Simulator Provides Guidance for Increasing CO$_2$ Slip in Gas Treating Applications

by Ralph H. Weiland and
John C. Dingman,
Optimized Gas Treating, Inc.

Accurate computer simulation can help gas processing facility designers take full advantage of amine absorber column internals when dealing with natural gas streams that contain both hydrogen sulfide and carbon dioxide.

When treating a gas stream containing both H$_2$S and CO$_2$, it can often be desirable to remove most of the H$_2$S but not all of the CO$_2$, only reducing the CO$_2$ content to a specific amount (typically 2 to 3 percent). Selective removal of H$_2$S with CO$_2$ rejection ("slip") results in lower solvent circulation rates, better quality sulfur plant feed, and concomitantly lower capital and operating costs. Producing a gas with specified levels of both CO$_2$ and H$_2$S can be achieved using "formulated" solvents, most of which are based on mixtures of MDEA and another primary or secondary amine used as an activator to adjust the level of CO$_2$ absorption. However, there are times when the maximum possible rejection of CO$_2$ consistent with any maximum H$_2$S specification is desirable. One example is tail-gas treating. Another is the treating of a gas stream with relatively low total acid gas content and a very high CO$_2$ to H$_2$S ratio where a higher than normally allowable CO$_2$ content output stream can be blended with other gas streams.

In high CO$_2$-rejection applications there is an optimal number of absorber column trays or an optimal depth of absorber packing that maximizes CO$_2$ rejection while still meeting the H$_2$S treating goal. The processing facility designer must determine the number of trays or depth of packing (of a specific type) and decide on how to provide enough flexibility to be able to handle the inevitable changes in the volumes and acid gas composition experienced over the life of most plants.

The reasons for selectivity differences between trays and random packings concern the effects of tray and packing hydraulics on mass transfer fundamentals, an important but often overlooked factor in gas treating. A computer simulator incorporating true mass transfer rates based on a detailed depiction of real trays and packing material, both depth and type, can provide far more rigorous predictive modeling of a process and its columns. As a result, such a simulator can be an extremely valuable tool for predicting sensitivity to variations in both design and operating parameters. A simpler, equilibrium model cannot achieve the same accuracy.

The ProTreat™ simulator, developed by Optimized Gas Treating, Inc. with financial support from the Gas Research Institute (now Gas Technology Institute), can be used to uncover ways to maximize CO$_2$ slip and relate the findings to column internals details and actual column structure. This article provides several examples of its application.

Understanding Selectivity

All alkaline solvents are thermo-dynamically selective towards CO$_2$ but kinetically selective towards H$_2$S. However, if we are to use this understanding to figure out how to increase CO$_2$ slip (i.e., to improve selectivity) then we must also recognize two other important facts about acid gas-amine systems: (1) CO$_2$ and H$_2$S react quite differently in alkaline solution, and (2) their physical absorption rates are controlled by resistances in entirely different phases.

How do these facts relate to selectivity? When CO$_2$ dissolves into the solvent, it binds chemically to the amine at finite rates of reaction, forming reaction products. At low temperatures, these reaction products are stable and require heat and stripping vapor to decompose them and reverse the reactions. On the other hand, when H$_2$S dissolves into an amine, it converts immediately to sulfide and bisulfide ions via instantaneous protonation reactions with hydrogen ions, without directly involving the amine at all. These protonation reactions are immediately reversible and the extent of reversibility depends on solvent alkalinity, not reaction kinetics. While CO$_2$ reacts relatively slowly and H$_2$S rapidly, the CO$_2$ forms stable reaction products, whereas, H$_2$S forms readily-

decomposed products in a reaction that depends only on alkalinity.

What this means is that if the gas mixture and the solvent are exposed to each other for only a short time, H_2S absorbs more rapidly than CO_2 because the instantaneous H_2S reaction keeps the H_2S concentration in the unreacted form low in the liquid and this maintains the driving force. However, the CO_2 reaction isn't fast enough to prevent the CO_2 concentration from building up and slowing down its absorption rate. The reaction kinetics have made the process selective towards H_2S. If, on the other hand, we allow the phases to remain in contact for a long time, both gases continue to absorb, but as the CO_2 absorbs it consumes amine and reduces the solvent's alkalinity. At some point, this reduction in alkalinity becomes too low to keep all the H_2S in a protonated form. Consequently HS^- and $S^=$ deprotonate and the H_2S starts to desorb. Meanwhile, the CO_2, still driven by the (almost) irreversible reaction, continues to absorb and react. Reaction equilibrium favors keeping CO_2 in solution even to the extent of releasing already-absorbed H_2S if necessary. Part of the trick to controlling selectivity is a combination of manipulating the factors affecting the chemistry (because changing the reaction kinetics profoundly affects the CO_2 absorption rate) and controlling contact times.

But the absorption of both gases, although greatly influenced by CO_2 reaction kinetics, is also controlled by diffusion. For CO_2, the diffusional resistance is predominantly in the liquid phase, while for H_2S it is in the gas phase. The other part of the trick then is that by carefully selecting the tower internals to favor mass transfer of an acid gas in one phase over the other, it should be possible to alter the relative absorption rates and hence the selectivity. This gives one an additional means to enhance CO_2 slip.

So, the secret to controlling selectivity lies in choosing an amine with the right alkalinity and the right reactivity towards CO_2, allowing gas-liquid contact for the right length of time, and using the right kind of equipment with the right internals. A mass transfer rate model is perfectly suited to dealing with such issues of all-important detail. Equilibrium stage models simply cannot capture these effects.

The Need for a Mass Transfer Rate Model

The rigorous, mass transfer rate approach used for all column calculations by ProTreat modeling is completely predictive, because it is not dependent on the availability or the need for empirical adjustments to simulate new applications correctly. In fact, there are *no* empirical adjustments in the ProTreat model. True mass transfer rate modeling is built on five key elements:

- Mass and energy balances around individual phases on a tray or in a packed segment

- Conventional thermodynamic phase equilibrium
- Equilibrium across vapor-liquid interfaces
- Effect of chemical kinetics on mass transfer rates, particularly in the liquid phase
- Mass and heat transfer rate models for transport across vapor-liquid interfaces.

There are intricate interrelated effects between these five key elements. They are affected by a variety of chemical and physical, phase and component transport properties such as chemical kinetics, diffusion coefficients, solvent viscosity, and other heat and mass transport properties, salting-out effects on acid-gas solubilities, and the mass transfer characteristics of the actual hardware being used.

The tower is modeled in full detail as a piece of real equipment, not as an idealization. From a separations standpoint, multi-pass trays perform differently from single-pass trays. Metal packing gives different results from plastics and ceramics. In addition, all solvent properties, including the changes in these properties caused by acid gas loading, affect mass transfer coefficients and thereby influence the
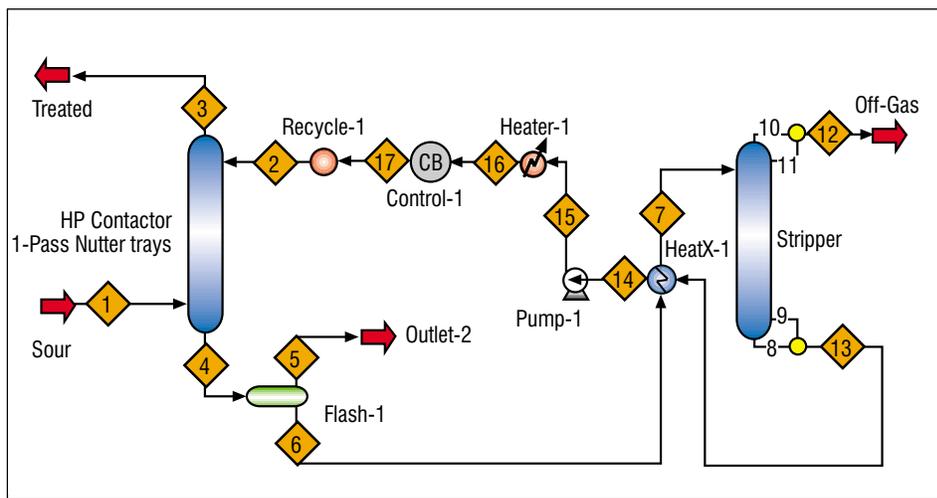

Figure 1: Process Flow Diagram

Table 1: Stream Conditions for Case Study 1

	Sour Gas (Inlet 1)	Lean Solvent (Stream 2)
Temperature (°F)	90	110
Pressure (psig)	900	900
Flow (MMscfd or US gpm)	20	Various
H_2S (vol% or loading)	1.0	Various
CO_2 (vol% or loading)	10.0	Various
Methane (vol% or loading)	85.0	
Ethane (vol% or loading)	4.0	
MDEA (wt%)		45

actual separation achievable with a specific column under a given set of operating conditions. A true mass transfer rate simulation uses a distributed parameter model: mechanistic, rich in detail, and fully predictive. This is in contrast to the nonpredictive equilibrium stage approach based on a lumped parameter model that assigns all the physical and chemical complexities to one or two parameters such as stage efficiencies for the acid gases and liquid residence times.

Case Study 1: Selective H_2S Removal from High-CO_2 Gas

This simulator case study describes removal of H_2S from a high pressure gas stream using a conventional flow scheme (Figure 1) with a 3-ft diameter column contactor containing Nutter trays or Raschig rings. The example demonstrates how trays compare with equivalent depths of a random packing, and the effect of tray count and packed depth on H_2S removal and CO_2 rejection. The feed streams to the contactor are detailed in Table 1. The effect of tray count on the H_2S content

of the treated gas, the percentage CO_2 slipped, and the quality of the off-gas from the regenerator (a potential Claus plant feed) are determined for several solvent rates.

Higher solvent flows always produce pipeline quality gas even at low tray counts and that the treated gas quality falls off rapidly as the tray count is reduced beyond a certain minimum (Figure 2). Very low solvent flows are incapable of meeting pipeline specifications at all.

CO_2 slip is rather insensitive to tray count at low solvent rates, and increasing the solvent rate in order to meet an H_2S specification causes reduced CO_2 slip (Figure 3). This results in regenerator off-gas of lower and lower quality because CO_2 pickup in the contactor increases (Figure 4). For this particular gas and solvent combination, trays typically slip only 30 percent to 50 percent of the CO_2 and produce a marginal quality Claus feed.

The effect of packed bed depth on the treated-gas H_2S content, CO_2 slip, and regenerator off-gas quality can all be illustrated using the simulator. Greater depths of packing (2-inch Raschig rings) and higher solvent flows
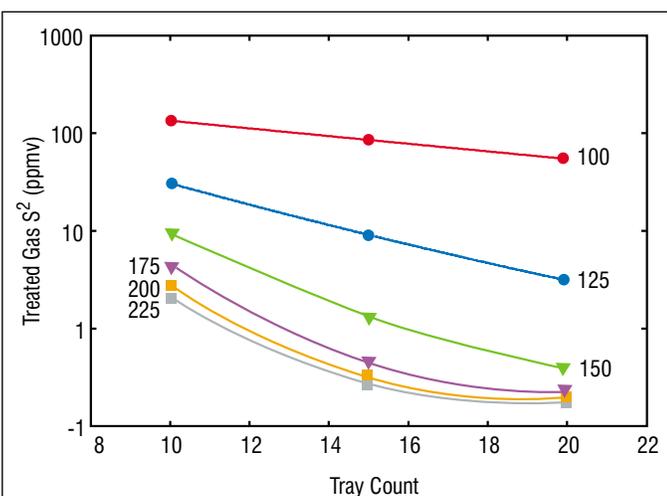
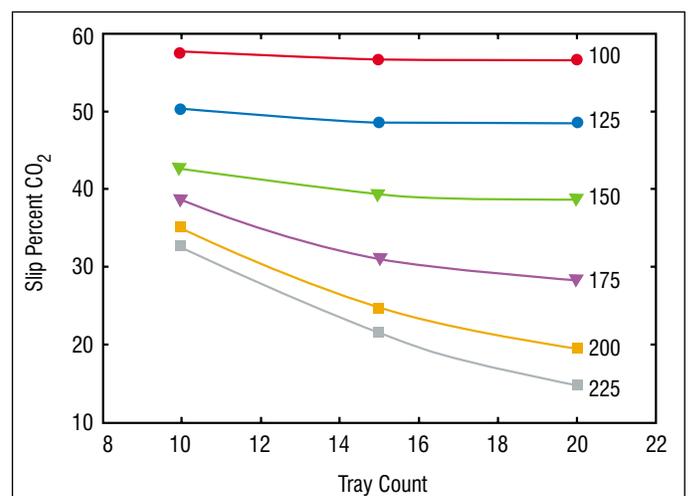**Figure 2: Effect of Number of Trays and Circulation Rate on Treated Gas H_2S Content**

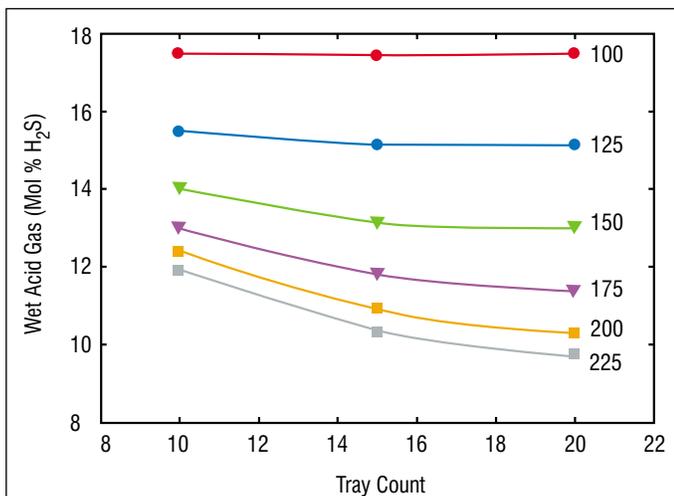**Figure 3: Effect of Tray Count on CO_2 Slip (Circulation Rate in US gpm)**

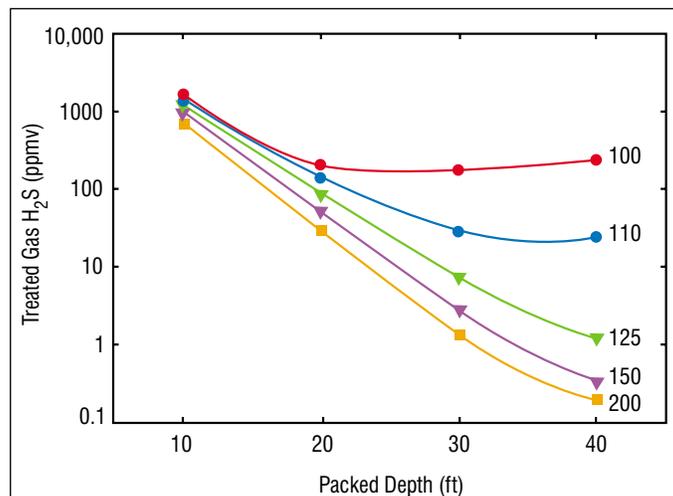**Figure 4: Increasing Tray Count Lowers Acid Gas Quality**

Figure 5: Effect of Packed Bed Depth on Treated Gas Residual H₂S

are needed to produce a treated gas containing less than 4 ppmv H_2S (Figure 5). This despite the fact that CO_2 slip with packing is very much higher than with trays, typically 70 percent to 90 percent (Figure 6). However, this is only first stage treating, and it may be quite satisfactory to leave considerably more H_2S in the treated gas, especially if the second stage regenerator off-gas is to be flared. At low solvent rates, as the

packed depth is increased, the sweet gas H_2S content first falls, reaches a minimum, and then begins to increase. The increase at higher bed depths is caused by increased absorption of CO_2 which prevents H_2S absorption.

Figure 7 shows a much improved quality of Claus plant feed (regenerator off-gas H_2S content). Note that the absorber packed bed depth affects enrichment, but solvent rate does not. Solvent rate affects only treated gas

purity. Obviously, packing produces a much better quality Claus plant feed.

Case Study 2: Regenerator Off-Gas Concentration

This case study depicts the enrichment of a dilute regenerator off-gas to make it a suitable sulfur-plant feed. The gas being enriched is essentially a wet H_2S-CO_2 stream at 110°F and 10 psig, flowing at 10 MMSCFD. The solvent is 40 wt percent MDEA at 120°F. A
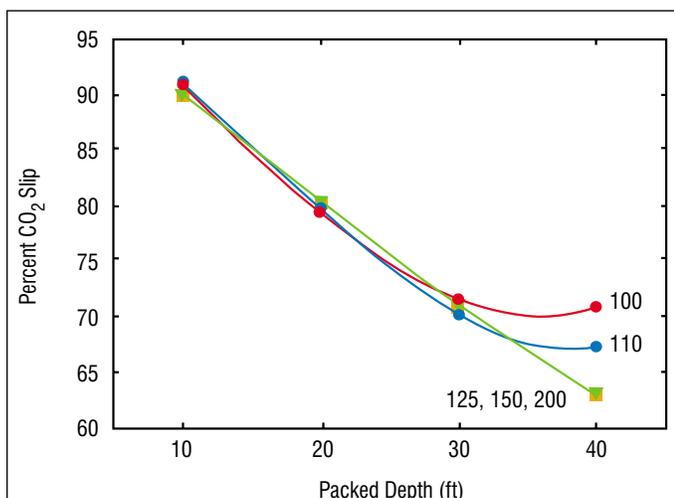
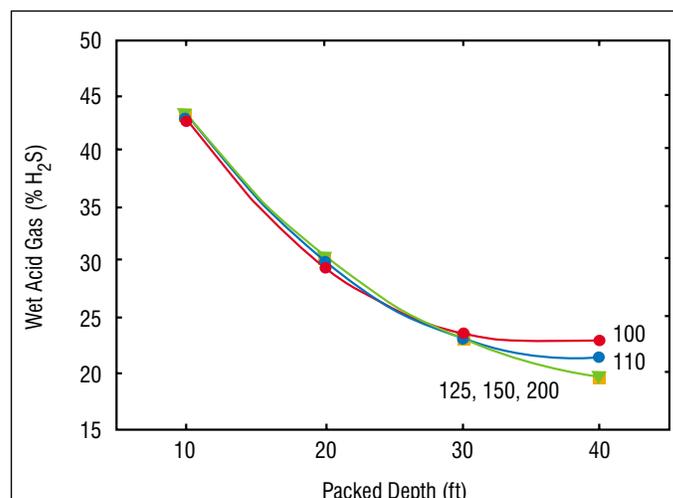

Figure 6: CO₂ Slip Improved by Shorter Packed Beds

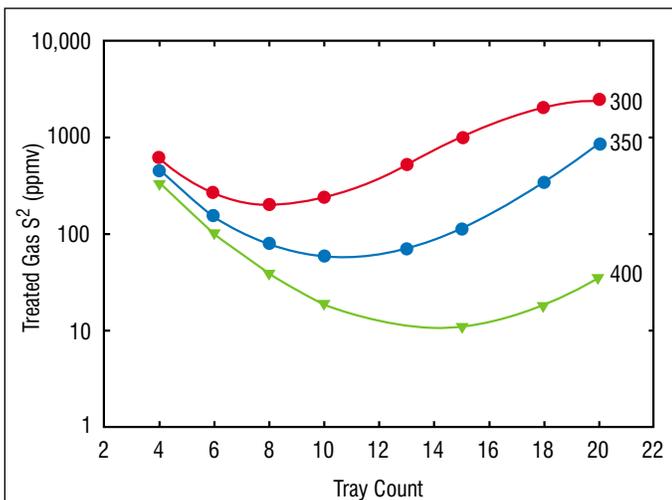**Figure 7: Quality of Wet Acid Gas at Various Circulation Rates**

Figure 8: Residual H$_2$S in Treated Gas at Three Circulation Rates (Feed Gas is Being Enriched From 1% H$_2$S in CO$_2$)
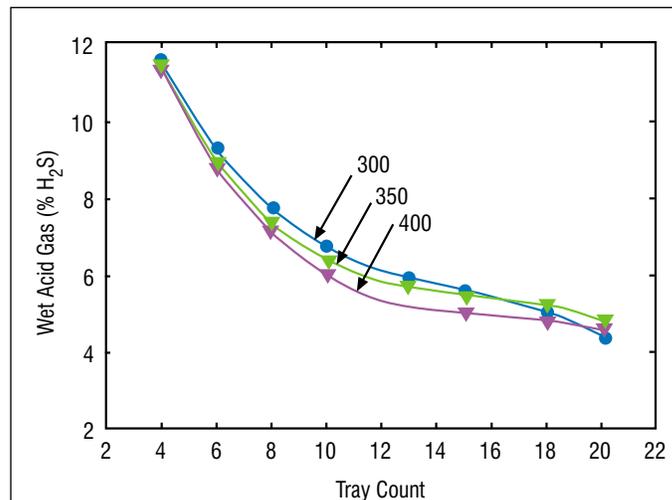

Figure 9: Effect of Tray Count on Enrichment of a 1% H$_2$S - in - CO$_2$ Feed Gas at Three Circulation Rates

conventional absorber-regenerator flowsheet is used with a 5-ft diameter regenerator containing 20 two pass Koch FLEXITRAYS. Note that the regenerator duties for trays and packing were 25 MMBtu/hr and 15 MMBtu/hr, respectively. These were chosen to give similar regenerator reflux ratios under worst-case conditions.

Three feed gas dry-basis analyses are considered: 1, 2, and 5 volume percent H$_2$S with the balance CO$_2$ and, for the case of 1 volume percent H$_2$S in the feed gas, three solvent rates are examined: 300, 350, and 400 US gpm. Both the trayed and packed contactors were sized for 80 percent flood as determined for the highest circulation rate.

Figure 8 shows the effect of tray count (Glitsch V-1 trays) and solvent flow on the residual H$_2$S in the treated gas. The absorber here contained two-pass Glitsch V-1 valve trays in a 5.5-ft diameter shell. Higher solvent rates give lower residual H$_2$S levels, as expected. However, in each case there is an optimal number of trays at which the H$_2$S content is minimum. For very small tray counts there is insufficient contact to get to very low H$_2$S levels and as the number of trays is increased, H$_2$S pickup improves; however, as the
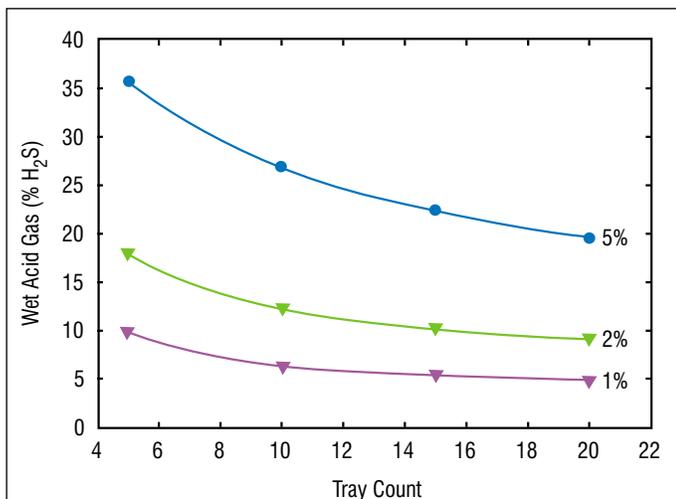

Figure 10: Effect of Tray Count on Enrichment of 1%, 2%, and 5% H$_2$S Feed Gas Streams at 350 US gpm
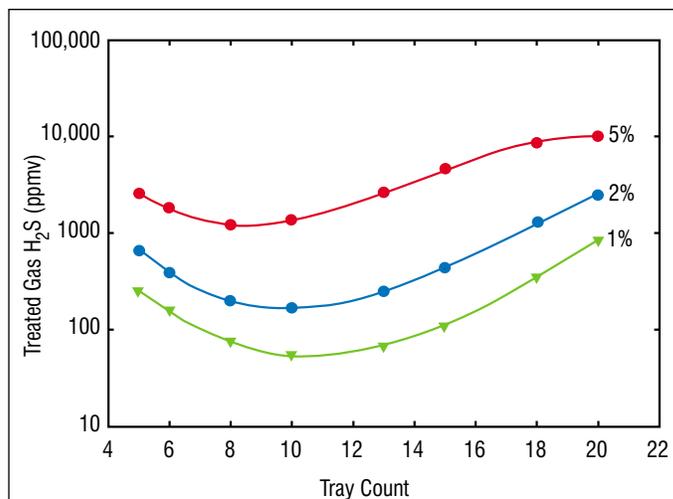

Figure 11: Treated Gas H$_2$S Content After Enrichment of 1%, 2%, and 5% H$_2$S Feed Streams with Solvent at 350 US gpm
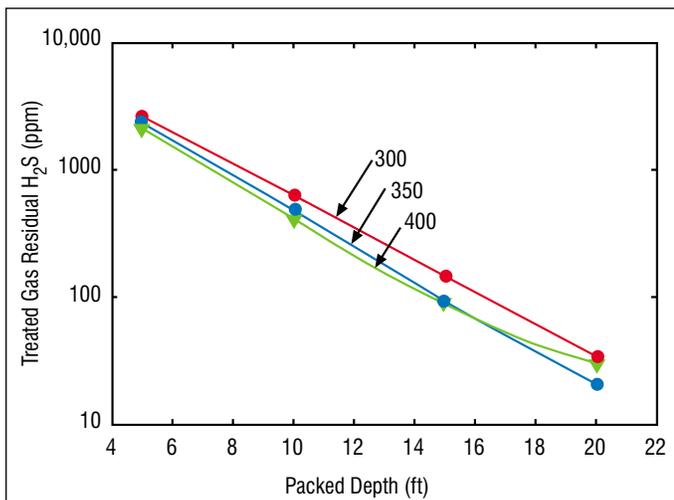
Figure 12: Effect of Bed Depth on Treated Gas Quality After Enrichment at Three Solvent Rates
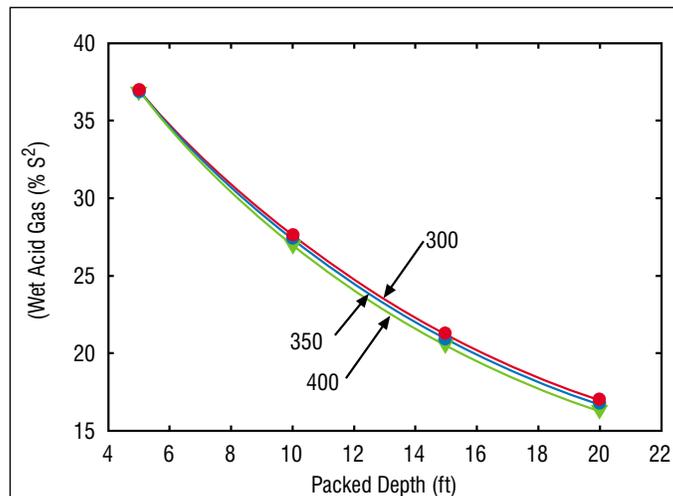

Figure 13: Enriched Wet Acid Gas Stream Obtained at Various Packed Bed Depths and Solvent Rates (Feed Gas Was 1% H$_2$S)

number of trays continues to increase, performance starts to deteriorate. This is because the increased contact results in increased CO_2 pickup which is detrimental to H_2S removal.

This can be seen in deteriorating sulfur-plant feed quality as the tray count is increased (Figure 9). Because higher solvent flows can pick up more acid gas, the optimum tray count for best H_2S removal is an increasing function of solvent flow. Of course, the asymptotic limit is zero enrichment which occurs when the tray count and solvent rate becomes high enough for total acid gas pickup.

The simulation can also show the effect of feed-gas H_2S content on the degree of enrichment as a function of tray count (Figure 10) and the corresponding treated gas residual H_2S concentration (Figure 11). Again, there is an optimal number of trays for maximum H_2S recovery. However, as expected from the kinetic preference for H_2S versus the thermodynamic selectivity for CO_2, the highest degree of enrichment corresponds to the fewest number of trays, but then the H_2S recovery is poor. Thus, when it comes to
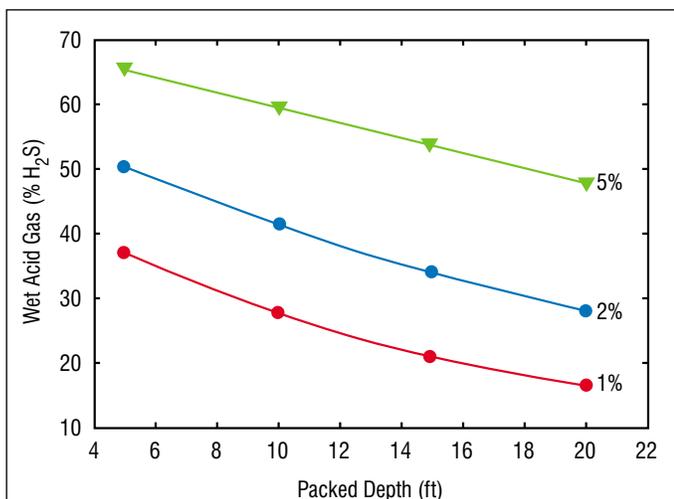

Figure 14: Effect of Packed Bed Depth on Enrichment Achievable From Feed Streams Containing 1%, 2%, and 5% H$_2$S in CO$_2$ (Solvent Flow of 350 US gpm)
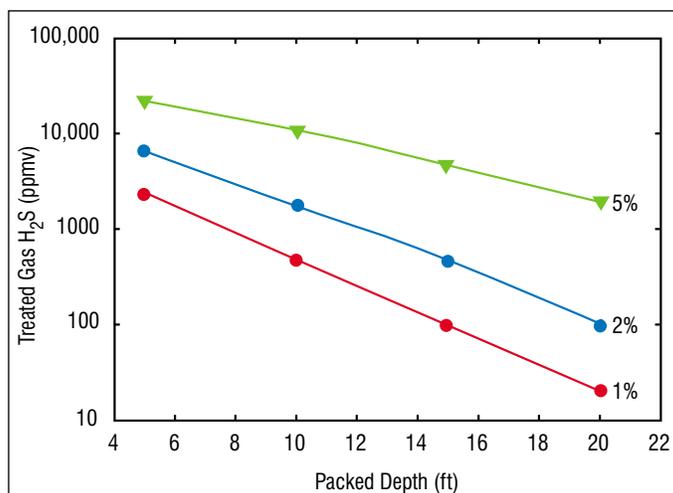

Figure 15: Residual H$_2$S in Treated Gas for Various Feed Gas H$_2$S Concentrations in a Packed Contactor With Solvent Flow of 350 US gpm

tray count, there is always a tradeoff between fractional recovery of H_2S and degree of enrichment.

As an alternative, the same acid gas enrichment operation was simulated using 2-inch steel Pall rings with 40 weight percent MDEA. In this case, the tower diameter required for 80 percent flood at the highest flows was only 4.5 feet. The residual H_2S in the treated gas decreases exponentially with increasing depth of packed bed (Figure 12). Solvent circulation rate appears to have very little effect on treated gas quality.

The quality of the enriched gas stream is shown in Figure 13. The improvement that packing affords over trays is remarkable. Referring to Figure 9, the best that could be achieved under these same circumstances using trays was about a ten-fold enrichment. Packing produced a thirty-fold enrichment, taking a stream of 1percent H_2S in 99 percent CO_2 and enriching it to about 30 mol percent H_2S. Depending on the solvent rate, trays may or may not achieve a cleaner treated gas; however, the cost is always a tremendously reduced quality of Claus sulfur plant feed.

Figures 14 and 15 show the enrichment possible with packing from acid gas streams containing 1 percent, 2 percent and 5 percent H_2S in CO_2, and the concomitant level of treating, respectively. Figure 14 shows that production of sulfur plant feed of outstanding quality from problem off-gas streams is quite achievable. As shown in Figure 15, residual levels of H_2S in the treated gas comparable to those produced with trays can also be reached.

What has been done here is to take a problem off-gas stream containing levels of H_2S that are hopelessly low for use in a sulfur plant (and probably too high for flaring or to make a sulfur scavenger economic) and produce a very high quality sulfur plant feed. The residue is a very dilute stream of H_2S in CO_2 which must be disposed of, but at these small concentrations of H_2S, both flaring and scavengers become more attractive.

Case Study 3: Performance Test of Commercial Absorber

The final example is a comparison of a ProTreat simulation with field performance data collected from a commercial contactor removing H_2S and CO_2 with 46.3 weight percent DGA. The contactor is 66 inches in diameter and contains 16 Nutter trays on 2 foot spacing. The plant performance test data (taken in 1982) included measured temperatures on three trays and the tower sump. Table 2 shows the feed stream conditions.

This column produced better than 1 ppmv H_2S treated gas, but unfortunately the gas was not analyzed for CO_2. The ProTreat simulation gave a treated gas containing 0.05 ppmv H_2S and 1.8 ppmv CO_2. These are very encouraging numbers, particularly in view of the fact that the model was not tweaked into agreement with any of the data—the simulated quality of the treated gas is a pure prediction.

No parameters have been fine-tuned to achieve agreement and the close match is completely natural. Even more impressive, however, is the agreement between the measured and simulated column temperature profiles (Figure 16). This plot shows the (unequal) vapor and liquid temperatures on each real tray in the column. The large square symbols are measured data.

For this performance test, the column was operating in a severely turned down condition, at 14.4 percent of jet flood and 11.3 percent of downcomer flood. Given that the tower was probably originally designed for 80 percent flood, this represents a 5.5 to 1 turndown ratio. Operation was certainly outside the recommended operating range and there was likely substantial weeping and possibly tray blow-dry.

Using ProTreat™

These three case histories provide support for the notion that rigorous simulation of amine treating units can be very important in maximizing their performance and that the ProTreat simulator can be used to uncover ways to maximize CO_2 slip and relate the findings to column internals details and actual column structure.

Table 2: Feed Stream Data for Performance Test

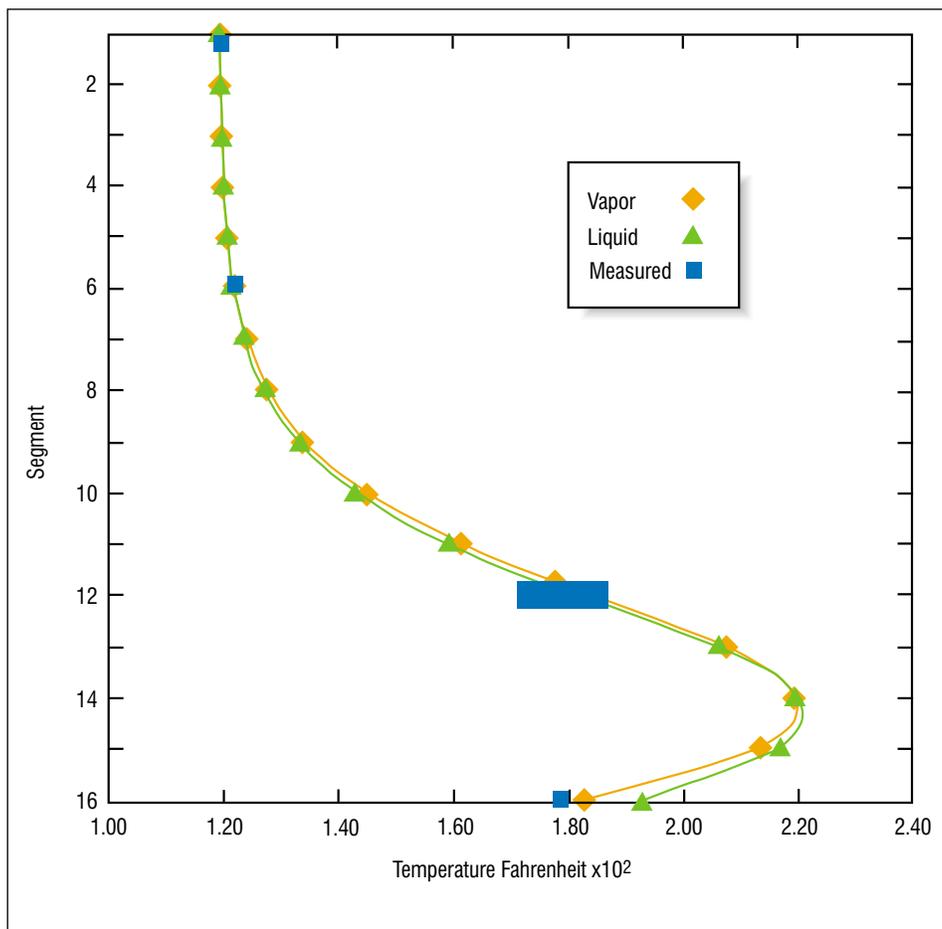|	Sour Gas (Inlet 1)	Lean Solvent (Stream 2)
Temperature (°F)	88	119
Pressure (psig)	980	980
Flow (MMscfd or US gpm)	17.22	
H_2S (vol% or loading)	0.38	0.0001
CO_2 (vol% or loading)	5.82	0.034
Methane (vol% or loading)	93.80	
DGA (wt%)		46.3

Figure 16: *ProTreat™* Simulated Vapor and Liquid Temperature Profiles Compared With Performance Test Data

ProTreat is a Microsoft Windows® based, flexible-flowsheeting package for amine gas treating designed to be run with Windows 95, 98 and NT. Data input is through Windows dialogs and includes on-line help features as well as extensive preprocessing validation of input data.

The model is available for licensing and currently is in use by a number of major oil and gas producing companies and amine suppliers. ■