

he corrosion that results from ammonia ingress and accumulation in refinery and biogas amine systems is a problem that may be exacerbated by the increasing utilisation of advantaged crudes with higher nitrogen content. Many refiners have instituted guidelines for purging amine regenerator reflux water for corrosion control. (The corrosion guideline is commonly understood to be <1 wt% ammonia in reflux water.) Historically, this has been done empirically based on periodic lab analysis and adjustment of the purge water rate.

Contemporary theories on the true amount of ammonia ingress and its material balance across refinery amine units have not been well understood, because until now the ability to model and simulate the disposition of ammonia in amine absorbers and regenerators has been lacking. This has changed with the advent of a

real rate based mass transfer model for ammonia transport in amine systems and for sour water stripping.

Using the well known ProTreat[™] mass transfer rate based process simulator, it is possible to addresses a number of questions and draw comparisons with measured plant data, including:

- How the choice of regenerator operating conditions affects the amount of accumulated ammonia in the amine system.
- The correspondence between this accumulated ammonia and the amount of ammonia rejection into the amine acid gas.
- Locating where ammonia levels build in regenerators, and whether the accumulation causes additional H₂S to

be trapped leading to higher lean loadings, reduced treating performance, or even regenerator flooding. The amount of ammonia that skates through refinery amine treaters.

Ultimately, the aim is to answer whether the ammonia balance on a refinery amine system can be fully characterised based on the knowledge of a few simple parameters. Using a simulation tool that treats ammonia (and the acid gases) as components whose movement

> between vapour and liquid phases is treated as a mass transfer rate process (rather than as one dictated solely by equilibrium) can help answer these questions.

Ammonia is a highly volatile amine without carbon; indeed, it can be viewed as the simplest possible amine. It has high affinity for water, provides the alkalinity required for H₂S absorption and reacts with CO₂

to form thermally reversible ammonium carbamate. The reaction products trap both ammonia and the acid gases and allow them to become much more concentrated. Thus, it is to be expected that ammonia will trap acid gases. The acid gases are corrosive to steel in aqueous solution and trapping them will result in increased corrosion rates. Furthermore, very high ammonia concentrations in the amine will solubilise hydrocarbons which, when the ammonia is stripped out, may reform as a separate organic phase and cause foaming.

Mass transfer rate based model

Carbon dioxide and hydrogen sulfide have quite different tray efficiencies in amine treating. Both are notoriously low and span a fairly wide range, depending on hydraulics and

and Ralph H. Weiland, Optimized Gas Treating Inc., USA, discuss the fate of ammonia in refinery amine systems the specific conditions on each tray. However, for ammonia they are completely unknown. Where ammonia migrates, where it accumulates in an absorber or regenerator, and how much acid gas it traps depend on the efficiency of its transfer between the phases on the trays. A real mass and heat transfer rate based model completely circumvents the need even to think in terms of efficiencies. let alone determine what values they might have. A mass transfer rate model directly calculates the transfer rate (of ammonia, H₂S and CO_{3}) between vapour and liquid. It does this from knowledge of the tray's mass transfer characteristics (gas side and liquid side mass transfer coefficients and interfacial area) and their dependence on hydraulics, physical properties and reaction kinetics. A conceptual parallel is the kind of heat transfer rate calculations that have been done for nearly a century when dealing with heat exchangers.



Figure 1. MDEA treating system with basic parameters.





Mass transfer involves multiple components (not just heat) through flexible, extensible interfaces (not just rigid tube walls or plates). From a computational standpoint this only makes mass transfer calculations a little more arduous than heat transfer: the principles, however, are the same.

The model treats water, CO_2 , H_2S and ammonia as components whose concentrations in the vapour and liquid are controlled by their rates of transfer between these phases. Phase equilibrium exists only right at the gas to liquid interface. In complete contradistinction from equilibrium stage models, here the mass transfer rates are controlled by the extent to which the components are not in equilibrium between the bulk phases.^{1,2}

Due to the fact that mass transfer rate models are completely mechanistic from the standpoint of the fundamental processes actually taking place, and because they use fundamental data on tray and packing mass transfer characteristics, they are entirely predictive in the fullest meaning of the word. The data needed to simulate a particular case corresponds only to what can be read from a process flow diagram (PFD) or tray vendor drawing. A real mass transfer rate model does not ask for efficiencies, packing height equivalent to a theoretical plate (HETP), residence times or ideal stage counts. It uses the actual tower internals details not just to find pressure drop and flooding parameters; it also performs the separation calculations and provides accurate answers without having to know the answers first. Once the calculations are done, the results can be used to back out what the tray efficiency is for each component on each tray. A mass transfer rate model eliminates guesswork, essentially creating a virtual plant.

Parametric study

A parametric study of the flowsheet shown in Figure 1 was carried out with a view to determining the effect of various operating parameters on the distribution of ammonia. These parameters included 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 - 140 °F, with lean amine always being 10 °F higher. Absorber pressures of 900, 450 and 125 psig were studied and the ammonia content of the raw gas ranged from 50 - 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. The details are too extensive to repeat, 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 ammonia does not significantly activate methyldiethanolamine (MDEA) at these levels.

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 tray 15 (blue points) can be seen. Below tray 15, ammonia absorbs from the gas quite rapidly because the coabsorbed acid gases convert ammonia to ammonium ion, ammonium bicarbonate, ammonium carbonate and ammonium carbamate. This 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 lean solvent and discharges it along with the treated gas. The solid red line in the figure indicates the ammonia concentration in the gas that would be in equilibrium with the liquid leaving the respective tray. It is quite apparent that each real tray, at least in the bottom part of the column, is far from an equilibrium stage. There is some departure from equilibrium even in the upper part of the tower. In fact, near the bottom of the column there is a factor of ten difference between actual and equilibrium ammonia levels in the gas.

Table 1. Effect of raw gas ammonia content andcondenser temperature: no purge									
NH ₃ conc. in feed (ppmv)	150	150	150	500	500	500			
Condenser temperature (°F)	120	140	160	120	140	160			
NH3 in treated gas (ppmv)	2.8	1.7	1.0	7.0	4.3	2.9			
NH ₃ in reflux water (wt%)	2.60	1.42	0.76	5.21	2.90	1.59			
Treated gas H ₂ S (ppmv)	8.0	7.8	7.7	8.2	8.0	7.8			
NH ₃ in lean amine (ppmw)	33.8	20.3	12.6	85.4	52.5	35.4			

Table 1 shows the effect on several performance parameters of:

- The ammonia concentration in the raw gas to the absorber.
- The condenser temperature.

As expected, high ammonia in the raw gas leads to more ammonia in the treated gas, increased ammonia in the reflux water from the condenser and more residual ammonia in the lean amine. However, higher condenser temperature lowers the residual ammonia in the lean amine by sending more ammonia to the sulfur recovery unit (SRU) with the acid gas and returning less to the column in the reflux water. In turn, reduced ammonia in the lean amine results in lowered ammonia levels remaining in the treated gas. The effect on residual H₂S in the treated gas is only marginally improved because of slightly lower H₂S lean loading: there is less reflux and ammonia with trapped H₂S to restrip.

Table 2. Effect of condenser reflux purging								
NH ₃ conc. in feed (ppmv)	500	500	500	500				
Reflux water purged (%)	0	15	75	51*				
NH ₃ in treated gas (ppmv)	7.0	4.7	1.8	3.5				
NH ₃ in reflux water (wt%)	5.21	3.87	1.6	0.99				
NH ₃ in lean amine (ppmw)	85.4	57.4	21.7	42.9				
NH ₃ in acid gas (vol%) (wet)	0.77	0.46	0.10	0.17				
*Flowsheet makeup water requirement added to reflux stream								

As Table 2 shows, reflux purging can be relatively effective at removing ammonia from the amine system. It lowers the ammonia content in the treated gas by more effectively stripping ammonia from the lean amine and also producing an acid gas with a lower ammonia content. Although not shown in Table 2, the effect of purging on H_2S leak in the treated gas, the acid gas loadings in the lean amine, and the CO_2 slip through the absorber, is negligible. The far right column in the table documents the results when fresh makeup water required for the unit's material balance is added to the reflux. It shows that this approach can lower ammonia to the SRU while also managing ammonia levels in the lean amine.

Figure 3 shows that the ammonia concentration in the liquid phase varies markedly and unexpectedly with position in the regenerator. Interestingly, accumulation is not restricted to the reflux wash section: quite significant accumulation occurs throughout much of the regenerator. In this example, it occurs to the extent that only the bottom six regenerator trays are truly effective in removing ammonia from the amine.



Figure 3. Ammonia concentration variation with position in the regenerator.

Figure 4 shows how the presence of a sizable amount of ammonia in the raw gas can lower the temperature profile in a regenerator. The cause is increased energy usage to remove ammonia and trapped H_2S . The result is poorer stripping of acid gases (and ammonia) from the amine.

The efficacy of the mass transfer rate model in actually predicting the behaviour and distribution of ammonia in amine systems is demonstrated in Figure 5, 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 the ProTreat mass and heat transfer rate based model using varying concentrations of ammonia in the raw gas to the amine plant shown in Figure 1, and with different numbers of wash trays in the 20 tray regenerator. The data points are actual measurements from a refinery amine system in which the regenerator 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 remarkable. All other things being equal, the number of wash trays (and therefore the number of stripping trays) does indeed make a difference to the way ammonia distributes itself between the lean amine and the reflux water, all of which is related to the trapping of H₂S by the ammonia in the system.



Figure 4. Effect of ammonia on regenerator temperature profile.



Figure 5. Plant performance data versus ProTreat mass and heat transfer rate based model predictions.

Conclusion

A high quality mass transfer rate model for ammonia and acid gas absorption, as well as for solvent regeneration, will accurately predict plant performance without knowing beforehand what the performance really is. There is no need to provide estimates for tray efficiencies or HETPs for packing, and absolutely no guesswork or fitting is required for simulations to match plant performance data with high accuracy. In this case, information on tray geometry was read from tray vendor drawings, and the raw gas flow rate, temperature, pressure and composition, together with the solvent flow and amine strength, were read from the plant distributed control system (DCS). The simulations predicted everything else. It is important to emphasise that in no sense were simulations fitted to plant performance measurements: each is completely independent from the other. Predicting plant performance is something that the ideal stage plus efficiency approach simply cannot do: with ideal stages, it is only possible to fit to performance data. Mass transfer rate based models, on the other hand, are comfortable predicting performance based on sound science and a mechanistic understanding of the fundamental transport processes at work.

ProTreat's mass transfer rate model for ammonia shows that relatively low levels of ammonia contamination in a sour gas can lead to comparatively high ammonia levels in reflux water, and to much higher levels than one might expect to find on the stripping trays themselves. Purging is thus an advisable strategy to minimise corrosion from the ingress of ammonia in refinery amine systems under virtually all circumstances. Purging reflux water will also minimise ammonia slip to treated gas, acid gas and lean amine streams. The mass transfer rate model provides useful guidance on the relationship between the ammonia levels in these very streams. However, as in most situations in gas processing, quantitative results depend very much on the specifics of the unit configuration. Therefore, they should be viewed on a case by case basis and generalised only with caution. 📊

References

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Optimized Gas Treating, Inc. 12337 Jones Rd., Suite 432 Houston, TX 77070

Telephone: +1 281 970 2700 Web: http://www.ogtrt.com