# Effect of Heat-Stable Salts on Amine Absorber and Regenerator Performance<sup>\*</sup>

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# Abstract

Absorption by thermally-regenerable aqueous amines is the dominant technology for removing  $CO_2$ ,  $H_2S$ , and other organic sulfur compounds from industrial gases. An amine <u>h</u>eat-<u>s</u>table <u>s</u>alt (HSS) is the thermally-unregenerable protonated form of the amine. Absorber and regenerator performance can be significantly influenced by the presence of even a relatively low concentration of HSS in the amine solvent.

The HSS is itself a product of the neutralization reaction between the alkaline amine and an organic or inorganic acid (the neutralizing agent). Unless deliberately added, such acids enter the solution either as the result of degradation of the amine, or by absorption of sulfur oxides or other acid-forming components from the raw gas being treated. However, the presence of HSSs is not always detrimental to amine unit performance. Under certain circumstances, HSSs can actually help to achieve a very low  $H_2S$  leak from an absorber, so sometimes partial neutralization with a mineral acid is done on purpose (so-called partially neutralized amines).

This paper describes the mechanism through which HSSs affect the solution chemistry, and alter the ability of the amine to remove acid gases and to be thermally regenerated. HSSs have been incorporated into the capabilities of ProTreat<sup>™</sup>, a mass and heat transfer rate-based amine-treating process-simulation software package. This simulator is used, with examples, to analyse the benefits and penalties associated with the intentional or unintentional presence of HSSs in the treating solution.

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# 1. Introduction

Twenty years ago, achieving the gas treating goals regularly reached today well beyond reach. The norm was complete removal of  $CO_2$  and  $H_2S$  using tried and true amines like MEA, DEA, DGA, and DIPA. Then MDEA began to be used and it was found possible to leave a certain amount of  $CO_2$  in the treated gas (and get paid for it). MDEA found quite extensive use in operations such as tail gas treating where efficient  $H_2S$  removal and high  $CO_2$  rejection were the goals. In the mid-80s mixtures of amines began to be used, formed mostly by adding varying amounts of reactive amines to MDEA (Chakravarty, Phukan and Weiland, 1985). Thus it became possible to control selectivity and to produce a gas having a specified composition with respect to *both*  $H_2S$  *and*  $CO_2$ . At about the same time, a patent was issued to Union Carbide Corporation (1984) describing the use of a mineral acid or other substance capable of neutral-izing some of the MDEA to its HSS<sup>1</sup>, in order to achieve higher levels of  $H_2S$  removal.

As an aid to understanding partial neutralization, we first show how MDEA (and certain other amines) achieve good  $CO_2$  slip, while other amines do not. The discussion centres on a true mass and heat transfer rate model for the columns, including the effects of chemical reactivity and reaction equilibrium, as well as the influence of explicit equipment design parameters. The column model is validated against detailed plant performance data. Then we examine how partial neutralization (inactivation) of the amine can be used to achieve the seemingly astonishing result of much *lower* H<sub>2</sub>S residual levels in the treated gas. Again, the approach taken is fundamental, this time at the level of shifting reaction equilibria and its influence on vapor-liquid equilibrium.

An example of the effect of the degree of neutralization on regenerator performance is given, following which anecdotal plant performance data for a fuel gas treater are compared with model predictions. Finally, we examine fundamental modeling predictions in terms of projected treating plant performance.

# 2. The Mass and Heat Transfer Rate Model Dissected

An understanding of new amine treating technologies can most easily be reached by concentrating on the process fundamentals, namely, the chemistry and physics of the processes themselves, and the way equipment selection can be used to influence process outcomes. This means taking a truly mechanistic approach in terms of mass and heat transfer rate fundamentals at the microscopic level.

Heat transfer and heat exchanger design are sufficiently simple and parallel to mass transfer to be useful in explaining the utility of treating mass transfer as a rate process. By the 1950's heat exchanger design had been put on a rational basis. Today, no one would contemplate designing a shell-and-tube exchanger, for example, without referring to the physical dimensions of the exchanger and its components (tube diameter, baffling arrangements, passes, and so on), using the physical and transport properties of the fluids, and estimating the shell-side and tube-side heat transfer coefficients needed for the overall heat transfer coefficient used in the heat-transfer-rate equation. Compared with mass separations in columns, most heat exchangers are pretty simple because there is only a single transferring quantity, namely heat. Mass transfer is so much more complicated, sometimes with a dozen or two species transferring, that until recently a theoretical stage approach was the only avenue open. The advent of high-speed desk-

<sup>&</sup>lt;sup>1</sup> The nomenclature of heat stable salts is somewhat confusing. If the amine is *purposely* neutralized, the protonated amine is termed the heat stable salt. If the treating solution is *contaminated* by organic acids, these acids sometimes are called heat stable salts. In this paper, HSS refers to the thermally-unregenerable protonated amine.

top computers, however, has offered the possibility of putting distillation and absorption calculations on the same sound, detailed-mechanistic footing as heat transfer. At the simplest level, mass and heat transfer rates depend on driving forces, transfer coefficients, and interfacial contact area:

# *Rate* = (*Coefficient*)×(*Area*)×(*DrivingForce*)

In heat transfer, the rate is the rate of heat transfer through the tube area that is driven by a (log mean) temperature difference between the shell-side and tube-side fluid temperatures. The overall heat transfer coefficient is derived from individual film coefficients on the shell- and tube-sides of the heat transfer surface, possibly including the resistance of the tube metal and scale deposits. Film coefficients depend on the fine details of the exchanger's construction, on fluid transport properties, and on flow rates. Mass transfer is completely parallel.

In treating, the absorption step involves removal of acid gases and other components from the gas phase by transport into the liquid phase. Figure 1 is a sketch of the vapor and liquid phases in contact on a tray or in a small section of packing. The gas-liquid interface separates the phases. An absorbing gas dissolves into the liquid at the interface, then diffuses across a thin layer of liquid (called the diffusion layer). As it diffuses, the gas meets the reactive amine component in the solvent, reacts with it, and generates heat and reaction products such as carbamate and carbonate. Reaction products diffuse into the bulk liquid while the liberated heat of reaction heats the liquid and also transfers into the vapor. What makes the mass and heat



# Figure 1 Schematic of absorption accompanied by diffusion with reaction

transfer rate model such an attractive tool is the fact that the model deals with the actual trays and packing in the detailed form these internals actually have in the column. For example, the transfer rate of an acid gas component through the vapor towards the interface depends on the diffusion coefficient of the acid gas and the driving force, but it also depends on the state of flow of the vapor phase, i.e., the vapor hydraulics. Phase hydraulics is highly equipment specific. All the other physical and chemical steps in the overall transfer process depend on the specific component, as well as on the amine, reaction kinetics, and very importantly, the hydraulic state of the fluids being contacted. In principle, all the pertinent parameters are just as calculable and determinate for mass transfer as they are for the more familiar heat exchange process. This is illustrated further in the equation of Figure 2, which describes the physical processes acting on an acid gas component once it enters the liquid phase. The generic equations used in the Pro-Treat<sup>™</sup> model apply to the biphase on each tray, or to each of numerous, very short segments of packing (essentially differential heights of packing) in a column. There are some features



Figure 2 Absorption rate of component "i" into the liquid

of the mass transfer rate equation for the liquid phase worth further elaboration. (1) The model directly calculates the transfer rates of the species (and heat) from one phase to the other. *The exiting liquid and vapor phases are not in equilibrium*. (2) Actual equipment design details and parameters are directly involved in determining the transfer rates, in other words, in determining the separation. Equipment details *are required* in order to evaluate the mass transfer coefficients and interfacial contact area. These parameters depend on the hydraulics of the contacting device, and the physical and transport properties of the fluids (phase density, surface tension, viscosity, diffusion coefficients). Obviously, hydraulics depend very much on the type and details of the contacting device. For trays, these coefficients might reasonably be expected to depend on tray type, passes, flow path lengths, type of tray deck opening, and weir geome-

try). For packing, the packing style (random vs. structured), type (specific brands of rings, saddles, structured packing), and their size and material will affect mass transfer performance. (3) Chemical reaction kinetics enhances the mass transfer rates. The reaction acts as a sink for dissolved acid gas, it steepens concentration gradients, and it speeds up diffusion of the acid gas through the liquid. The enhancement factor is a well-defined and readily calculated quantity; *it is not a correction factor* and it should not be classed with tray efficiencies and HETPs. (4) Phase equilibrium is an important factor because it determines the relationship between the concentrations of the acid gases in the bulk vapor and liquid phases. (5) Although not explicitly shown in the figure, component balances must still be closed, but now around each phase rather than around the tray or packed segment as a whole. Further model details can be found elsewhere (Weiland et al., 1985; Vickery et al., 1988; Weiland and Dingman, 1995).

The results of an enormous amount of laboratory and large pilot-scale research have been made available publicly so that the ProTreat mass transfer rate model can be used quite effectively to *predict* column (and plant) performance completely without recourse to experience with similar plants. There are no adjustable parameters and there are *no translations from theoretical stages to real trays and real packed beds*. As will be shown in subsequent sections, ProTreat's mass and heat transfer model faithfully mirrors the realities of processing in actual plant equipment.

# 3. Selective Treating Using MDEA

In the present context, selective treating means removing as *much* of the  $H_2S$  from a gas as possible, while simultaneously removing as *little* of the  $CO_2$  as possible. This is distinct from what we will call *targeted* removal, in which a gas with specific, target levels of both  $H_2S$  and  $CO_2$  is produced.

In some situations selectivity is not wanted (total acid gas removal is required); in others, selectivity is not really possible. For example, a gas containing 20% H<sub>2</sub>S and 0.5% CO<sub>2</sub> cannot be treated to a 4 ppmv H<sub>2</sub>S specification without removing essentially all the CO<sub>2</sub> as well. In such instances, the kind of model used for the absorber has little bearing on the simulated treated-gas purity because the column is lean-end pinched. Suppose, however, that the sour gas is 2% H<sub>2</sub>S and 3.5% CO<sub>2</sub>. This is a low enough H<sub>2</sub>S/CO<sub>2</sub> ratio that the gas can be treated selectively using MDEA, with a substantial part of the CO<sub>2</sub> slipping through the column. The mass-transfer rate-based simulation of a 26-tray column treating 950-psig gas of this composition using 50 wt% MDEA is shown in Figure 3. Note that the CO<sub>2</sub> profile is plotted on a linear scale; whereas, the H<sub>2</sub>S concentration scale is logarithmic. The column is slipping about 40% of the CO<sub>2</sub> but is achieving close to the target 4 ppmv H<sub>2</sub>S. The simulated temperature profile is compared with field data for this tower in Figure 4—the agreement is quite remarkable.

All amines are capable of selective treating to some extent. This is because the finite-rate kinetics of reaction between  $CO_2$  and the amine favors  $H_2S$  absorption, while the thermodynamics always favors  $CO_2$ . The less reactive the amine, the better the selectivity, a fact that is taken to its logical limit with MDEA which does not form reaction products with  $CO_2$  at all.

The reaction between dissolved molecular H<sub>2</sub>S and the solvent is simple ionic dissociation:

$$H_2S \Leftrightarrow H^+ + HS^-$$

The extent of the reaction is influenced by the solution pH and, of course, this is controlled largely by the alkaline amine. In fact, the amine is a substantial sink for the  $H^+$  ions formed by molecular  $H_2S$  absorption and dissociation. The ionization reaction is instantaneous but readily reversed just by a shift in pH. When  $CO_2$  reacts with an amine, on the other hand, it forms a carbamate, and the carbamate formation reaction is not nearly so easily reversed:

$$2RNH + CO_2 \Leftrightarrow RNCOO^- + RNH_2^+$$

Carbamate formation is possible only with primary and secondary amines, i.e., with amines having a labile hydrogen. The faster that dissolved, molecular<sup>2</sup>  $CO_2$  reacts with the amine, the faster it is removed from solution, the steeper its concentration gradient *near* the interface, the faster its transfer rate *away from* the interface and, therefore, the faster it absorbs. MDEA does not form reaction products with  $CO_2$ . However,  $CO_2$  reacts with the hydroxyl ion formed by the dissociation of water, and MDEA is known to be a catalyst for this reaction:

$$H_2O \Leftrightarrow H^+ + OH^-$$

$$CO_2 + OH^- \Leftrightarrow HCO_3^-$$

MDEA is also a sink for the coproduced  $H^+$  ions. Thus, as far as the chemistry is concerned, MDEA achieves its selectivity by being non-reactive with CO<sub>2</sub> and is, at best, a catalyst for the CO<sub>2</sub> hydrolysis reaction. It has a number of other desirable properties for amine treating, including a relatively lower enthalpy of reaction with CO<sub>2</sub>. But by being nonreactive and, therefore, allowing substantial amounts of CO<sub>2</sub> slip (i.e., CO<sub>2</sub> non-absorption), more amine is available for H<sub>2</sub>S pickup and solvent rates can be greatly reduced. With reduced solvent rates come lower reboiler heat loads, reduced solvent pumping requirements, and smaller columns (both height and diameter!). Choice of amine is not the only parameter one can use to obtain and control selectivity. ProTreat's mass transfer rate model teaches us that equipment selection is an important element, too.



Figure 3 Mole % CO<sub>2</sub> (left) and H<sub>2</sub>S (right) in the vapor phase of a contactor using 50 wt% MDEA to treat 950 psig gas containing approximately 2% H<sub>2</sub>S and 3.5% CO<sub>2</sub>. The column contains 26 Nutter Float Valve trays. Note the logarithmic mole fraction scale for H<sub>2</sub>S, but the linear scale for CO<sub>2</sub>.

<sup>&</sup>lt;sup>2</sup> This is the *only* form of  $CO_2$  that exists in, and can therefore transfer from, the vapor phase. Therefore, it is the form pertinent to  $CO_2$  mass transfer, in both absorption and stripping.



# Figure 4 Simulated liquid (▲) and vapor (♦) temperature profiles compared with field data (■) for the conditions described in Figure 3.

The mass transfer rate of an acid gas from the bulk vapor to the interface, and from the interface to the bulk liquid is given, respectively, by the following two expressions:

$$Rate = k_{G,i}a(y_i^{bulk} - y_i^{lnt})$$
$$= E_i k_{Li}^o a(x_i^{lnt} - x_i^{bulk})$$

(The rates are equal because whatever leaves the vapor must enter the liquid.)

Kinetics affects liquid-phase mass transfer through the enhancement factor, *E*. The contacting equipment affects both the liquid and vapor phase mass transfer through the mass transfer coefficients  $k_G$  and  $k_L$  and the interfacial area, *a*. In amine treating, H<sub>2</sub>S absorption is gas-phase controlled while CO<sub>2</sub> absorption is controlled by liquid-phase resistance. It also happens that the liquid flow on trays is highly turbulent but the liquid flow over packings is relatively quiescent. Therefore, choice of the type and design of tower internals can be expected to affect not only selectivity but also the ability of the column to treat the gas satisfactorily.

MDEA and other tertiary amines are fairly selective towards  $H_2S$  because they do not react directly with  $CO_2$ . Some of the most severe applications for selective treating using MDEA are sulfur-plant tail-gas treating, and concentrating regenerator offgas to produce either a richer Claus plant feed or an  $H_2S$  stream suitable for down-well disposal. In both cases, too many trays or too much packing is as fatal to performance as too little. As the tray count rises,  $CO_2$ continues to absorb and eventually reaches the stage of lowering solution pH so much that already-absorbed  $H_2S$  strips out on the bottom trays of the contactor. Figure 5 is an example from regenerator offgas upgrading (20 psig gas containing 80%  $CO_2$  and 20%  $H_2S$  without hydrocarbons, being treated with 50 wt% MDEA). A minimal  $H_2S$  leak of 830 ppmv can be achieved with 12 trays and the rich solvent, when regenerated, would produce a Claus plant feed with an  $H_2S/CO_2$  ratio of 14/10 starting from a 20/80 offgas, i.e., a seven-fold enrichment. The more illustrative lesson from the calculations, however, is that using too many trays can result in  $H_2S$  stripping in the lower part of the column and can push  $H_2S$  out the top. The resulting  $H_2S$  bubble can be seen in Figure 5 for the 20-tray case. Too few trays result in high  $H_2S$  leak. Although regenerating the rich solvent would produce an  $H_2S/CO_2$  ratio of 23/10—nearly a 12-fold enrichment—it is a fact that the residual gas must also meet disposal requirements. An 830-ppmv  $H_2S$  gas cannot be disposed of unless it is a very small part of a larger, very-dilute stream.



Figure 5 Profiles of mole %  $H_2S$  in vapor in an absorber having various tray counts ( $\bullet$ -5, O-10,  $\nabla$ -12,  $\nabla$ -15,  $\blacksquare$ -20 trays). Column is removing  $H_2S$  from a 20 psig regenerator offgas containing 80% CO<sub>2</sub> and 20%  $H_2S$ , water saturated but without hydrocarbons or fixed gases.

Selectivity in gas treating is achieved by bringing together quite a number of individually complex rate and equilibrium processes into an orchestrated whole. But most important is the inescapable fact that *selective treating can be satisfactorily modeled only as a mass transfer rate process* in which all the elements participate—one simply cannot assign tray efficiencies or ignore tower internals details and expect to come up with a reliable prediction.

Perhaps the most common application of selective purification is sulfur-plant tail gas treating and it is exactly here that using a partially-neutralized amine can yield striking benefits.

#### 4. Partially Neutralized Amines

Partially neutralizing an amine (for example, with an acid) can allow unusually low  $H_2S$  levels to be reached in the treated gas. This counterintuitive behavior was probably discovered by accident, through a plant upset that resulted in formation of a substantial amount of the heat stable salt of the amine. More amine was added to the solvent to make it up to its original strength, and surprisingly,  $H_2S$  removal was greatly improved. How? The answer is in the regenerator.

Consider a tertiary amine as an example. When ionization of  $H_2S$  in water is combined with proton acceptance by the amine, the net overall reaction is:

$$H_2S + RN \Leftrightarrow RNH^+ + HS^-$$

The equilibrium constant for the reaction is:

$$K = \frac{a_{RNH^+}a_{HS^-}}{a_{RN}a_{H_2S}}$$

It easily can be seen that if the concentration of the protonated form of the amine can be increased, the equilibrium concentration of HS<sup>-</sup> will decrease in proportion, i.e., equilibrium H<sub>2</sub>S loading will drop. This has greatest potential impact at very low loadings because here is where the protonated amine concentration normally would be quite small (e.g., 0.001 mol/mol), but has been artificially made quite large. Consequently, there is a *dramatic* decreased equilibrium concentration of HS<sup>-</sup> in solution and, therefore, a *dramatic* decrease in solution loading with respect to H<sub>2</sub>S. The reaction equilibrium has been shifted towards *much* lower H<sub>2</sub>S loadings. This can lead to a regenerated solvent with more than an order-of-magnitude lower H<sub>2</sub>S loading and, therefore, with the ability to remove H<sub>2</sub>S to much lower levels. The effect is very pronounced at the lean end of the regenerator (especially the reboiler) where the protonated amine and HS<sup>-</sup> concentrations are already fairly small. Here, artificially enhancing the protonated amine concentration from a very small value to a relatively very large one results in a very large decrease in H<sub>2</sub>S loading of the lean solvent.

It is noteworthy that there is a similar reduction in residual  $CO_2$  loadings because protonated amine is also a species in  $CO_2$  reaction equilibrium. Although tertiary amines do not react directly with  $CO_2$ , they still act as proton acceptors:

$$CO_2 + RN + H_2O \Leftrightarrow RNH^+ + HCO_3^-$$

with the reaction equilibrium constant:

$$K = \frac{a_{RNH^+} a_{HCO_3^-}}{a_{RN} a_{H_2O} a_{CO_2}}$$

Again, one sees that by independently increasing the protonated amine concentration, especially at low loadings where the concentration of this species is normally quite small, a substantial decrease in the already-small  $HCO_3^-$  ion concentration will be required to balance it.

The potential impact of solvent protonation on regeneration is clear. However, its potential effect on absorption is apparently the opposite of what is wanted because amine protonation results in *higher* acid gas backpressures at equilibrium. In the following, we will examine a stand alone regenerator, then look at an absorber whose performance is degraded by the presence of HSSs, and finally simulate a complete tail gas treating unit to see what effect various levels of protonation have on the H<sub>2</sub>S leak.

#### 4.1. Standalone Regenerator

The amine treating process simulation package ProTreat<sup>™</sup> was used to simulate a regenerator, automatically sized for 70% jet- and downcomer-flood (roughly 17.5-ft diameter). It contains 10 sieve trays (12 gauge, 3-pass with ½-inch holes and 12% open area) on 24-inch tray spacing. Rich solvent is fed to the top tray, and operating conditions are shown in Table 4. The total MDEA concentration (protonated plus unprotonated forms) is fixed at 45 wt% and various degrees of neutralization from zero through 25% are used. All other conditions remain unchanged from case to case.

	0 1
Solvent feed	4233 USgpm
Solvent temperature	190°F
Solvent CO <sub>2</sub> load	0.4 mol/mol
Solvent H <sub>2</sub> S load	0.1 mol/mol
MDEA concentration	50 wt%
Reboiler Duty	275 MMBtu/hr

Table 4	Physical and operating details of the column used in modeling
	the effect of amine protonation on regenerator performance

Figure 6 shows simulated lean solvent loads (mol/mol) as a function of the percent of the total MDEA neutralized. The impact of partial neutralization is quite remarkable. By neutralizing 25% of the MDEA, the residual  $H_2S$  and  $CO_2$  loadings have both been reduced by a factor of 50!



Figure 6 Effect of partial neutralization of MDEA on the residual loadings of  $CO_2$ and  $H_2S$  in the regenerated solvent; see Table 4 for operating data.

# 4.2. Effect of Solvent Contamination by HSSs on Absorber Performance

One of the absorbers in a refinery fuel-gas treating system using MDEA was revamped from packing to high-performance trays in an attempt to produce treated gas below 4 ppmv  $H_2S$ . However, after the revamp, the column still failed to meet requirements. Process simulation indicated for the measured lean solvent quality, the absorber should have been producing gas with about 2 ppmv  $H_2S$ . Instead, the  $H_2S$  leak was 27 ppmv.

Detailed solvent analysis showed the presence of 0.25 wt% acetate and 1.6 wt% formate. When the absorber was simulated using these levels of the HSSs in the solvent, ProTreat predicted an  $H_2S$  leak of 32 ppmv, in close agreement with the measured plant performance.

# 4.3. Effect of Partial Neutralization on Tail Gas Unit Performance

In this example the simple recycle flowsheet shown in Figure 7 is used to treat the tail gas described in Table 5. The contactor contains 12 FLEXITRAYS on 2-ft spacing in a 7.5-ft diameter column. It operates with a bottom pressure of 2.25 psig below the bottom tray. The regenerator is 6-ft diameter with 20 trays and rich solvent is fed to tray 4 from the top. Reboiler duty is set at 9 MMBtu/hr and the operating pressure is 15 psig below the bottom tray. Figure 8 shows the effect on  $H_2S$  leak of partial neutralization using various amounts of phosphoric acid at constant MDEA concentration of 37 wt%.



# Figure 7 Flow sheet for tail-gas treating unit simulation

Tail Gas	
H <sub>2</sub> S (%)	1.3
CO <sub>2</sub> (%)	8.8
Nitrogen (%)	89.9
Temperature (°F)	86
Pressure (psig)	2.25
Flow (MMscfd)	10.5
Solvent	
Flow rate (USgpm)	178
MDEA Total Concentration (wt%)	37

#### Table 5 Tail gas analysis and stream conditions



Figure 8 Effect of partial neutralization on H<sub>2</sub>S leak for data in Table 5

Because the *total* amine concentration is held constant, the concentration of the *free* amine capable of participating in the reactions decreases as the solvent becomes more neutralized. All the basic data used for the simulation correspond to an actual plant.

With the addition of enough phosphoric acid to produce two percent neutralization, the  $H_2S$  leak falls dramatically from 21.5 ppmv to 2.5 ppmv. This is the result of greatly reduced residual  $H_2S$  loadings of the lean solvent (from 0.0016 mol/mol to 0.000033 mol/mol). Indeed, as the percent neutralization continues to be increased, the lean loadings keep falling, almost to the point where the lean solvent is nearly devoid of  $H_2S$  (and  $CO_2$ ). However, beyond 3% neutralization the  $H_2S$  leak takes a turn upwards and keeps rising with continued addition of phosphoric acid. The upturn is caused by the fact that as the solvent is neutralized, the concentration of reactive (unprotonated) MDEA decreases. The solution alkalinity, a controlling factor in determining the  $H_2S$  absorption rate, falls. The minimum in the curve is a classic indicator of competing effects at work. On the one hand, increasing neutralization improves the quality of the lean solvent; on the other, it turns more and more of the reactive amine into the inactive protonated form.

The normal recommendation for partially neutralized solvents is to replenish the neutralized part of the amine with fresh, thereby maintaining the *free* amine concentration in the lean solvent roughly constant. In the present case, however, this provides only a small additional reduction in  $H_2S$  leak (always less than 0.1 ppmv), partly because the percentages neutralized are fairly small. When thought of in terms of the difference in pH between a 37 wt% and a 40 wt% MDEA solution, for example, the smallness of the benefit is no surprise.

This example shows that partially neutralizing an amine, in this case MDEA, can result in *greatly* reduced  $H_2S$  leak from tail-gas treating units, and that the reduction is directly attributable to greatly improved solvent regeneration. Reducing  $H_2S$  leak by a factor of ten is quite achievable.

# 5. Summary

This paper has attempted to develop a basic understanding of (1) the factors that affect selectivity and (2) how the presence of amine heat stable salts can cause poor sour-gas contactor and treating plant performance in some cases, and tremendous reductions in  $H_2S$  leak in others. The following conclusions can be drawn:

- MDEA (and certain other amines) achieve good CO<sub>2</sub> slip because of a favorable balance between chemical reactivity and phase equilibrium.
- Selectivity is a balance between the mass transfer *rates* of the acid gases competing for the amine in the solvent. It is much more than a matter of acid gas partial pressures and reaction rates. Mass transfer rates depend on transport properties and physical equipment, too.
- The type of equipment (trays versus packing) and the detailed equipment design parameters play just as important a part in setting individual column and overall plant performance as do kinetics and thermodynamics.
- ProTreat's true mass and heat transfer rate model has no more difficulty with packed columns than with trayed ones, and the model finds unusual situations such as acid gas enrichment just as easy to handle as traditional absorbers.
- Comparison with detailed absorber temperature profiles and qualitative observations of plant behavior show that a mass and heat transfer rate based simulator reproduces field performance with uncanny accuracy.
- Just neutralizing part of the amine sometimes can give tremendous reductions the in H<sub>2</sub>S leak from absorbers. With MDEA, for example, it is often possible to achieve well below a few parts per million H<sub>2</sub>S in the treated gas, whereas, a hundred or so parts per million is the norm with conventional MDEA.
- The mechanism by which partial neutralization achieves this amazing result is through the formation of a substantial concentration of a protonated form of the amine that has been rendered heat-stable (unregenerable) by the stable nature of the neutralizing agent. This large stable concentration of protonated amine shifts the chemical reaction equilibria concerned with amine protonation. At low acid gas loadings the shifted equilibria favor free dissolved H<sub>2</sub>S and CO<sub>2</sub> concentrations lowered by several orders of magnitude.

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