

Column Design Using Mass Transfer Rate Simulation

by

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Presented at the 80th Annual Gas Processors Association Convention
In San Antonio, TX March 12, 2001

ABSTRACT

The solution to the dilemma of translating theoretical stages into actual trays and packed bed depths is to use detailed mass transfer, rate-based simulation. This completely new approach to simulating complex chemically-reactive, nonideal separations is particularly suited to amine treating operations. This paper uses the *ProTreat*TM simulation package to look at three examples of commercial columns in CO₂ removal and selective H₂S treating. Comparisons with plant performance test data, and especially column temperature profile data, are used to demonstrate the benefits of modeling actual column internals using mass transfer rate-based process simulation. No input of empirical efficiency information is required. Tower internals performance is directly modeled, and translation from theoretical stages to the real world of packing and trays never arises.

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INTRODUCTION

In recent years there have been at least three major advances in gas sweetening technologies at the process level:

- More easily regenerable solvents have been developed
- Solvents having greater selectivity have been commercialized
- Desirable properties of individual solvents have been exploited by creating solvents with two or three amines

These approaches have led to significant reductions in process energy requirements, primarily by increasing CO₂ rejection and tailoring CO₂ slip. Reduced energy requirements are mainly a consequence of lowered solvent circulation rates.

There has also been a remarkable new advance in process simulation capability, namely, the development of a completely new approach to column modeling and analysis—the *ProTreat*TM mass transfer rate based tower model. This model does for mass transfer columns what modern heat transfer methodology has done for heat exchanger design. It models towers in full detail, as real physical equipment as opposed to a theoretical-stage idealization of reality. The key concept is mass transfer rate.

ABSORPTION AND STRIPPING AS MASS TRANSFER RATE PROCESSES

In processes for total acid-gas removal, treated gas quality is completely determined by phase equilibrium, provided the column contains enough trays or packed depth. This is not the case in selective treating. Here, the extent to which each acid gas is removed is related directly to its mass transfer rate, as well as to the mass transfer rates of each of the other absorbing acid-gas species. The separation is a rate process rather than one dominated by phase equilibrium.

An appreciation of the fact that all alkaline solvents are thermodynamically selective for CO₂ but kinetically selective for H₂S is vital to understanding the importance of mass transfer rates to contactor performance. For a given lean-solvent acid-gas loadings, a high enough tray count or a deep enough packed bed guarantees that the treated gas leaves the contactor in equilibrium with the lean solvent (or for low solvent rates, that the rich solvent leaves in equilibrium with the sour gas). However, as the tray count is reduced (or the bed shortened) the treated gas becomes further and further removed from equilibrium. The thermodynamics of acid gas-amine systems is such that CO₂ is the preferred solute because it absorbs by forming a fairly stable chemical bond with the amine. However, the CO₂-amine reaction is of finite rate and, in fact, is quite slow in MDEA, for example. On the other hand, H₂S ionizes instantaneously (to bisulfide ion); it does not react with the amine at all, it forms no chemical bonds, and the ionization reaction is immediately reversible. Thus, the chemical reaction kinetics are much faster for H₂S; therefore, CO₂ absorbs more slowly.

At short contact times (read low interfacial areas, small tray counts, short packed beds) H₂S absorbs at a higher rate than CO₂, and so H₂S is preferentially absorbed. At long contact times (high interfacial areas, many trays, deep beds), CO₂ absorbs more completely, albeit more slowly, and CO₂ is preferentially absorbed. Thus, control over selectivity can be achieved by choosing an amine (or a multiple-amine mixture) with the right reactivity toward CO₂, allowing contact in a column with the right number of trays

or the right depth of packing, and choosing the kind of column internals that favor either CO₂ or H₂S absorption. Selectivity depends on rates—not just reaction rates, but mass transfer rates—which implies dependence on all the factors that affect the mass transfer characteristics and mass transfer performance of the actual physical hardware in which the process is carried out. Equilibrium stage models simply cannot capture these effects.

The currency of equilibrium stage models is the number of theoretical stages—the currency of internals vendors and gas processors is actual tray counts, types, and passes and volumes and depths of packing of specified size, type and material. With ideal stages, translation between the two is forever an open question. A true mass transfer rate model, on the other hand, always deals in real trays and real packing—there is never a question about how many trays are needed or what depth of packing to install.

It is equally important to be able to model solvent regeneration accurately if for no other reason than the fact that the loading of the lean solvent produced by the stripper directly and significantly affects contactor performance. Not only does it affect its ability to meet treated gas specifications, but also the actual treated gas composition. Equilibrium stage models don't work very well here either because the reactions and the tower internals type and details affect mass transfer in just as important ways as in absorption. None of the trays in a stripper come even close to an equilibrium stage, and the desorption rate of each acid gas affects the rate of the other. From a technical standpoint, the *ProTreat* mass transfer rate based stripper model treats regenerators every bit as rigorously as absorbers. It produces the best possible predictions of regenerator performance without the need for empirical adjustment. And when absorber and stripper models are tied together in a recycle flowsheet, the best possible prediction of treating-plant performance is obtained without applying user-supplied or internally-generated empirical corrections of any kind. This complete freedom from empiricism allows the engineer to design and predict the performance of new facilities for which absolutely no operating data or field experience exists.

CASE STUDIES

This section compares *ProTreat* simulation with performance test data collected from three separate treating facilities run by different operating companies. The first data set is for the Worland, Wyoming plant of Texas Gulf Sulphur, as reported in an excellent article by Estep et al¹. For the second and third data sets, we are not permitted to identify ownership and location. The first two data sets report only overall column and plant performance. For the third data set, however, detailed contactor temperature profiles were collected and these provide a rather stringent test of *ProTreat* modeling accuracy.

Case Study 1: Worland, Wyoming Plant of Texas Gulf Sulphur

Texas Gulf Sulphur's Worland, Wyoming gas plant was built in 1950. The general process flow diagram for the acid gas treating section of the plant is shown in Figure 1. Two parallel regenerators supply a high pressure and a low pressure contactor with nominally 15 wt% lean MEA. This is a somewhat unusual plant in that the contactors and regenerators are all packed to a depth of 40 feet with 3-inch and 2-inch metal Raschig rings, respectively. The high pressure contactor and both regenerators are 9-foot diameter; the low pressure contactor is 3-foot diameter. The paper provides a wealth of construction detail but unfortunately the regenerator operations are insufficiently described to allow them to be confidently simulated. However, the operation of both contactors from a process standpoint is well documented.

Contactor simulation is based on the known status of the lean amine to the absorption section of

¹ Estep, J. W., G. F. McBride, Jr., and J. R. West, *Sulfur From Natural and Refinery Gases*, Advances in Petroleum Chemistry and Refining, Vol. 6, Ch. 7, pp. 314–466 (1962)

the plant. Basic flows and acid gas/amine contents of the absorber feed streams are shown in Figure 1. The gas compositions shown in Table 1 are intended only to indicate the hydrocarbon makeup of these streams—the acid gas content is different from the table values and is as shown in Figure 1. In the paper, two sets of performance data are given, together with a different set of (incomplete) data on the process flow diagram. The present comparison is for the higher of the two flow rates in their Table XVII, i.e.,

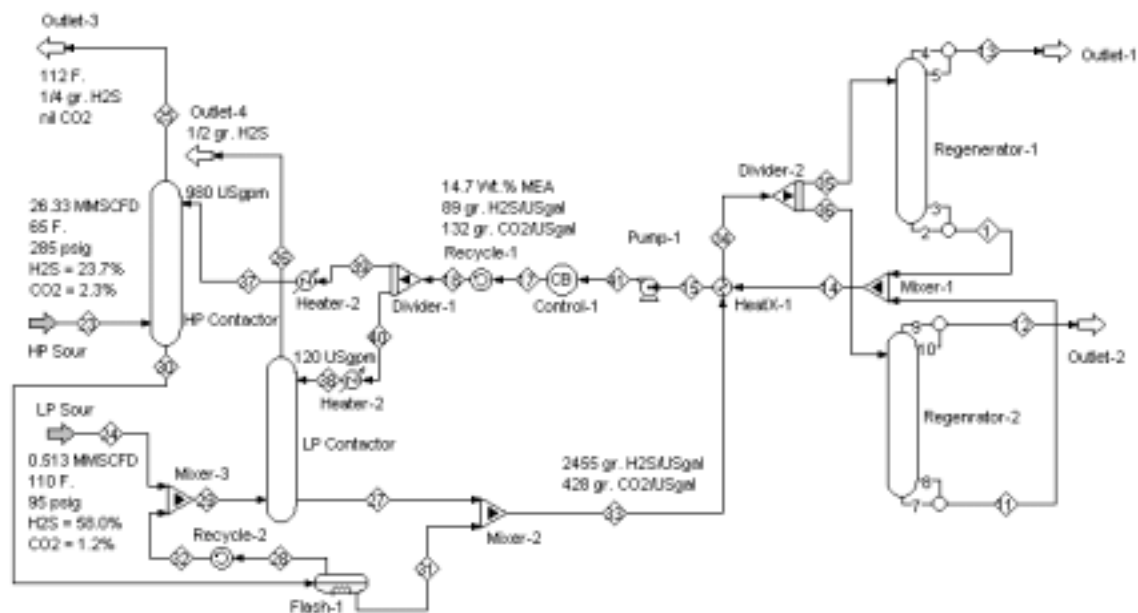


Figure 1. Process Flow Diagram of the Texas Gulf Sulphur Worland, Wyoming Plant

for a total amine flow of 1,100 USgpm. It should be noted that this plant treats very high sulfur content gas, 24% H₂S and 58% H₂S in the high and low pressure gases, respectively, in this particular test. Note too, that the low pressure contactor sour gas feed is supplemented with off-gas from the flash unit on the high pressure contactor's rich solvent product stream. Thus, the two contactors are tied together, not just by the simple connection of sharing a common lean solvent stream, but by the low pressure column being feed by the high pressure column's rich amine flash gas.

Table 1. Typical Sour Gas Analysis

COMPONENT	MOLE PERCENT	
	HP SOUR	LP SOUR
Hydrogen sulfide	30.2	62.5
Carbon Dioxide	2.6	4.9
Methane	57.2	8.4
Ethane	6.3	5.2
Propane	1.4	4.6
Isobutane	0.6	2.5
n-Butane	0.7	7.5
Pentane	0.6	3.4
Hexanes	0.4	1.0

A comparison between overall performance test data (treated gas composition and temperatures, and rich amine compositions and temperatures) and simulation results is drawn in Table 2. The simulation closely matches the measured treated gas purities and the combined rich amine stream acid gas contents. Examination of the gas-phase H₂S concentration profile in the low pressure contactor showed that the contactor is greatly over designed in terms of packed depth—the H₂S level flat-lined long before the gas

reached the top of the column. Therefore, the low pressure treated gas purity from the actual plant is entirely dependent on the lean quality. In terms of modeling, this means that the simulated treated gas purity is a function strictly of the accuracy of the phase equilibrium (VLE) model, independent from the column model used. The low pressure column is a test of the VLE model, not of the mass transfer rate based column model. Such is not the case in the high pressure absorber. Here, the simulated H₂S profile in the gas continued to fall over the whole packed bed, tailing off only a little as the gas approached the top of the column. The comparison between measurement and simulation in this case is a test of both the VLE model and the model for the column itself and shows excellent model validation.

Table 2. Comparison Between Performance Data and Simulation

	TREATED GAS		RICH AMINE	
	MEASURED	SIMULATED	MEASURED	SIMULATED
HP Contactor				
H ₂ S	0.25 gr./100ft ³	0.31 gr./100ft ³		2802
CO ₂	Nil	0.25 ppmv		471
LP Contactor				
H ₂ S	0.50 gr./100ft ³	0.73 gr./100ft ³		1151
CO ₂	Nil	0.28 ppmv		160
Total Rich Amine <33>				
H ₂ S			2455 gr./USgal	2641 gr./USgal
CO ₂			428 gr./USgal	440 gr./USgal

Case Study 2: A DEA Unit Removing CO₂

This example is a single absorber and a single regenerator in a conventional recycle flowsheet for CO₂ removal using nominal 50 wt% MDEA. The process flow diagram is shown in Figure 2 and the raw gas and lean solvent conditions are shown in Table 3.

The contactor and regenerator both contained 20 single-pass Nutter Float Valve trays. The contactor was 36-inches ID. The regenerator diameter is unknown but for simulation, it was sized at about 30-inches for 70% jet and downcomer flood. Steam flow to the reboiler of the regenerator was measured at 75 lb/min steam on the shell-side; pressure on the process side was 15 psig.

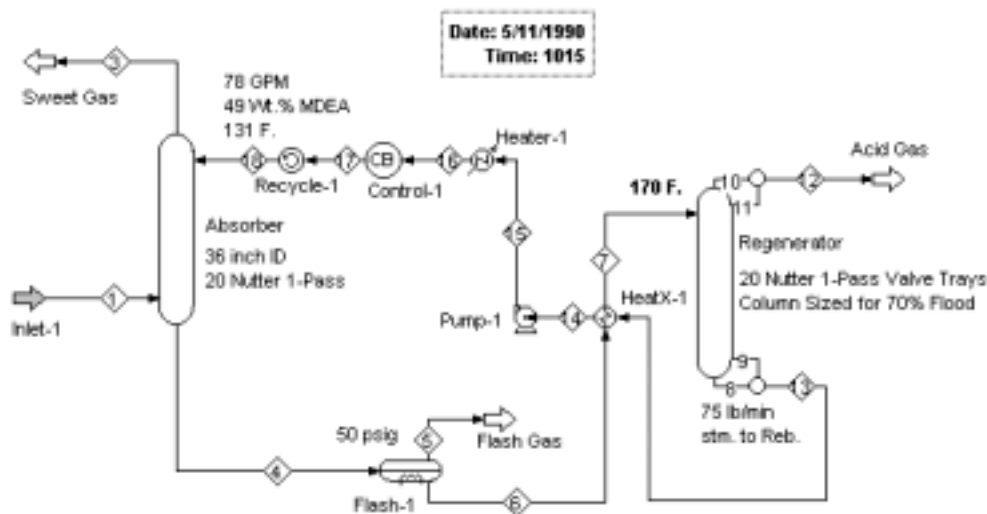


Figure 2. Process Flow Diagram for Case Study 2

Table 3. Case Study 2 Inlet Stream Conditions

	SOUR GAS	LEAN SOLVENT
Temperature (°F)	68	131
Pressure (psig)	1059	1245
Flow rate (MMSCFD or USgpm)	15.3	78
CO ₂ (mole %)	4.18	Unknown
Methane (mole %)	95.134	0
Ethane (mole %)	0.294	0
MDEA (wt %)	0	49

Data were collected to measure overall contactor performance. Table 4 shows a comparison with *ProTreat* simulation results. The match is exceedingly good with all measurements being reproduced by

Table 4. Comparison Between Process Measurement and *ProTreat* Simulation

	MEASURED DATA	SIMULATION
Treated Gas Flow	14.7	14.9
Treated Gas Temperature (°F)	N/A	138
Treated Gas mole % CO ₂	1.2	1.20
Lean Amine Loading (mol/mol)	N/A	0.013
Rich Solvent Temperature (oF)	124	125
Net CO ₂ Pickup (mol/mol)	0.31	0.31

the simulation. Figure 3 shows the absorber temperature profile to be large and broad, peaking a little below the center of the column. However, in this case, the more interesting unit is really the regenerator, for which there is unfortunately almost no data.

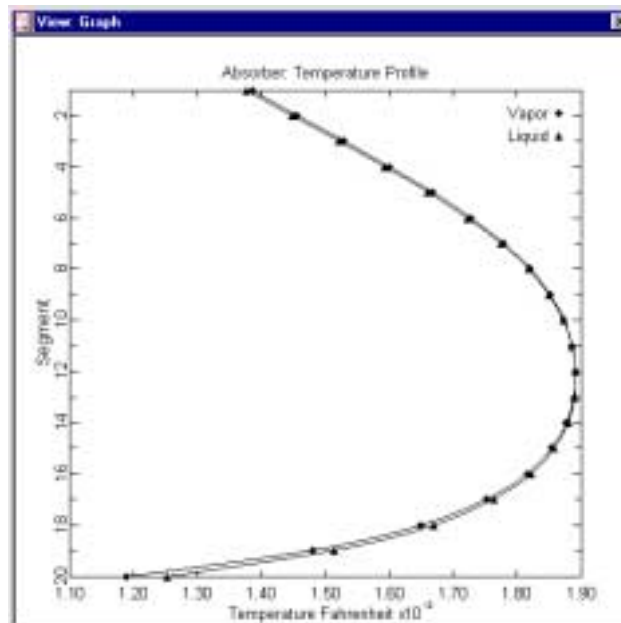


Figure 3. Absorber Temperature Profile—Case Study 2

The rich feed to the regenerator was preheated via cross-exchange to an estimated 170°F and entered the column on Tray 1. With a 75 lb/min steam flow to the reboiler, simulation gave the temperature profile shown in Figure 4 with a simulated reflux ratio of only 0.13. The reason for the low reflux ratio is apparent.

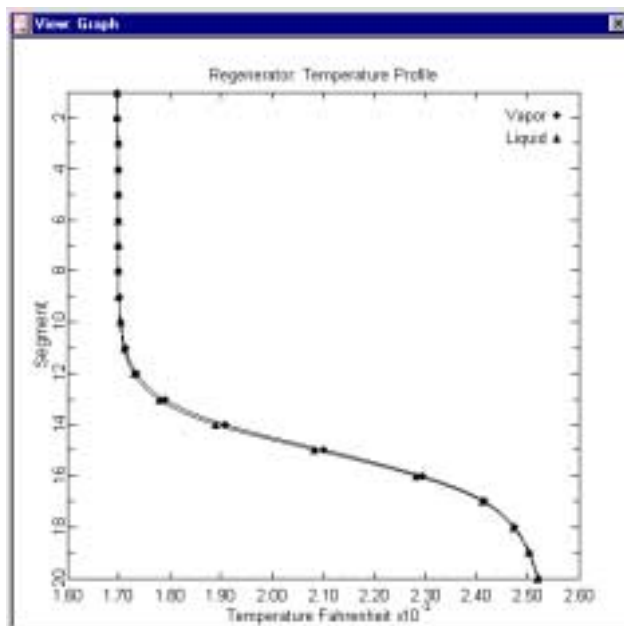


Figure 4. Simulated Regenerator Temperature Profile with 170°F Rich Amine Feed

Condensation of a sizable fraction of the water vapor flow though the column is used to heat the relatively cold feed to its bubble point, and the cold liquid has to travel half way down the column before finding enough condensable water vapor to even begin heating it. The upper one-half of the column does no stripping at all—the CO₂ loading leaving Tray 12 is identical to the feed loading (see Figure 5). The

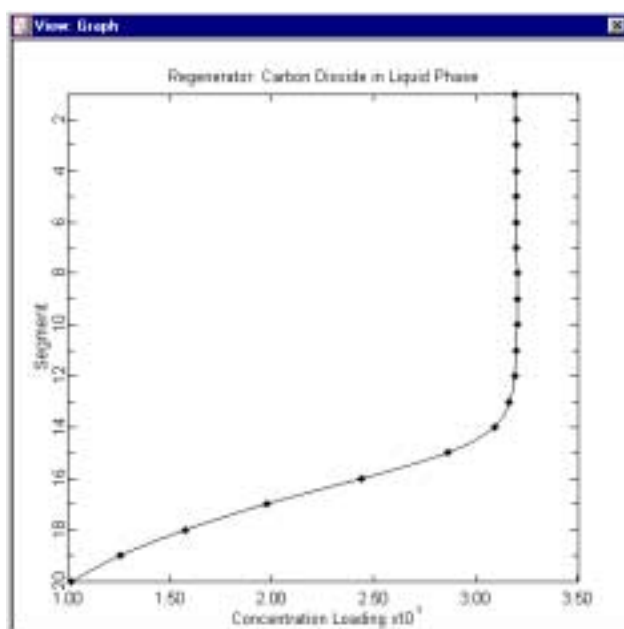


Figure 5. Simulated Regenerator Loading Profile With 170°F Rich Amine Feed

loading of the solvent leaving Tray 20 is 0.102 and leaving the reboiler it is 0.013 for a net change of 0.089 mol/mol across the reboiler. For comparison, Figures 6 and 7 show the simulated temperature and loading profiles when the rich feed is preheated to 190°F. The reflux ratio is now 0.50, the temperatures change rapidly over the top few trays, and the profile looks more like what would be expected. Liquid leaving Tray 20 has a CO₂ loading of 0.0159 mol/mol and the lean from the reboiler is at 0.0039 mol/mol—the net

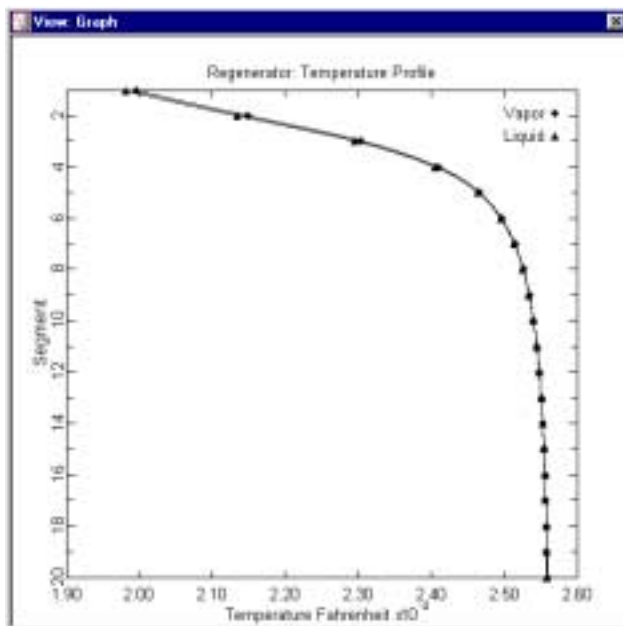


Figure 6. Simulated Regenerator Temperature Profile With 190°F Rich Amine Feed

stripping in the reboiler is now only 0.012 mol/mol, or 13% of the cold-feed value. Note that there has been no change in reboiler heat input between these two cases, although for the hot-feed case there is an extra

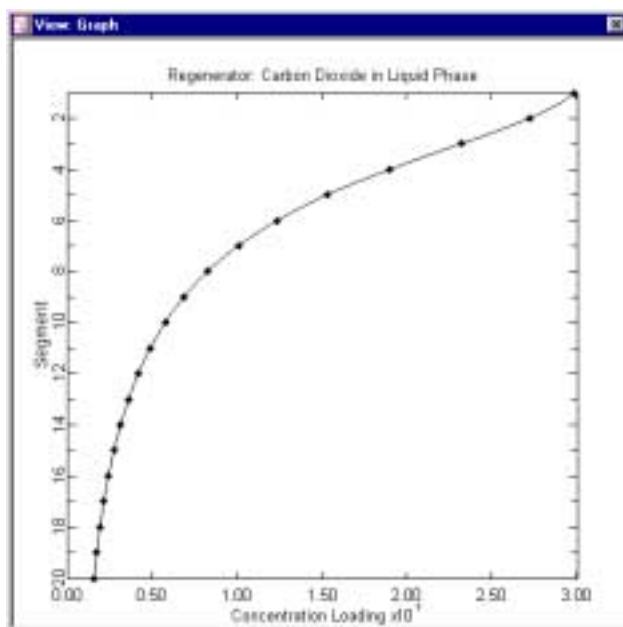


Figure 7. Simulated Regenerator Loading Profile With 190°F Rich Amine Feed

0.44 MMBtu/hr load on the trim cooler while supplying extra heat to the regenerator. Basically, the choice is between taking the extra heat out by condensing more vapor and doing a poorer stripping job in the regenerator (with increased stripping in the reboiler—vapor is 6% CO₂), or taking the heat out in the trim cooler and lowering the CO₂ level in the (corrosion-prone) reboiler to only 0.79% in the vapor. An apparent saving in cross-exchanger area and reduced demand on the trim cooler have a potentially serious hidden penalties, namely increased corrosion and poor stripping.

Case Study 3: A High Pressure MDEA Contactor Treating Natural Gas

This study consists of three sets of overall performance data and detailed temperature profiles for a 7.5-ft ID contactor containing 26 Nutter Float Valve trays processing a natural gas stream at 940 psig. This contactor was one of two parallel units, each treating 200 MMSCFD of gas using a nominal 45 wt% MDEA solution at 750 USgpm. Table 5 shows feed stream conditions. The lean solvent temperature was varied among the data sets (94°F, 108°F and 113°F); otherwise, no other parameters were purposely changed. However, it is unlikely that vapor and liquid flows and compositions remained constant during the entire duration (at least two or three days) of test data collection, so it is unfortunate that only a single set of flows and compositions is available for all three cases.

Table 5. Inlet Stream Conditions for Case Study 3

	SOUR GAS	LEAN SOLVENT
Temperature (°F)	83	Various
Pressure (psig)	940	940
Flow rate (MMSCFD or USgpm)	200	750
Water (mole %)	0.12	
H ₂ S (mole % or mole loading)	1.83	0.0011
CO ₂ (mole % or mole loading)	3.40	0.0050
Methane (mole %)	88.28	
Ethane (mole %)	4.51	
Propane (mole %)	1.18	
n-Butane (mole %)	0.20	
i-Butane (mole %)	0.26	
Nitrogen (mole %)	0.22	
MDEA (wt %)	Nil	50

Table 6 shows that the simulation slightly over predicts the treated gas purity. However, in view of the fact that a single solution analysis and a single gas analysis were used for all three performance tests, the departure of the prediction from the test measurements must be viewed as exceedingly small. This is

Table 6. Measured vs Simulated Treated-Gas Purity

TEST	LEAN SOLVENT TEMPERATURE (°F)	MEASURED PPMV H₂S	SIMULATED PPMV H₂S
3-1	94	4	4.3
3-2	108	7	5.8
3-3	113	13	6.5

even more emphatically the case when one considers that these simulations are pure predictions—there has been absolutely no tweaking of any model parameters to achieve agreement. It is true that the results were known beforehand; however, the ProTreat tower model has no knobs or dials that can be used to

improve agreement or in any way alter the results. These are *predictions*, not fits to the data and they would have been the same whether the results were known or not.

Measured temperatures within the contactor provide an even more stringent assessment of simulation accuracy. Starting from tray 5 from the top, temperature was measured on every fourth tray through the column. Figures 8 to 10 show a direct comparison between the measured data and simulated temperature profiles. For tests 3-1 and 3-2 the agreement is astonishingly good and the worst deviation is perhaps 3°F or 4°F on the steeply rising shoulders of the profiles. Agreement with data shown for the hottest lean solvent in Figure 10 is not as good. It can be seen from Figures 11 and 12 that the large temperature bulge greatly slows H₂S absorption in the center of the column and almost completely stops CO₂ pickup there.

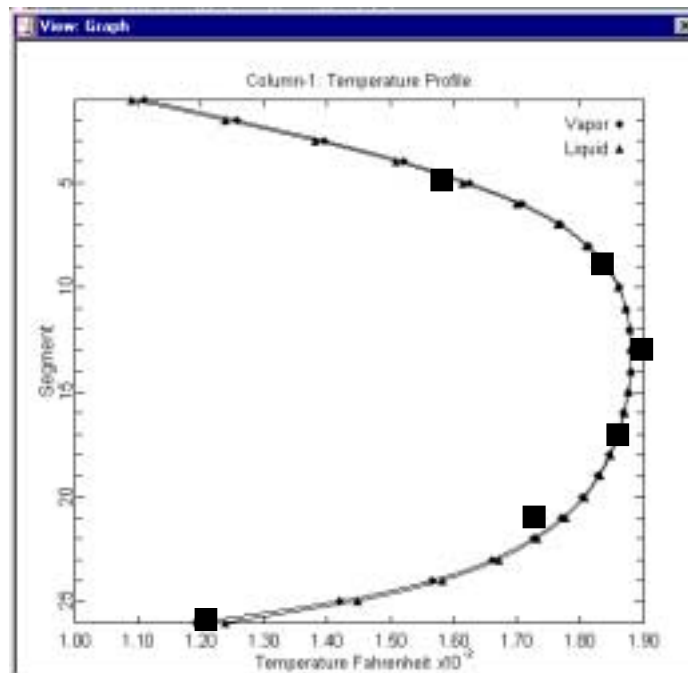


Figure 8. Case Study 3: Measured (■) vs Simulated Contactor Temperatures for Lean Solvent Temperature of 94°F

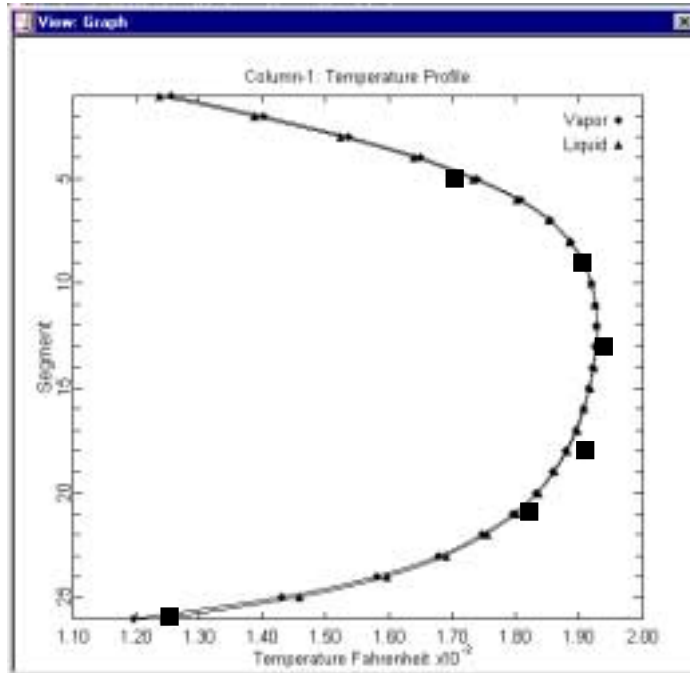


Figure 9. Case Study 3: Measured (■) vs Simulated Contactor Temperatures for Lean Solvent Temperature of 108°F

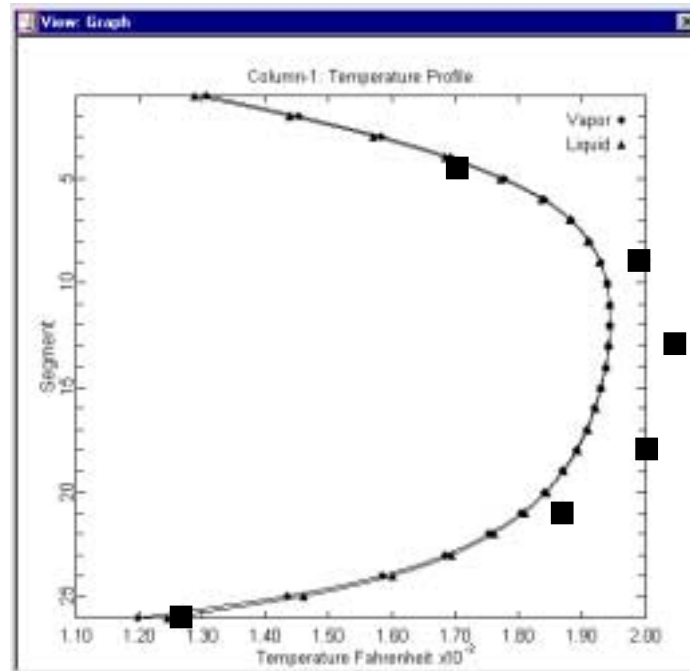


Figure 10. Case Study 3: Measured (■) vs Simulated Contactor Temperatures for Lean Solvent Temperature of 113°F

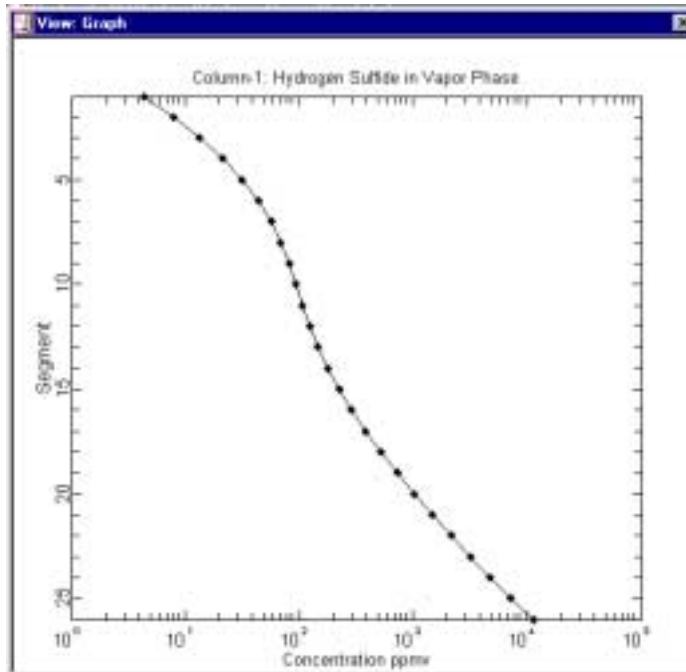


Figure 11. Case Study 3: Simulated H₂S Profile for Lean Solvent Temperature of 94°F

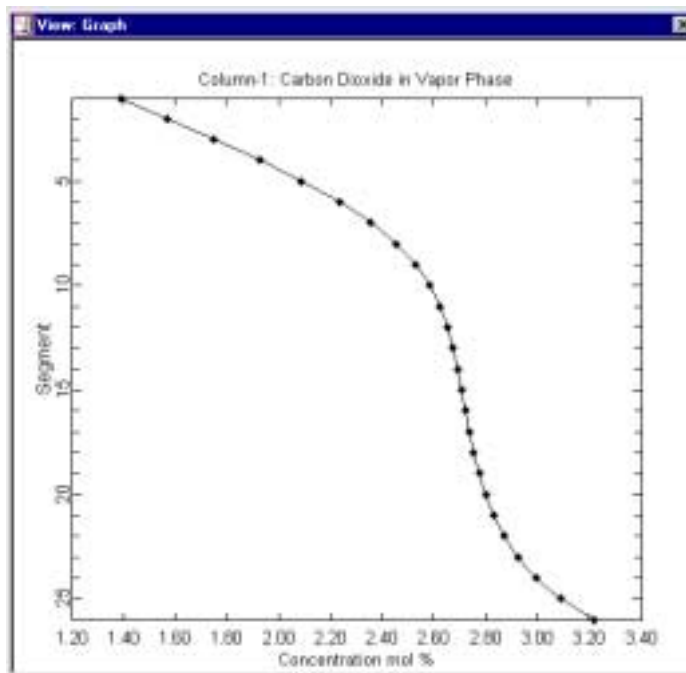


Figure 12. Case Study 3: Simulated CO₂ Profile for Lean Solvent Temperature of 94°F

SUMMARY

Good quality commercial performance test data are extremely scarce, especially test data in which absorber temperature profiles have been measured. With enough empirical adjustment, almost any model can be forced to fit overall performance data in terms of outlet stream compositions and temperatures. However, a fit to the endpoints says nothing about what happens inside the column itself. Thus, temperature profiles are a stringent test of any model because it is a lot harder to fudge simulated internal temperatures.

ProTreat simulations compare extremely well with every set of overall column performance test data presented here. Even more impressive, however, is the generally excellent agreement between simulated and measured temperature profiles, especially in the selective treating application of Case Study 3. All the simulations presented are predictions—there are no adjustable parameters, no efficiencies, no tray holdups, nothing to tweak. There is no empiricism in true mass transfer rate based tower modeling. The mass transfer rate based tower model does the mass transfer equivalent of detailed heat exchanger design, but in the context of gas treating with amines. This freedom from empiricism allows the engineer to predict more accurately the performance of completely new facilities for specific preliminary process and mechanical design for which absolutely no current or similar operating data or experience exist.

ACKNOWLEDGEMENT

ProTreat was developed with the partial financial support of the Gas Research Institute under Contract Number 5092-222-2409, Dennis Leppin, GRI Project Manager.