

Column design using mass transfer rate simulation

This article looks at examples of commercial columns used in CO₂ removal and selective H₂S treating, comparing performance test data to demonstrate benefits of modelling actual column internals using mass transfer rate process simulation

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At least three major advances in gas sweetening at the process level have been made in recent years: more easily regenerable solvents developed, solvents having greater selectivity have been commercialised, and 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 new advance in process simulation capability, the development of a completely new approach to column modelling and analysis in the form of the ProTreat mass transfer rate-based tower model. This models towers in full detail as real physical equipment as opposed to a theoretical-stage idealisation of reality. The key attribute is that the mass transfer rate model uses actual trays and packing for simulation of columns.

Thus, if a column contains 2-pass trays in one section and 4-pass trays in another, or trays in one section and packing in another, it is modelled exactly that way. Attention to this variety of design detail within a column is obviously important to actual column performance, and equally important to column simulation. Avoiding the use of calculations based on theoretical stages is of the utmost importance when dealing with applications involving either selective H₂S removal or customised CO₂ slip, because the internals and their mass transfer characteristics determine to a major extent, the actual H₂S and CO₂ treating levels achieved.

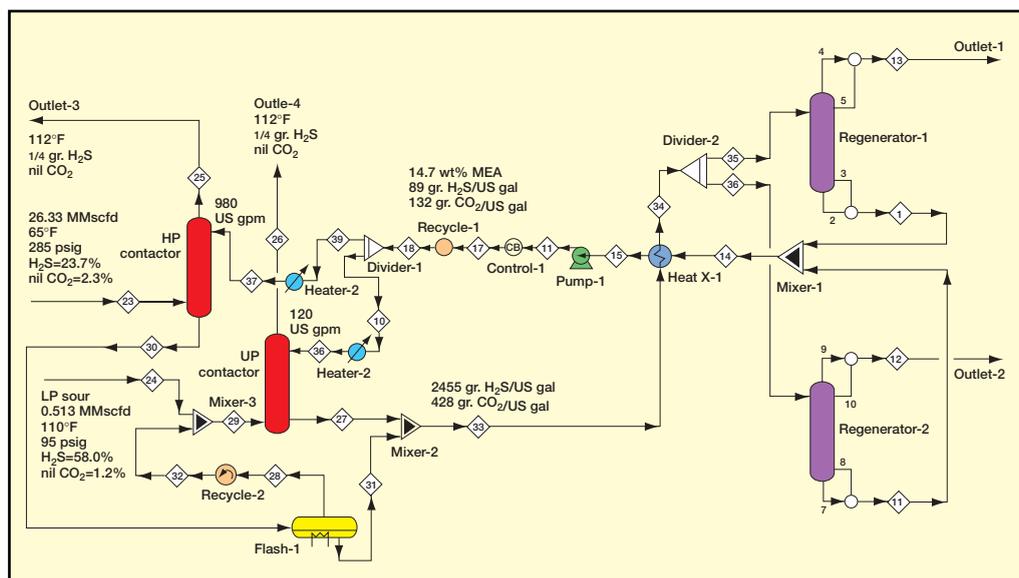


Figure 1 Process flow diagram of Texas Gulf Sulphur plant.

Absorption and stripping

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. But the CO₂-amine reaction is of finite rate and, in fact, is quite slow in MDEA, for example. On the other hand, H₂S ionises instantaneously (to bisulphide ion); it does not react with the amine at all, it forms no chemical bonds, and the ionisation 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

Component	Mole per cent	
	HP sour	LP sour
Hydrogen sulphide	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

Table 1

trays or the right depth of packing, and choosing the kind of column internals that favour 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 do not work very well here either, because the reactions, the tower internals type, and details affect mass transfer in ways just as important 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 Pro-Treat mass transfer rate-based stripper model treats regenerators as rigorously as absorbers and produces the best possible predictions of regenerator performance without the need for empirical adjustment. When absorber and stripper

	Treated gas		Rich amine	
	Measured	Simulated	Measured	Simulated
HP Contactor:				
H ₂ S	0.25gr/100ft ³	0.31gr/100ft ³	–	2802
CO ₂	Nil	0.25ppmv	–	471
LP Contactor:				
H ₂ S	0.50gr/100ft ³	0.73gr/100ft ³	–	1151
CO ₂	Nil	0.28 ppmv	–	160
Total Rich Amine <33>:				
H ₂ S	–	–	2455gr/USgal	2641gr/USgal
CO ₂	–	–	428 gr/USgal	440gr/USgal

Table 2

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

The case studies that follow compare mass transfer rate-based 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 article by Estep et al[Sulfur from natural and refinery gases; *Advances in Petroleum Chemistry*, 1962].

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 modelling accuracy.

Case study 1

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 (previous page). 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 40ft with 3in and 2in metal Raschig rings, respectively. The high pressure contactor and both regenerators are 9ft in diameter; the low pressure contactor is of 3ft 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 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

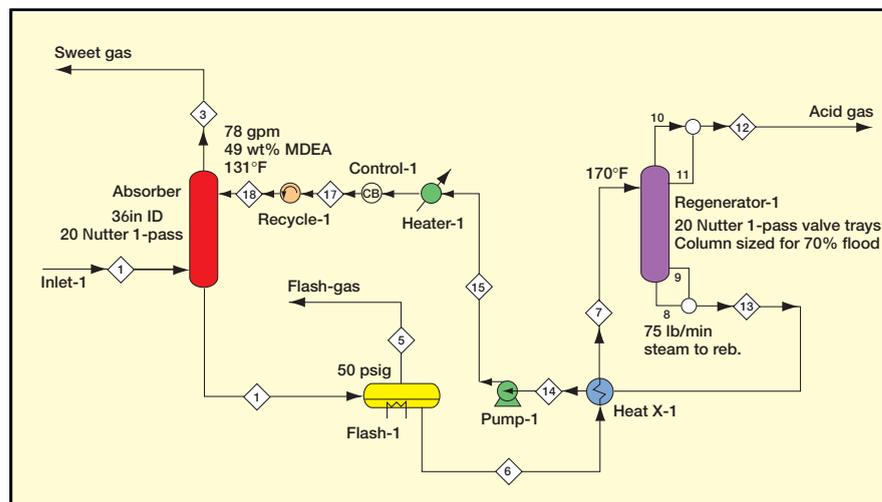


Figure 2 Process flow diagram for Case study 2

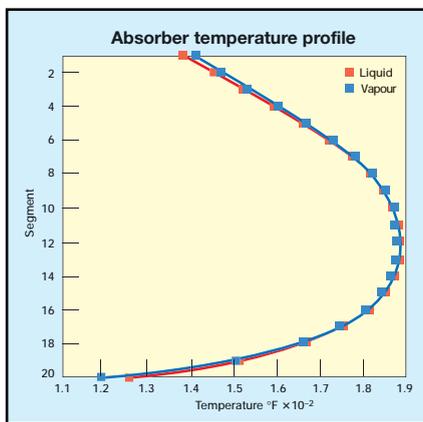


Figure 3 Absorber temperature profile

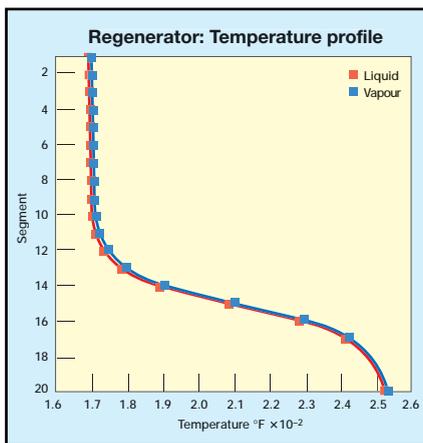


Figure 4 Simulated regenerator temperature profile with 170°F rich amine feed

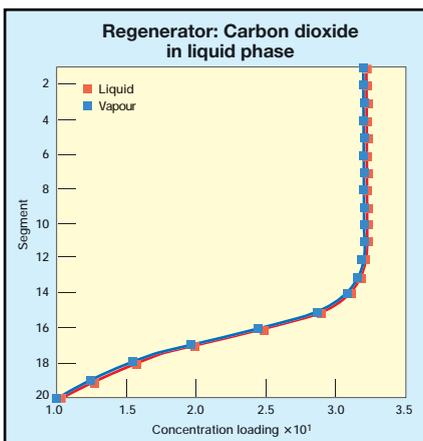


Figure 5 Inlet stream conditions for Case study 3

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, ie for a total amine flow of 1100 USgpm.

It should be noted that this plant treats very high sulphur content gas, 24 per cent H₂S and 58 per cent 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 offgas

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 fed by the high pressure column's rich amine flash gas.

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 modelling, 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.

Case study 2

This example is a single absorber and a single regenerator in a conventional recycle flowsheet for CO₂ removal using nominal 50 wt% MDEA. The

Comparison of process measurement and ProTreat simulation		
	Measured data	Simulation
Treated gas flow	14.7	14.9
Treated gas temperature (oF)	N/A	138
Treated gas mole% CO ₂	1.2	1.20
Lean amine loading (mol/mol)	N/A	0.013
Rich solvent temperature (°F)	124	125
Net CO ₂ pickup (mol/mol)	0.31	0.31

Table 4

Cast 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

Table 3

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 proprietary single-pass Nutter float valve trays. The contactor was 36in ID. The regenerator diameter is unknown but for simulation, it was sized at about 30in for 70 per cent jet and downcomer flood. Steam flow to the reboiler of the regenerator was measured at 75lb/min steam on the shell-side; pressure on the process side was 15psig.

Data were collected to measure over-

Case study 3: Inlet stream conditions

	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	-
Propane, mole%	1.18	-
n-Butane, mole%	0.20	-
i-Butane, mole%	0.26	-
Nitrogen, mole%	0.22	-
MDEA, wt%	Nil	50

Table 5

Measured vs simulated treated-gas purity

Test	Lean solvent temp, °F	Measured ppmv H ₂ S	Simulated ppmv H ₂ S
3-1	94	4	4.3
3-2	108	7	5.8
3-3	113	13	6.5

Table 6

all contactor performance. Table 4 shows a comparison with ProTreat simulation results. The match is exceedingly good with all measurements being reproduced by the simulation. Figure 3 shows the absorber temperature profile to be large and broad, peaking a little below the centre of the column. However, in this case, the more interesting unit is really the regenerator, for which there are unfortunately almost no data.

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 75lb/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.

Condensation of a sizable fraction of the water vapour 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 vapour 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 (Figure 5). The loading of the solvent leaving tray 20 is 0.102, and leaving the reboiler is 0.013, for a net change of 0.089 mol/mol across the reboiler.

Case study 3

This study consists of three sets of overall performance data and detailed temperature profiles for a 7.5ft ID contactor containing 26 proprietary Nutter float valve trays processing a natural gas stream at 940psig. This contactor was one of two parallel units, each treating 200 million scfd 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 vapour 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 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 even more emphatically the case when one con-

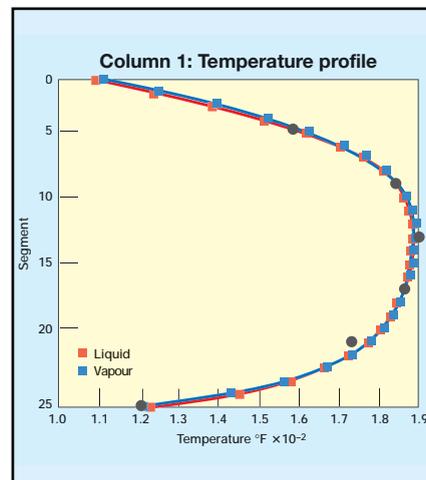


Figure 6 Measured data vs simulated contactor temperatures for lean solvent temperature of 94°F

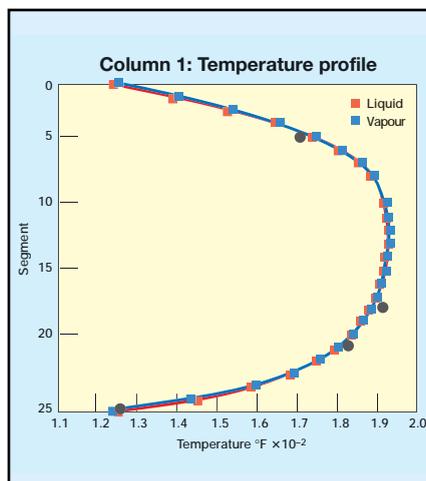


Figure 7 Measured data vs simulated contactor temperatures for lean solvent temperature of 108°F

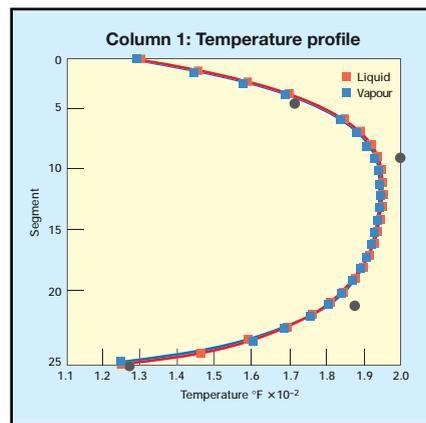


Figure 8 Measured data vs simulated contactor temperatures for lean solvent temperature of 113°F

siders 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 already known or not.

Measured temperatures within the contactor provide an even more stringent assessment of simulation accuracy. Starting with tray 5 from the top, temperature was measured on every fourth tray through the column. Figures 6 to 8 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 8 is not as good.

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 modelling. 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.

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