The CONTACTOR™

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# Ammonia Distribution in Refinery Amine Systems

We have recently added ammonia to ***ProTreat***™ as a component whose distribution between phases is determined, not just by equilibrium solubilities, but by mass transfer rates. As a result, we are in the process of discovering a lot of rather surprising things about where ammonia concentrates in amine systems, and about how to design and operate sour water strippers (the topic of a forthcoming issue of ***The Contactor***™).

Ammonia can be viewed as the simplest possible amine. It is volatile, has high affinity for water, provides the alkalinity required 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, and the acid gases in aqueous solution are corrosive to steel so trapping them will increase 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, $CO_2$, $H_2S$ 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,. The ***ProTreat*** mass transfer rate model does not ask for efficiencies, packing HETPs, residence times or ideal stage counts. It is fully predictive in the truest sense of the word. Answers are obtained *without having to know the answers first*. The ***ProTreat*** mass transfer rate model completely eliminates all guess work—it is a virtual plant.

### Case Study

A parametric study of the 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 or not water 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.

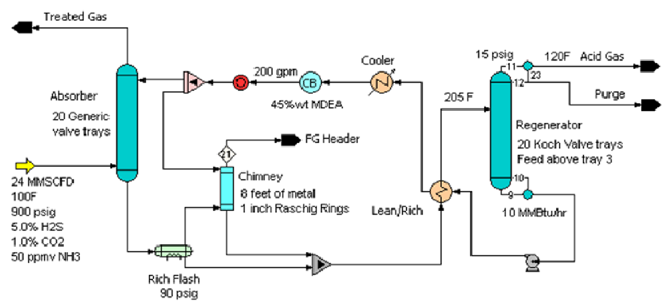


**Figure 1 MDEA Treating System with Basic Parameters**

The details are too extensive to repeat 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 $CO_2$ 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 as shown in Figure 2. Here, a minimum in the ammonia concentration around tray15 (blue points) can be seen. 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 lowers the ammonia equilibrium pressure and promotes 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 in the treated gas. The solid red

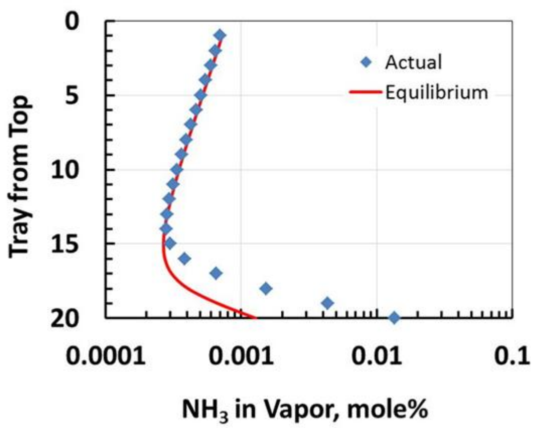


**Figure 2 Typical Gas-phase Ammonia Profile in Acid Gas Absorber**

line indicates the 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!

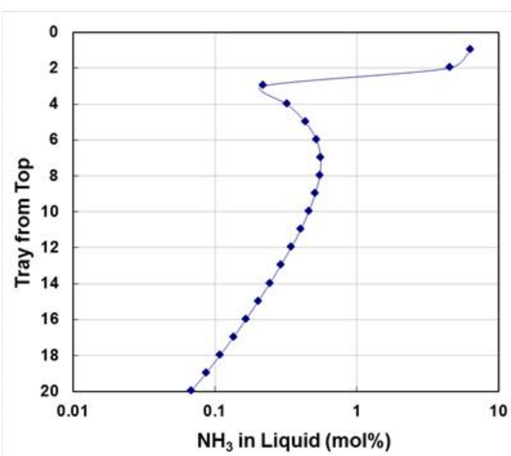


**Figure 3 How Ammonia Concentration Varies with Position in the Regenerator**

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.

The ability of the mass transfer rate model actually to predict the behaviour and distribution of ammonia in amine systems is demonstrated in Figure 4 where the ammonia in the stripped amine is shown 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 quite remarkable.

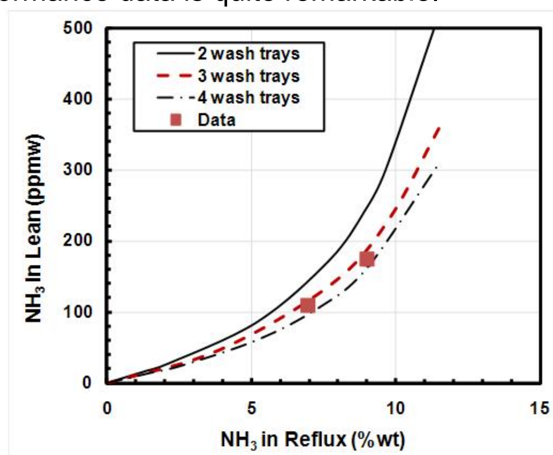


**Figure 4 Plant Performance vs. *ProTreat* Rate-Based Model Predictions**

**Summary**

Without guesswork of any kind, the ***ProTreat*** mass transfer rate model accurately predicts plant performance without prior knowledge of that performance. 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 well-advised strategy to minimize corrosion.

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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 www.ogtrt.com/seminars.

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