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Contaminated Solvents — Ammonia Buildup

ProTreat® determines the distribution of ammonia between phases, not just by equilibrium solubilities, but by mass transfer rates. This approach can reveal a lot of rather surprising things about where ammonia concentrates in amine systems, and about how to design and operate sour water strippers.

Ammonia can be viewed as the simplest possible amine. It is volatile, but has high affinity for water, provides additional alkalinity for significant H_2S absorption, and reacts with CO_2 to form thermally reversible ammonium carbamate. The reaction products trap both ammonia and the acid gases — the acid gases in aqueous solution are corrosive to steel so trapping them increases corrosion rates. Furthermore, high ammonia concentrations in the amine can solubilize hydrocarbons, and when ammonia is stripped, a second organic phase may form, causing foaming.

ProTreat's mass transfer rate model treats water, CO₂, H₂S and ammonia as components whose concentrations in the vapor and liquid are controlled by their rates of transfer between these phases. The model is completely mechanistic and uses only fundamental data on tray and packing mass transfer characteristics. **ProTreat**'s mass transfer rate model does not ask for efficiencies, packing HETPs, residence times or ideal stage counts. Being fully predictive, the mass transfer rate model completely eliminates all guess work—it is a virtual plant.

Case Study

A parametric study of the conventional flowsheet shown in Figure 1 was carried out with a view to determining the effect on the distribution of ammonia of various operating parameters such as sour gas temperature and pressure, the ammonia content of the raw gas, the condenser temperature and whether was purged from the regenerator. Sour gas temperatures ranged from 100°F to 140°F with lean amine always 10°F higher. Absorber pressures of 900, 450 and 125 psig were studied, and the ammonia content of the raw gas ranged from 50 to 500 ppmv (dry basis). The regenerator was simulated with condenser temperatures of 120, 140 and 160°F, and the simulations were performed with and without condensate (reflux) purge to remove ammonia.



Figure 1 MDEA Treating System with Basic Parameters

The findings are too extensive to enumerate here, but from the study it could be concluded that:

- Higher raw gas temperature and lower pressure reduce ammonia removal from the gas,
- Fractionally less ammonia is removed when the ammonia content of the raw gas is low,
- Ammonia slip into the treated gas is controlled by ammonia levels in the lean amine,
- The presence of ammonia only marginally increases CO₂ pickup so at these levels, ammonia does not significantly activate MDEA.

One of the more interesting findings is the ammonia profile in the absorber gas (Figure 2). There is a minimum in the ammonia concentration around tray 15 (blue points). Below tray 15, ammonia absorbs from the gas quite rapidly (raw-gas ammonia concentration is 500 ppmv) because the co-absorbed acid gases convert ammonia to ammonium ion, ammonium bicarbonate, ammonium carbonate, and ammonium carbamate, which lower the ammonia equilibrium pressure and promote its absorption. Above tray 15, however, the gas (which is lean in ammonia when it leaves tray 15) strips ammonia from the solvent and emits it with the treated gas. The solid red line shows the



Figure 2 Typical Gas-phase Ammonia Profile in Acid Gas Absorber

ammonia concentration in the gas that would be in equilibrium with the liquid leaving the respective tray. Near the bottom of the column there is a factor of ten difference between actual and equilibrium ammonia levels in the gas, pointing to a severe mass transfer resistance!



Figure 3 How Ammonia Concentration Varies with Position in the Regenerator

Figure 3 shows that ammonia concentration in the amine varies markedly with position in the regenerator, and *in an unexpected way*. Accumulation is not restricted to the reflux wash section quite significant accumulation occurs throughout much of the regenerator to the extent that in this example case only the bottom six regenerator trays are truly effective in removing ammonia from the amine. Figure 4 shows the ability of the mass transfer rate model to predict the behaviour and distribution of ammonia in amine systems. Here, ammonia in the stripped amine is plotted against the ammonia concentration in the reflux water. The lines on this plot were generated by ProTreat with different numbers of wash trays in the 20-tray regenerator. **The data points are actual measurements** from a refinery MDEA system in which **the regenerator in fact had three wash trays**. Remembering that no artificial data input such as tray efficiencies were used in the simulations, the agreement between the pure predictions of the **ProTreat** mass transfer rate model and actual performance data is stunning.



Figure 4 Plant Performance vs. *ProTreat* Rate-Based Model Predictions

Summary

ProTreat's mass transfer rate model accurately predicts plant performance without prior knowledge. Ammonia can be hard to strip from an amine treating solution, and fairly low levels of ammonia contamination in a sour gas can cause higher than expected levels on the stripping trays themselves. Reflux water purging is a strategy to minimize corrosion.

To learn more about this and other aspects of gas treating, plan to attend a workshop in Houston or Abu Dhabi in 2011-12. For details, please visit https://ogtrt.com/training.

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