Effective Amine Technology:

Controlling Selectivity,
Increasing Slip, and
Reducing Sulfur[1]

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ABSTRACT

Twenty years ago, achieving the gas treating goals regularly reached today was virtually uni-maginable. 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 vary-ing amounts of reactive amines to MDEA. 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. A rather inter-esting additive was a mineral acid or other substance which was capable of neutralizing some of the MDEA. In addition, a class of sterically-hindered amines was developed to target selective removal applications—we will not deal with these sterically-hindered amines here. The focus of the paper is the development of a fundamental understanding of how modern amine solvent technologies work and validation of this understanding through computer simulation and, where possible, comparison with actual plant performance data.

This paper first discusses how MDEA (and certain other amines) achieve good CO_2 slip, while other amines do not. The development embraces chemical reactivity and equilibrium consid-erations, as well as the influence of detailed equipment design parameters. The engineering basis for our understanding is validated against actual plant performance data, including de-tailed tower temperature profiles.

The use of reactive amines as activators or promoters for MDEA is considered next. We dis-cuss in detail the basic mechanism by which these promoters function and the various ways in which they can influence selectivity. The basic understanding developed in the paper is illus-trated with detailed tower simulation.

Finally, we examine how partial neutralization (inactivation) of the amine can be used to achieve the seemingly astonishing result of much *lower* H_2S 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. Although no plant performance data using a partially neu-tralized solvent are currently available to us, we examine fundamental modeling predictions in terms of projected treating plant performance.

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1. Introduction

Twenty-five years ago, using aqueous amines to achieve a 4 ppmv H_2S specification in the treated gas was invariably accompanied by the nearly complete, simultaneous removal of CO_2. From a process standpoint, as long as the contactor had enough trays and the regenerator was reboiled hard enough to yield a sufficiently lean amine, pipeline quality gas could be easily produced. Today, the gas processing industry routinely requires that various amounts of CO_2 are left in the gas, and demands that the treated gas meet ever more stringent quality specifications, especially in low pressure applications like tail gas treating. In addition, reducing energy consumption has become a focus. This has brought about the use of new amines, the development of blended amine technology, and the use of special additives to enhance H_2S removal. Understanding how these technologies work and simulating them is the focus of this paper.

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 desktop computers, however, has offered the possibility of putting distillation and absorption calculations on the same sound, detailed-mechanistic footing as heat transfer.

This paper uses the mass and heat transfer rate approach to develop a basic understanding of how modern amine-treating technologies work. The next section provides an overview of the necessary mass transfer rate fundamentals. This allows us to investigate CO_2 slip using MDEA, and the influence of equipment parameters on selectivity in §3. Blended amines are explored in §4 and the paper concludes by discussing the use of special additives to enhance H_2S removal in §5.
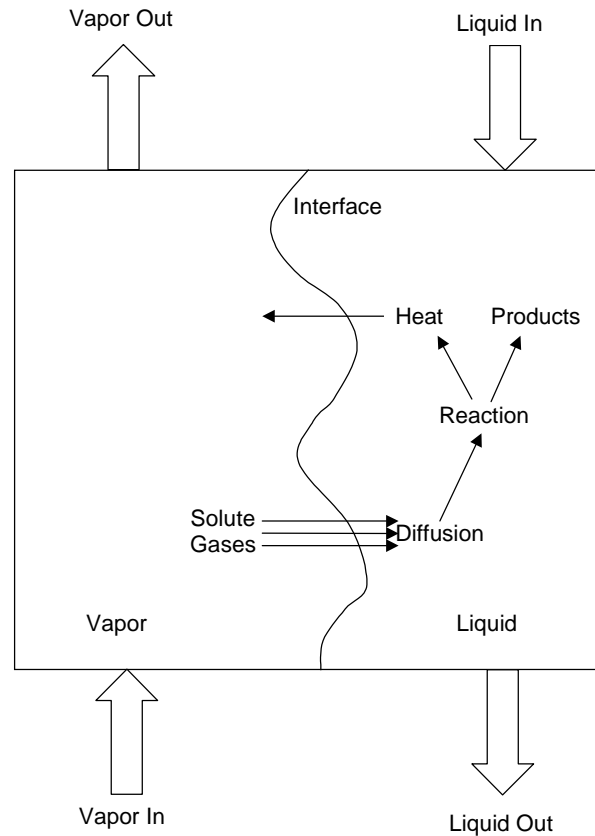
2. The Mass and Heat Transfer Rate Model Dissected

At the simplest level, mass and heat transfer rates depend on driving forces, transfer coefficients, and interfacial contact area:

$$Rate = (Coefficient) \times (Area) \times (DrivingForce)$$

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

Figure 1   Schematic of absorption accompanied by diffusion with reaction

vapor. What makes the mass and heat transfer rate model such an attractive tool is the fact that the extent to which a tray or packing element is effective in removing a species is actually calculated for the tray or element as it really exists 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 are 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 ProTreat™

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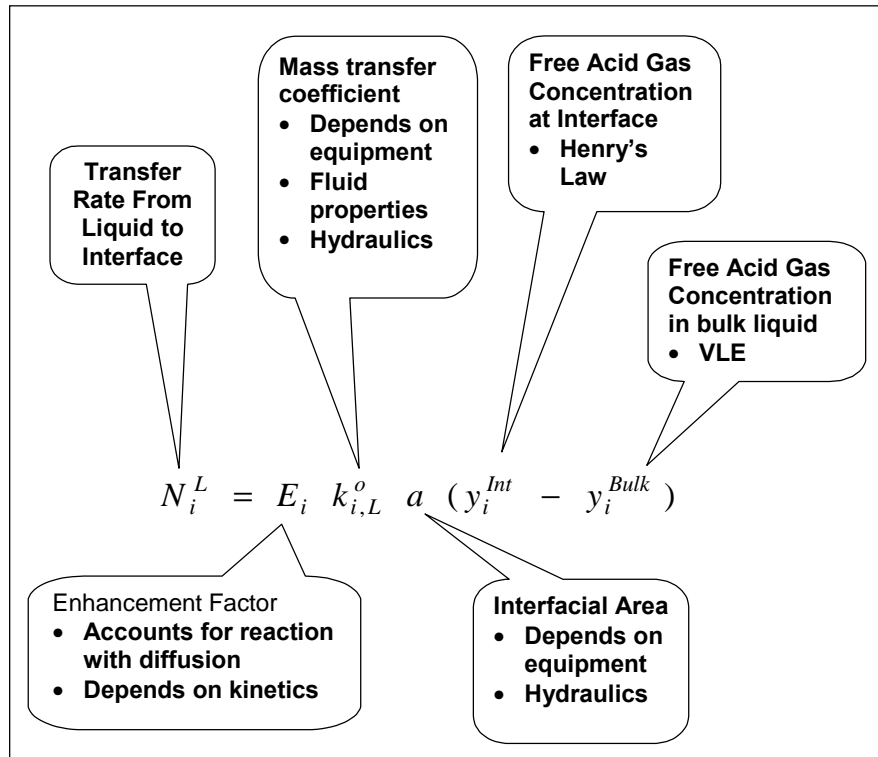
Figure 2   Absorption rate of component "i" into the liquid

There are some features of the mass transfer rate equation for the liquid phase that are 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 on 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 geometry). For packing, the packing style (random vs. structured), type (specific rings, saddles, other shapes), 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 balance 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 in the

proceedings of earlier conferences (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 has been done and made available publicly that the ProTreat mass transfer rate model can be used quite effectively to *predict* column (and plant) performance 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 this paper, 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 containing specific, target levels of both H_2S and CO_2 is produced, and which is discussed later.

When selectivity is not necessary and total acid gas removal is sought, the kind of model used for the absorber has little bearing on the simulated treated-gas purity. For example, Figure 3 shows the profiles of CO_2 and H_2S in a column using DGA to treat a gas for total acid gas removal. The treated gas purity is mainly a function of the lean amine quality, something determined entirely by regenerator operation (and most reliably simulated using *mass transfer rates*).
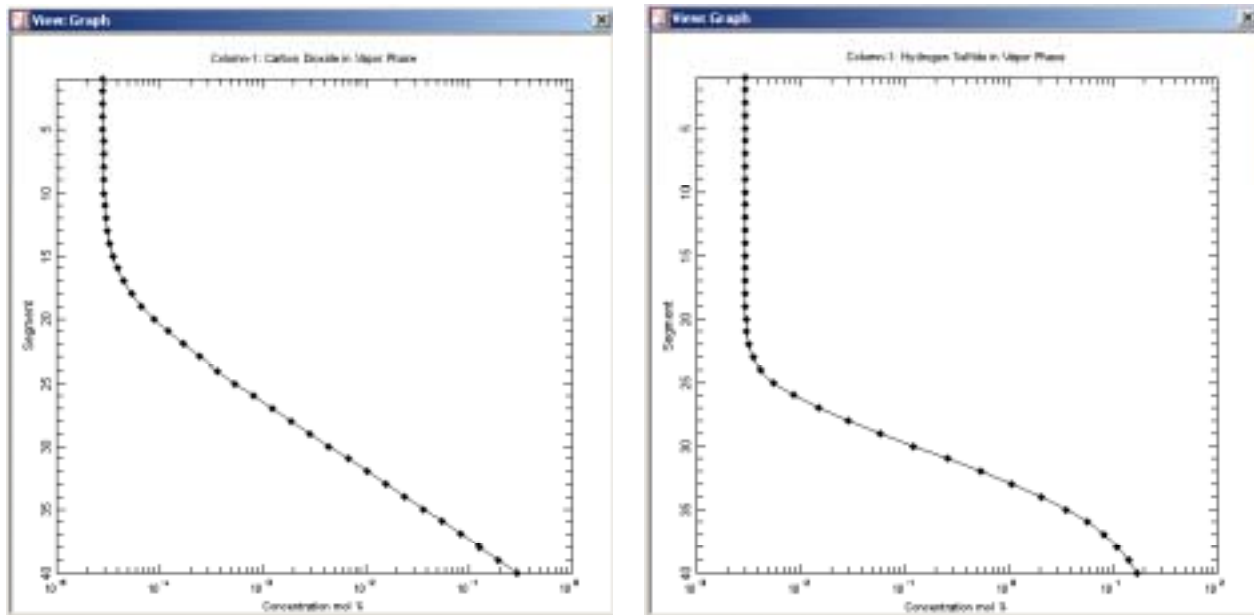
Figure 3   Mole fraction profiles of CO_2 (left) and H_2S (right) in the vapor phase of a contactor using 50 wt% DGA to treat 120 psig gas containing 20% H_2S and 0.5% CO_2. The column is packed with 40 feet of #2.5 CMR random packing and each 'segment' actually contains one foot of packing. Note the logarithmic mole fraction scale.

The sour gas in the example of Figure 3 is not a particularly good candidate for selective treating because the H_2S/CO_2 ratio is so high it would be virtually impossible to reach 4 ppmv H_2S in the treated gas without also removing essentially all the CO_2, even with MDEA. Suppose, however, that the sour gas is 2% H_2S and 3.5% CO_2. This gas has a low enough H_2S/CO_2 ratio that it can be treated selectively with MDEA, with a substantial part of the CO_2 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 Figures 4 and 5. Note that in Figure 4 the CO_2 profile is linear, whereas the H_2S profile is logarithmic. The column is slipping about 40% of the CO_2 but is achieving close to the target 4 ppmv H_2S. The simulated temperature profile is compared with field data for this tower in Figure 5—the agreement is quite remarkable.
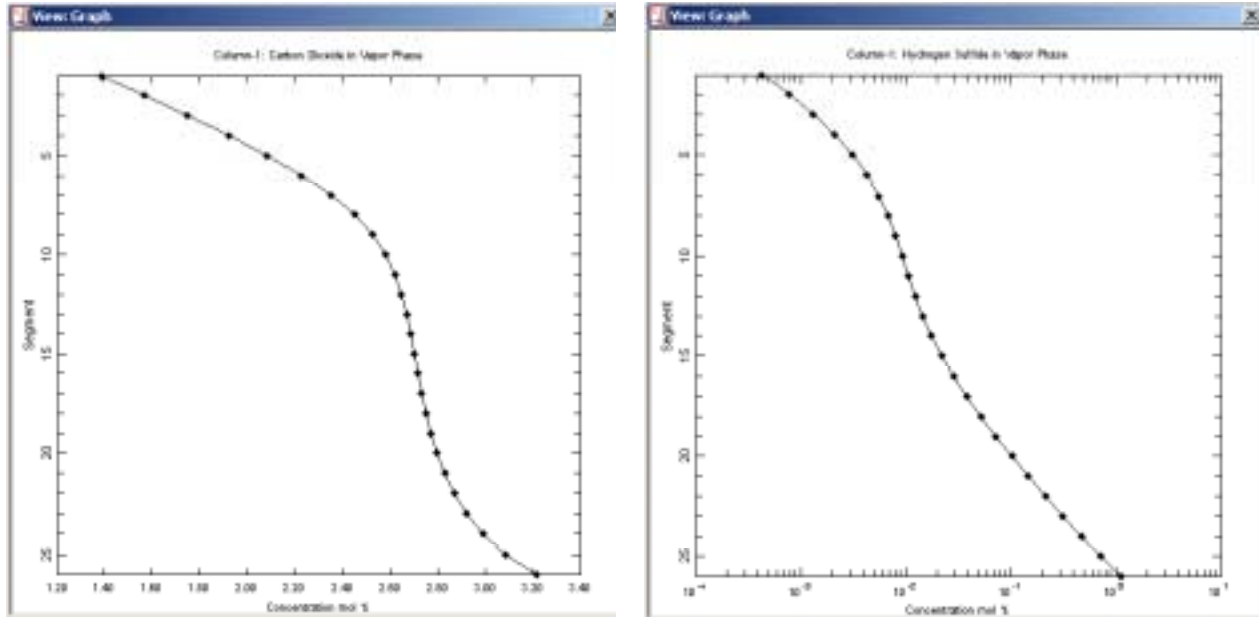
Figure 4   **Mole % CO_2 (left) and H_2S (right) in the vapor phase of a contactor using 50 wt% MDEA to treat 950 psig gas containing approximately 2% H_2S and 3.5% CO_2. The column contains 26 Nutter Float Valve trays. Note the logarithmic mole fraction scale for H_2S, but the linear scale for CO_2.**

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_2S 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[2] CO_2 reacts with the amine, the

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[2] 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.

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
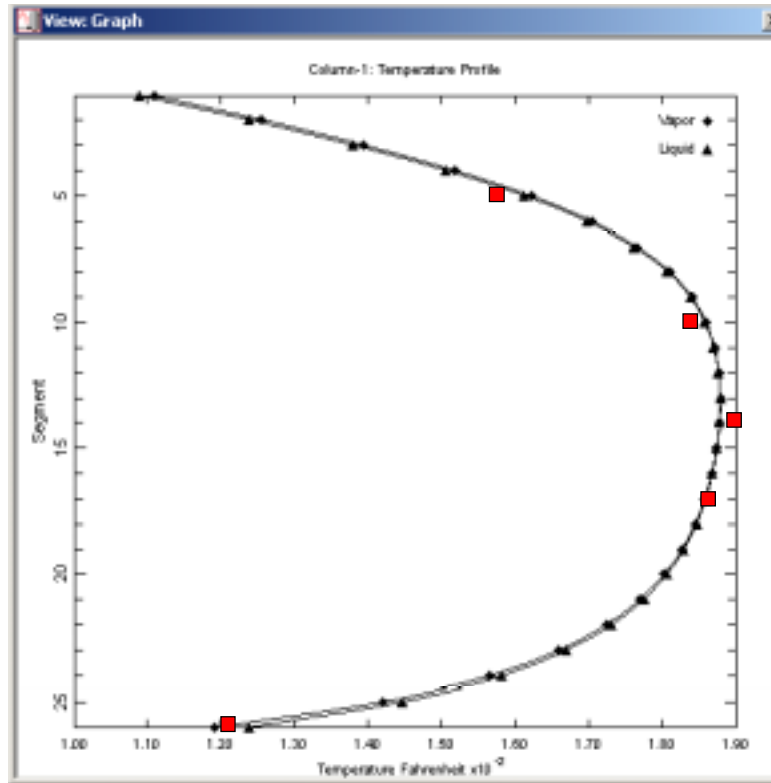
Figure 5 **Simulated liquid (▲) and vapor (◆) temperature profiles compared with field data (■) for the conditions described in Figure 4.**

dissociation of water, and MDEA is known to be a catalyst for this reaction:

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

$$CO_2 + OH^- \Leftrightarrow HCO_3^-$$
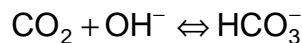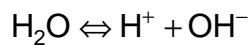
MDEA is also a sink for the coproduced H^+ ions. Thus, as far as the chemistry is concerned, MDEA achieves its selectivity by being non-reactive with CO_2 and is, at best, a catalyst for the CO_2 hydrolysis reaction. It has a number of other desirable properties for amine treating, including a relatively lower enthalpy of reaction with CO_2. But by being nonreactive and, therefore, allowing substantial amounts of CO_2 slip (i.e., CO_2 non-absorption), more amine is available for H_2S 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!). But 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 might be an important element, too. How can this be?

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:

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

(The rates must be equal because what 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_2S absorption is gas-phase controlled while CO_2 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 tower internals type and design can be expected to affect not only selectivity but also the ability of the column to treat the gas satisfactorily.

To illustrate, the 26-tray column described in Figure 4 is operating at 82% of jet flood. Suppose we wanted to increase the throughput substantially. One option might be to replace the trays with packing. Indeed, at the same gas and solvent rates, 52-feet of #40 IMTP metal packing will allow the column to operate at only 61% of flood so from a hydraulic standpoint, packing looks like a viable option. What is the impact on treating? The column was simulated by subdividing the 52-foot packed bed into 150 segments (each about 4-inches high) and running the same gas and liquid feeds. The column could not treat the gas. The CO_2 slip was indeed increased, as shown in the left portion of Figure 6. In fact, slip increased from 40% to 71%. The right hand part of this figure shows the profile of mole % H_2S in the vapor. But a 52-foot bed of IMTP could not do better than 0.13 mole % H_2S in the treated gas—the target is 0.0004 mole %. Against what appeared to be reasonable expectations, revamping the tower with packing failed!
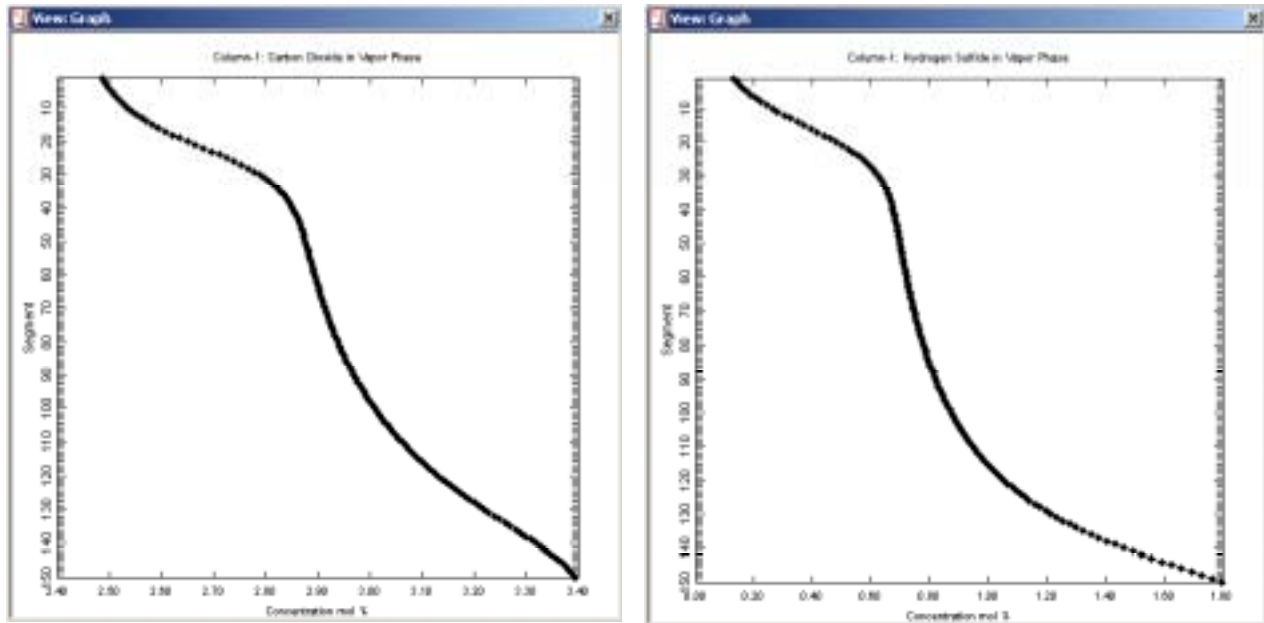
Figure 6   **Mole % CO_2 (left) and H_2S (right) in the vapor phase of the contactor of Figure 4 revamped with 52 feet of #40 IMTP metal packing instead of 26 trays. All feed flows and compositions are unchanged from the original column. With this packing, the column produces a treated gas containing 1,300 ppmv H_2S.**

The temperature profile with packing is also instructive. As can be seen in Figure 7, the profile is completely different from what was observed with trays. The bulge temperature is much higher with packing (225.5⁰F 1/3rd of the way from the top, vs. 188⁰F ½ way down the trayed column). Note however, that the bottom (rich amine) temperature is quite a bit lower when the column is packed (103⁰F vs. 124⁰F), which is consistent with the greatly increased CO_2 slip.
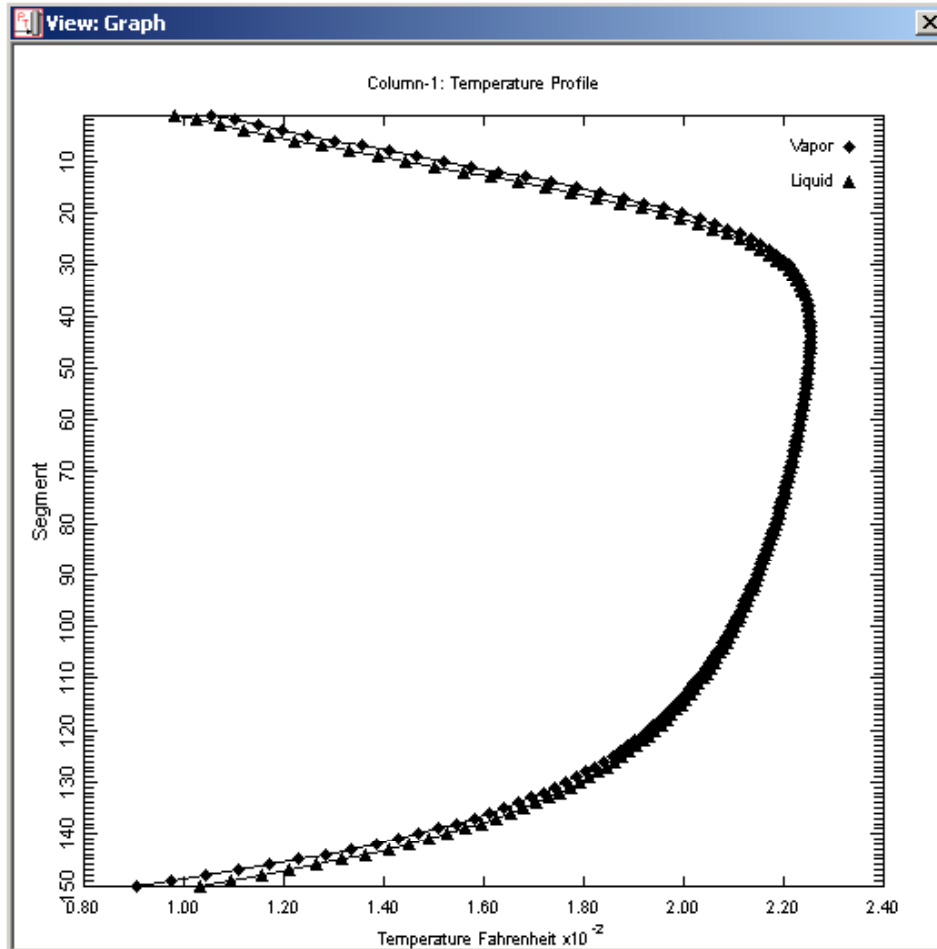

Figure 7   Simulated liquid (▲) and vapor (◆) temperature profiles in the 26-valve tray column of Figure 4, revamped with 52 feet of #40 IMTP packing.

Temperatures reach much higher levels with packing because of the differential or continuous contacting nature of packing. There is no large-scale bulk-phase mixing of large volumes of liquid (and vapor) as there is on trays. The mixing of large liquid volumes tends to reduce the mixing-cup temperature, something that just does not occur with continuous contacting. The higher temperatures retard H_2S absorption by shifting the VLE towards lower equilibrium H_2S loading, i.e., reduced driving force for absorption.

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 a richer Claus plant feed. 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 8 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 8 for the 20-tray case. Too few trays results 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.
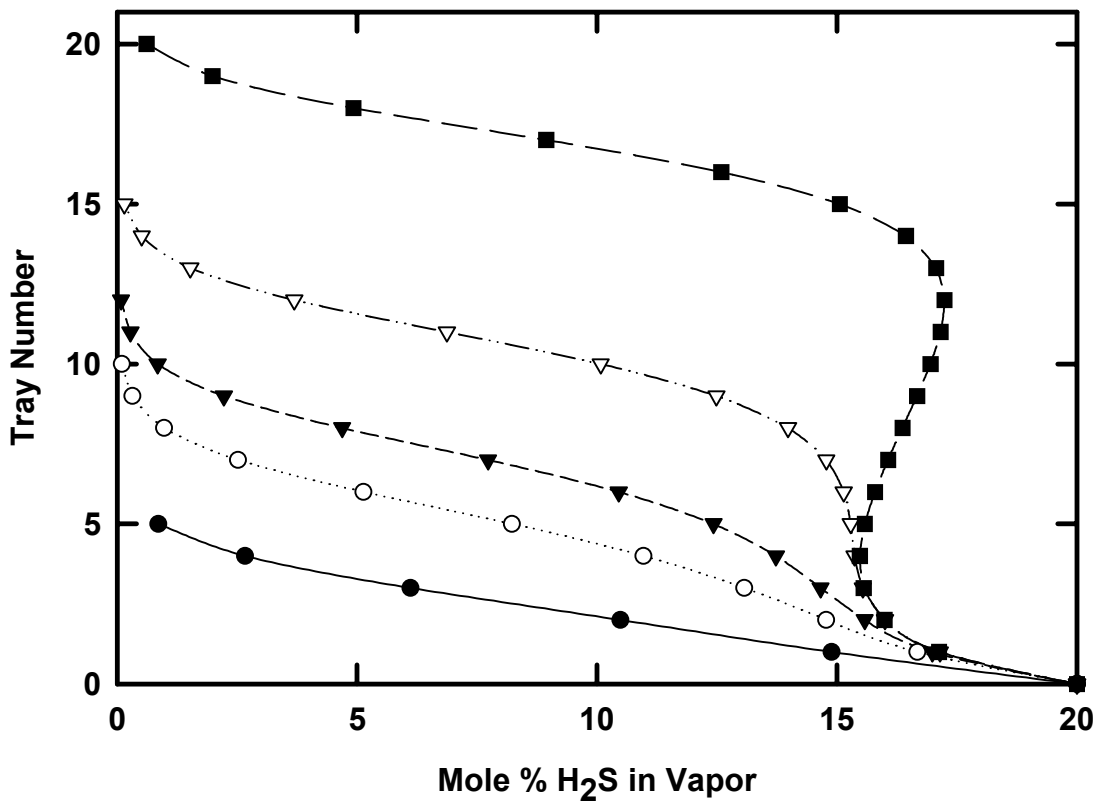
Figure 8   **Profiles of mole % H_2S in vapor in an absorber having various tray counts (●–5, ○–10, ▼–12, ▽–15, ■–20 trays). Column is removing H_2S from a 20 psig regenerator offgas containing 80% CO_2 and 20% H_2S, water saturated but without hydrocarbons or fixed gases.**

Figure 9 shows that the optimal tray count for maximum H2S removal is about 12.
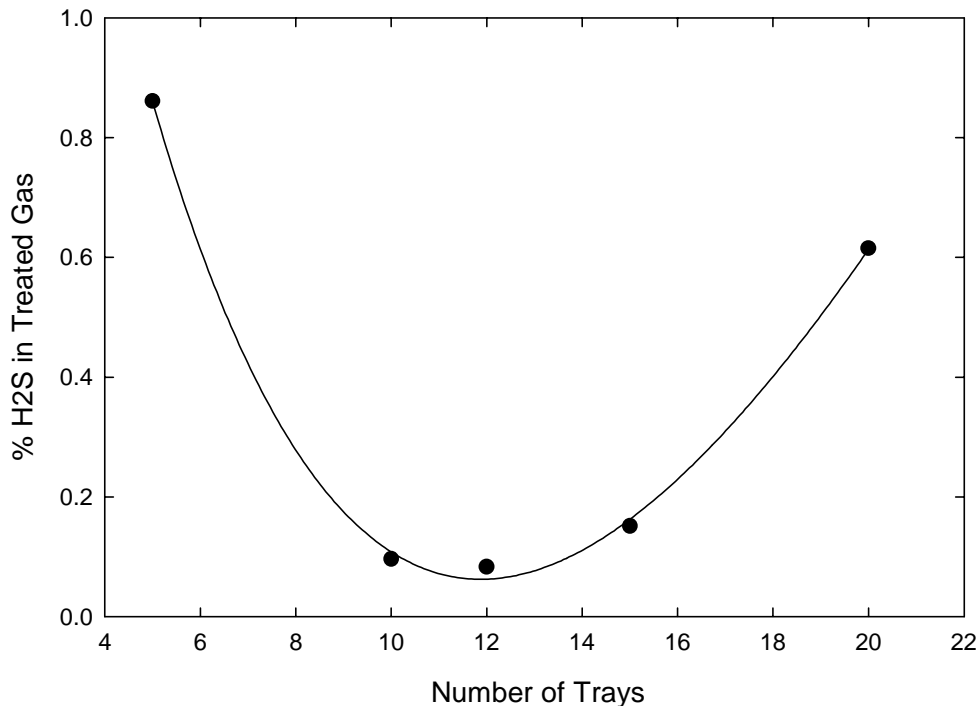
**Figure 9   Optimal tray count for offgas enrichment.**

4. Solvents Containing Mixtures of Amines

An innovation of the 80's was the development and commercialization of mixed amines, also called blended amines, or formulated solvents. Mixed amines are almost invariably based on MDEA, with various amounts of primary or secondary amines as so-called promoters or activators. With the blend formulation as an additional variable, it is possible, at least in principle, to produce a treated gas having predetermined residual amounts of both H_2S and CO_2. Thus, we no longer have to accept the residual amount of CO_2 that treating to 4 ppmv H_2S leaves in the gas. Using the right amount of additive lets us control the CO_2 level, too. But controlling selectivity is not the only application for blended amines technology.

MDEA is nonreactive towards CO_2 and, therefore, it absorbs it rather more slowly than do the primary and secondary amines; consequently, more trays or more packed bed depth is needed for CO_2 removal. However, the enthalpy of reaction is lower with MDEA, making it attractive from a reboiler energy consumption standpoint. Solvent regeneration typically accounts for some 80% of the energy used in gas treating. In general, the reboiler duty is reduced but not as much as one would hope, because the more reactive additives require more stripping energy. DEA and DGA are commonly-used in substantial concentrations with MDEA for bulk CO_2 removal. Piperazine in amounts of a few percent is also commonly used as an activator with MDEA. Piperazine, a common anthelmintic, has limited water solubility; however, it reacts rapidly with CO_2 and is widely used at concentrations of only 3 to 7 wt% with MDEA in ammonia synthesis gas purification.

The mode of action of the reactive amine is as a transporter or carrier for CO_2, essentially via a shuttle mechanism. Upon first dissolving into the solvent, the free CO_2 diffuses away from the

interface towards the bulk liquid. Along the way, it meets large amounts of MDEA and smaller amounts of the additive. Being unable to react with the MDEA, and finding only relatively small amounts of hydroxyl ion (with which it *can* react), most of the CO_2 reacts with the additive. The reaction product (the carbamate of the reactive amine) then continues to diffuse into the bulk liquid and eventually it dissociates, converting its CO_2 into carbonate. The liberated H+ ion reacts with the more plentiful MDEA and the released additive is free to return to the interfacial region to react with more, freshly-arriving CO_2. The mechanism in operation, particularly at the lean end of the column, is illustrated in Figure 10.
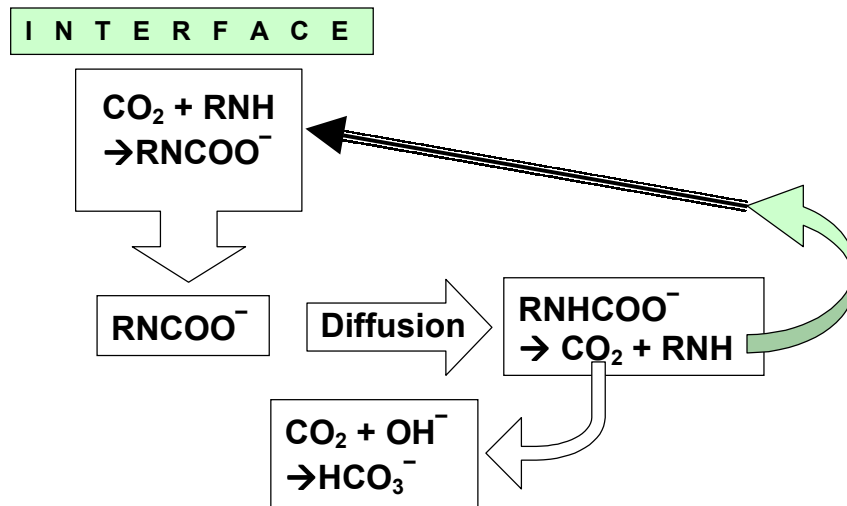
Figure 10   Shuttle mechanism for the action of a reactive amine additive in a mixture with MDEA

Besides directly affecting the mass transfer rate, the reactive amine also affects the vapor-liquid equilibrium (VLE) in the system. Modern activity coefficient models such as Electrolyte-NRTL, Pitzer, and Deshmukh-Mather can account for the effect of the second amine using only single-amine data (i.e., without amine mixture data) by neglecting binary interaction between molecules involving the two types of amine. If mixture data are available, interactions can be regressed for the model, but in all likelihood the corrections will be smaller than the inherent scatter in the VLE data, and so amine-amine interactions can continue to be ignored.

Quantities of a reactive amine affect the VLE and they increase mass transfer rates, especially for CO_2, by changing the effective chemical reaction rate. The question is what the real effect is on the absorption and regeneration processes, i.e., on the treated gas composition. The only public performance data for treating with a mixed amine solvent in a commercial column was presented at an earlier Gas Conditioning Conference (Harbison and Handwerk, 1987). The ability of the mass transfer rate model to predict the field data was addressed subsequently (Weiland and Dingman, 1995) and will not be repeated here. However, it is instructive to examine some what-if scenarios for a situation amenable to treating with a mixed solvent.

The column being considered is 3-feet diameter containing 20 generic valve trays and operating at 120 psig. The 94°F gas is 12 mole % CO_2 and 10 mole % H_2S flowing at 650 lbmol/hr. We will look at several solvent compositions, all using DEA + MDEA, to produce treated gas containing 4 ppmv H_2S and 2 mole % CO_2. Solvent regeneration will not be considered, and the lean sol-

vent loading is held constant at 0.02 mole CO_2/mole amine and 0.0005 mole H_2S/mole amine where moles of amine refers to the total amine present.

Table 1 shows the CO_2 concentration in the treated gas as a function of solvent rate for a 20 wt% MDEA + 30 wt% DEA treating solution.

Table 1   Treated-Gas CO_2 and H_2S Content vs. Flow Rate of a 20 wt% MDEA + 30 wt% DEA Solvent

Solvent Rate (USgpm)	CO_2 (Mole %)	H_2S (ppmv)
100	5.69	19,640
120	4.78	1,200
125	4.11	45.8
130	3.31	4.38
135	2.68	3.02
150	2.04	2.68

A solvent rate of 150 USgpm for this solvent blend leaves about 2% CO_2 in the gas and treats to less than 4 ppmv H_2S. The effect of blend formulation at 150 USgpm solvent rate is shown in Table 2.

Table 2   Treated-Gas CO_2 and H_2S Content vs. Blend Formulation at 150 USgpm Solvent Rate

MDEA:DEA (wt%)	CO_2 (Mole %)	H_2S (ppmv)
0:50	0.135	1.4
10:40	1.20	2.4
20:30	2.04	2.7
30:20	3.47	3.2
40:10	5.34	4.0
50:0	6.45	5.5

Obviously the solvent rate is high enough to allow the 4 ppmv H_2S specification to be met for almost any solvent blend, but the blend formulation has a significant effect on the CO_2 content of the treated gas. No attempt has been made to optimize the formulation and solvent rate, and indeed, without simultaneously dealing with solvent regeneration, to do so would be meaningless. Nonetheless, the data in these tables suggest that about 2% CO_2 and 4 ppmv H_2S could be produced using a 10 wt% MDEA + 40 wt% DEA blend at about 130 to 135 USgpm (disregarding any process consequences of such a high DEA concentration). Table 3 compares absorber performance at these two flow rates.

Table 3   Effect of Solvent Rate on Treated-Gas CO_2 and H_2S Content for a 10:40 MDEA:DEA Blend

Solvent Rate (USgpm)	CO_2 (Mole %)	H_2S (ppmv)
130	2.69	89
135	1.87	3.1

At these conditions, only a small change in solvent rate causes a disproportionate change in both the CO2 and H2S levels in the treated gas. The reason is apparent from Figure 11.
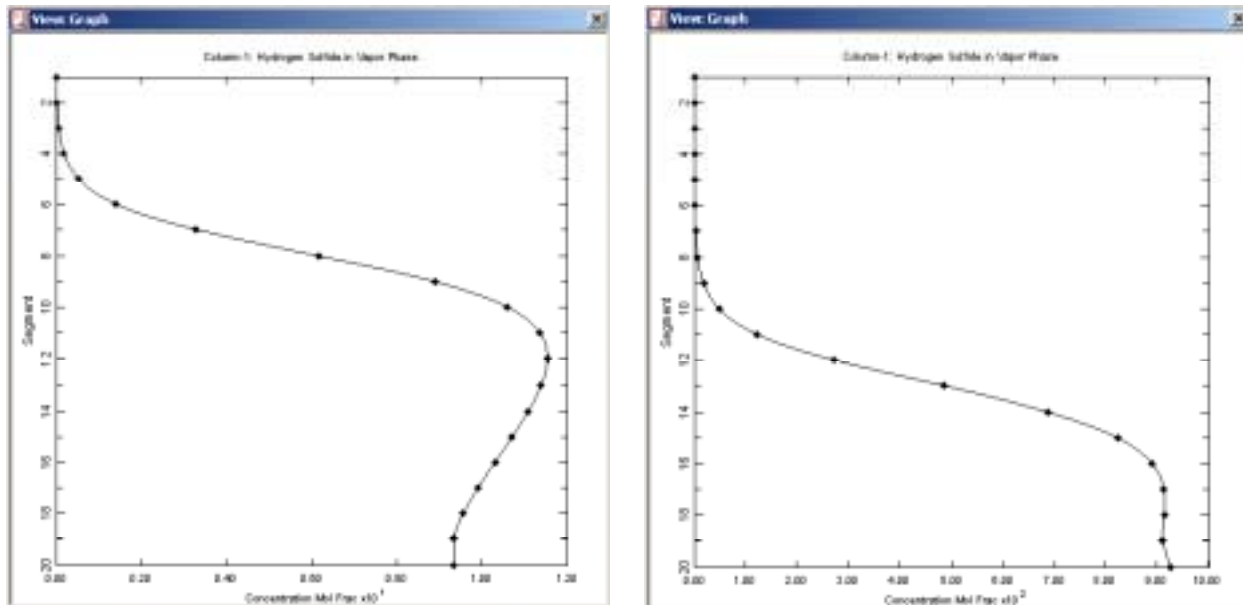
Figure 11   Absorber H₂S profile at 130 USgpm (left) and 135 USgpm (right) solvent flows. Only a relatively slight reduction in solvent flow creates a sizable H₂S bubble in the column which greatly increases the H₂S leak (from 3 ppmv to 89 ppmv).

Under these conditions, the column operates on the verge of H₂S breakthrough because an H₂S bubble is either just on the verge of forming, or has already formed. Such a bubble renders a substantial part of the column ineffective for H₂S removal. Part of the problem is that at the lower flow rate, the temperature bulge spreads out over the entire lower half of the column; whereas, at the higher flow the temperature bulge is confined to the lower quarter.

Using an amine blend allows column operation to be "tuned" to produce a gas meeting both H₂S and CO₂ targets. Of course, once having established the blend formula, normal control schemes will be used to ensure the H₂S specification. The treated-gas CO₂ content will not be controllable except by adjusting the blend composition from time to time.

5. Partially Protonated (Neutralized) Amines

Partially neutralizing an amine (for example, with an acid) can allow amazingly low H₂S 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 the original strength, and voila—H₂S removal was greatly improved. How? The secret is in the regenerator.

Consider a tertiary amine as an example. When ionization of H₂S in water is combined with proton acceptance by the amine, the net overall reaction is:

$$H_2S + RN \Leftrightarrow RNH^+ + HS^-$$
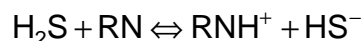
The equilibrium constant for the reaction is:

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

It can be readily seen that if the protonated form of the amine is increased, the concentration of HS^- must decrease. In a regenerator, this means that the H_2S loading will be decreased. This have greatest potential impact at low loadings—where the protonated amine concentration normally would be quite small, it artificially has been made quite large. Consequently, there is a dramatic decreased equilibrium concentration of HS^- in solution and, therefore, a dramatic decrease in solution loading with respect to H_2S. The reaction equilibrium has been shifted towards much low H_2S loadings. This can lead to the regenerated solvent having more than an order-of-magnitude lower H_2S loading and, therefore, the ability to remove H_2S to a very much lower level. The effect is very pronounced at the lean end of the regenerator where the protonated amine and HS^- 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_2S loading of the lean solvent.

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

$$CO_2 + RN + H_2O \Leftrightarrow RNH^+ + HCO_3^-$$
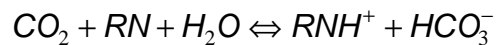
and the reaction equilibrium constant is:

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

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

The potential impact of solvent protonation on solvent regenerability is clear, but its potential effect on absorption is apparently the opposite of what is wanted because amine protonation results in higher acid gas back-pressures at equilibrium. However, in those applications where amine protonation is a useful technology (for example, tail gas treating) CO_2 removal is not a goal at all—the targeted component is H_2S and, in fact, reducing CO_2 pickup via amine protonation can be only beneficial to H_2S removal.

No plant performance data involving partially acidified amines are known to the authors. Nonetheless, ProTreat's mass transfer rate model is quite capable of predicting its effect. For illustrative purposes, we first consider the case of an isolated regenerator, then look at the effect of various degrees of protonation on overall amine plant performance.

5.1.   Standalone Regenerator

The amine treating process simulation package ProTreat™ was used to simulate a regenerator. This example regenerator was automatically sized for 70% of jet and downcomer flood (roughly 17.5-ft diameter). It contained10 sieve trays (12 gauge, 3-pass with ½-inch holes and 12% open area) on 24-inch tray spacing. Rich solvent feed was to the top tray. The operating conditions of the regenerator are shown in Table 4. The total MDEA concentration was kept fixed at 45 wt%

and various degrees of neutralized from zero through 25% were used. All other conditions remained the same from case to case.

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

Solvent feed	4233 USgpm
Solvent temperature	190ºF
Solvent CO_2 load	0.4 mol/mol
Solvent H_2S load	0.1 mol/mol
MDEA concentration	50 wt%
Reboiler Duty	275 MMBtu/hr

Figure 12 shows simulated lean solvent loads 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!
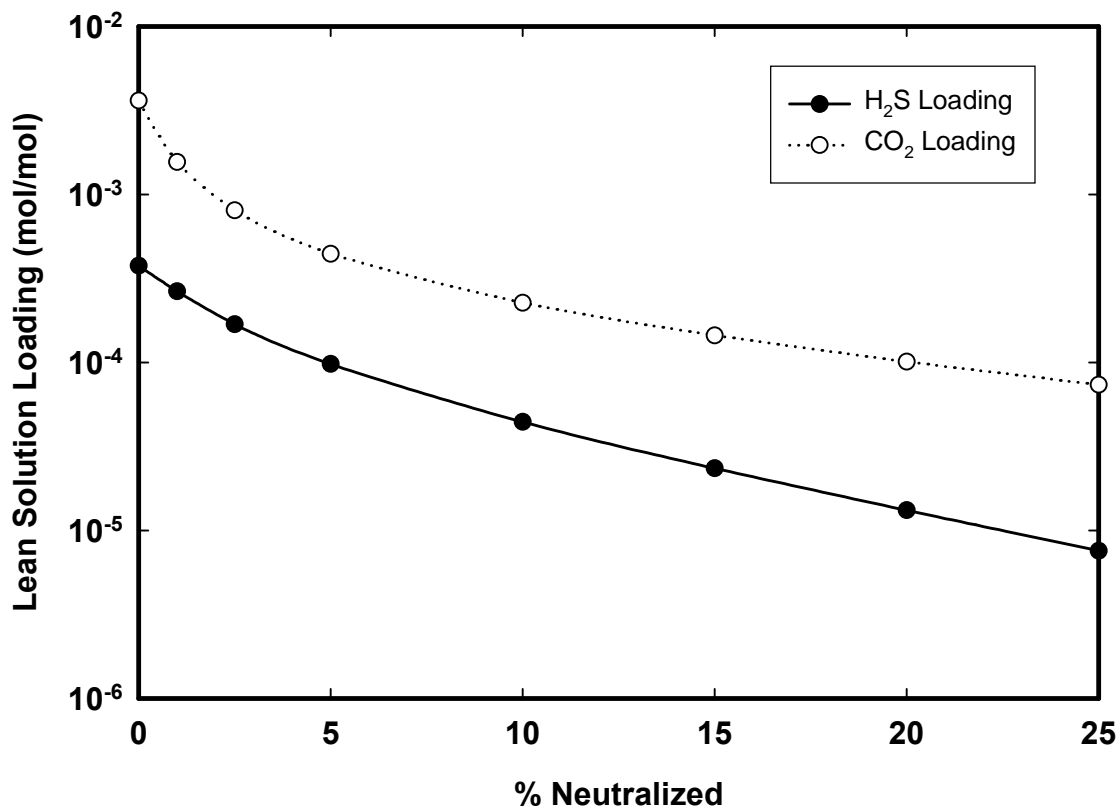
Figure 12   **Effect of partial neutralization of MDEA on the residual loadings of CO_2 and H_2S in the regenerated solvent; see Table 4 for operating data**
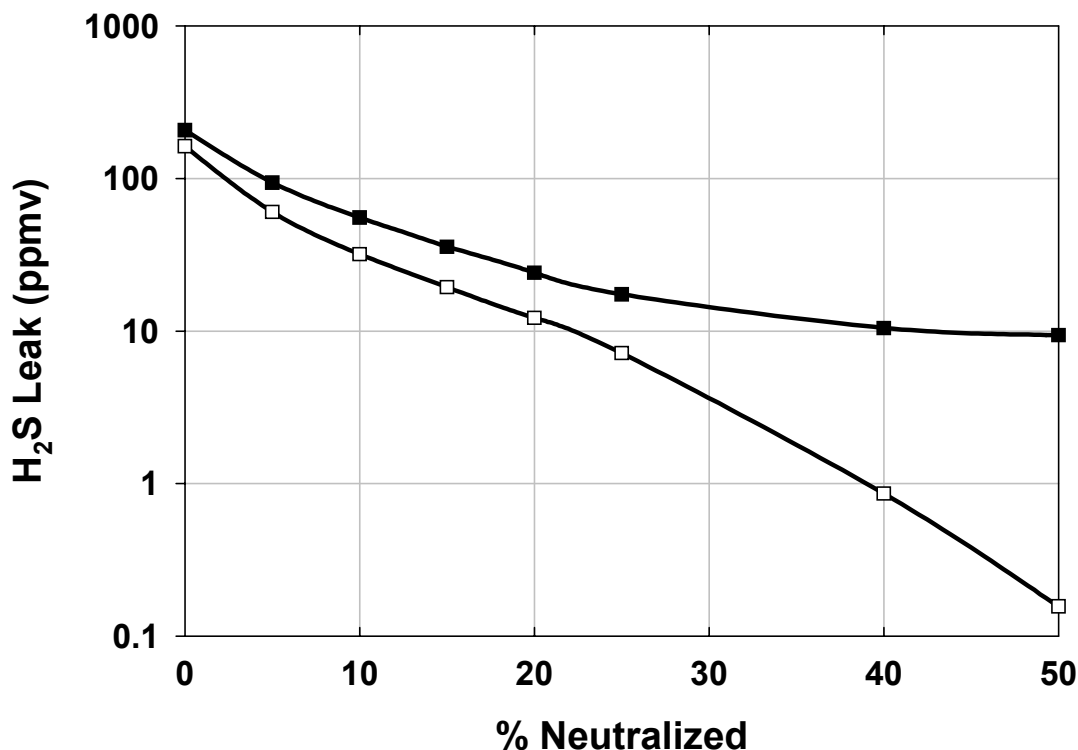
5.2. Effect of Partial Neutralization on Tail Gas Unit Performance

In this example a simple recycle flowsheet is used to treat the tail gas described in Table 5. The contactor contains Nutter trays on 2-ft spacing in a 6-ft diameter column. It operated with a bottom pressure of 1 psig below the bottom tray. The regenerator was automatically sized for 70% of jet and downcomer flood (2.5-ft diameter); it contained 20 trays with rich solvent feed to tray 4 from the top. Reboiler duty was set at 4 MMBtu/hr and the operating pressure was 12 psig below the bottom tray. Figure 13 shows the H_2S leak from absorbers with 10 and 20 trays.

Table 5   Tail gas analysis and stream conditions

Tail Gas	
H_2S (%)	1
CO_2 (%)	9
Nitrogen (%)	90
Temperature (°F)	80
Pressure (psig)	2
Flow (MMscfd)	8
Solvent	
Flow rate (USgpm)	120
MDEA Total Concentration (wt%)	50

Figure 13   Effect of partial neutralization of 50 wt% MDEA on the H_2S leak from 10-tray (■) and 20-tray (□) absorbers treating tail gas (1% H_2S, 9% CO_2) at 1 psig bottom pressure

The impact of neutralization on H_2S leak from the contactor is shown in Figure 12 (note logarithmic scale on the ordinate axis) for contactors with 10 and 20 trays. Here, the degree of neutralization was varied while maintaining the *total* amine concentration constant at 50 wt%. Thus, as the solvent became increasingly neutralized, the concentration of the *free* amine capable of participating in the reactions decreased.

It can be seen that neutralizing 50% of the MDEA (i.e., replacing 50 wt% of the total MDEA in the solvent with its neutralized or protonated counterpart) reduces the H_2S leak from about 210 ppmv to less than 10 ppmv when 10 trays are used, and from 163 ppmv to 0.16 ppmv with 20 trays. At the same time, the CO_2 slip falls from 92.04% to 88.85% and from 85.7% to 80.4% in the 10- and 20-tray cases, respectively—CO_2 pickup increases, but only a little.

With only 10 trays, the absorber is far from lean-end pinched—the lean quality affects the driving force for mass transfer but, in and of itself, it does not limit the H_2S content of the treated gas. Thus, in this case the improved gas quality is predominantly a consequence of higher mass transfer rates (via a greater driving force), not of removing an operating pinch. On the other hand, with 20 trays, the lean end operates closer to pinch (although still removed from it) and the extraordinary improvement in H_2S leak is a result of both higher mass transfer rates, and having relieved the lean-end pinch.

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. However, in the present example, even the rich solvent is extremely lightly loaded (i.e., the solvent strength is very high for the gas being treated) so that lowering the amine concentration by itself has very little effect on contactor performance[3]. This example does not imply that the neutralized amine never needs to be replenished—it depends on the application and its specifics. What the example shows is that partially neutralizing an amine, in this case MDEA, can result in tremendously reduced H_2S leak from tail-gas treating units, and that the reduction is directly attributable to greatly improved solvent regeneration.

6. Summary

This paper has attempted to develop a basic understanding of how some modern amine treating technologies work and to enhance understanding through computer simulation. The following conclusions can be drawn:

- MDEA (and certain other amines) achieve good CO_2 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.

- A true mass and heat transfer rate model has no more difficulty with packed columns than with trayed ones, and it finds unusual situations such as acid gas enrichment just as easy to handle as a traditional absorber.

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[3] In fact, the H2S leak *dropped* from 208 ppmv to 203 ppmv when the MDEA concentration was decreased from 50 wt% to 25 wt%. We ascribe this to the solvent viscosity being three times lower at the lower solvent strength.

- 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.

- Promoters and activators used in mixed amine systems work by a shuttle mechanism. Promoters affect thermodynamics, but more importantly, they allow the reactivity of the mixture as a whole towards CO_2 to be closely controlled.

- Tremendous reductions in H_2S leak from absorbers can be had just by neutralizing part of the amine. With MDEA, for example, we have shown that it is possible to achieve well below a few parts per million H_2S in the treated gas, whereas, a few hundreds of parts per million is the norm with conventional MDEA solvents.

- The mechanism by which partial neutralization achieves this amazing result is through the formation of a substantial concentration of a heat stable (nonregenerable) protonated form of the amine. 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_2S and CO_2 concentrations lowered by one or two orders of magnitude.

7. References

Harbison, J.L.; Handwerk, G.E.; *Selective Removal of H_2S Utilizing Generic MDEA*, Proceedings of the 37th Annual Lawrence Reid Gas Conditioning Conference, Norman, Oklahoma, March 2-4 (1987).

Vickery, D. J., S. W. Campbell and R. H. Weiland, *Gas Treating with Promoted Amines*, Proceedings of the 38th Annual Lawrence Reid Gas Conditioning Conference, Norman, Oklahoma, March 7-9 (1988).

Weiland, R.H. and J. C. Dingman, *Effect of Solvent Blend Formulation on Selectivity in Gas Treating*, 45th Annual Lawrence Reid Gas Conditioning Conference, Norman, Oklahoma, March, 1995.

Weiland, R. H., H. Sardar and M. S. Sivasubramanian, *Simulation of Commercial Amine Treating Units*, Proceedings of the 35th Annual Lawrence Reid Gas Conditioning Conference, Norman, Oklahoma, March 4-6 (1985).