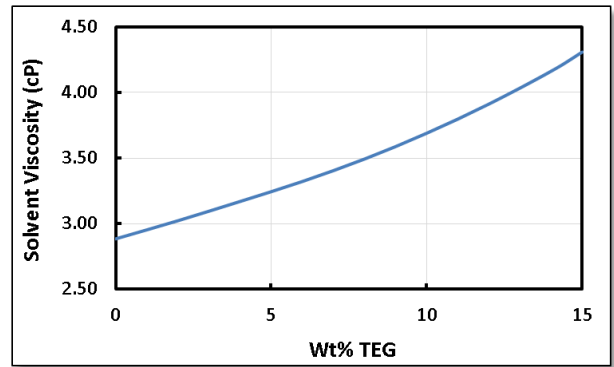


**Figure 2    Effect of TEG on Lean Solvent Viscosity**

Figures 3 and 4 show how TEG reduces bulge temperatures and lowers $CO_2$ pickup in the absorber because of slower reaction kinetics.
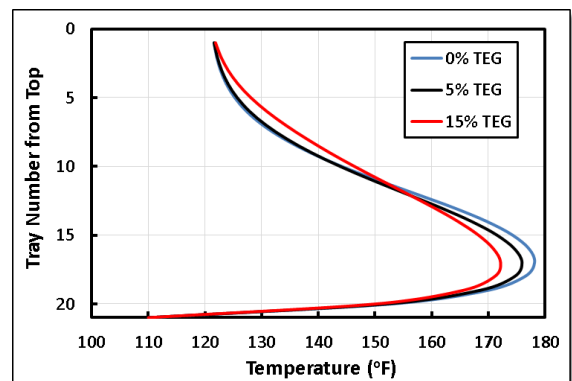


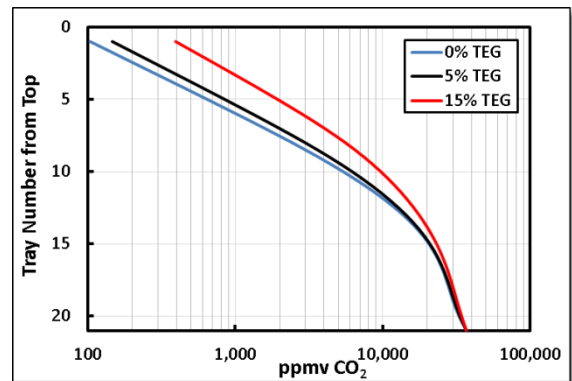**Figure 3        Absorber Temperature Profiles**



**Figure 4        $CO_2$ Profiles in the Gas**

If TEG levels are allowed to build up in an amine system, there can be serious consequences for treating. ProTreat® can accurately and reliably predict these consequences.

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