

Originally appeared in:
July 2011, pgs 43-49.
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What are the benefits from mass transfer rate-based simulation?

Models are highly detailed and predictive

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Alkanolamines have been successfully used for 80 years for sweetening hydrocarbon products. Despite the longevity and track record of amine treating as a process, it is common to find that calculation methods rely heavily on rules-of-thumb and the now-antiquated approximation of ideal or theoretical stages. The advent 30 years ago of high-speed, desktop computing power makes this approach not just severely limiting, but also unnecessary.

Designing for mass transfer. Compared with mass separations, heat transfer is a relatively simple operation involving transferring the single entity, heat. Mass transfer, on the other hand, involves transporting many components as well as heat. It also involves complex phase-equilibrium thermodynamics, as well as chemical reaction equilibrium and kinetics. Conceptually, the difference between heat and mass transfer is computational, rather than fundamental. The beauty of mass transfer rate-based simulation is that separations equipment can be designed and analyzed completely without recourse to theoretical stages, tray efficiencies and transfer unit heights. The separation is calculated directly without appealing to such artificialities, using only equipment parameters that can be measured with a ruler. Heat exchangers are never treated as equilibrium stages, and mass-transfer calculations don't have to be either. After 25 years of successfully applying mass transfer rate-based simulation tools to such diverse operations as azeotropic and extractive distillation, three-phase distillation, distillation with catalytic chemical reaction and reactive amine-based gas absorption, the need for efficiencies and residence-times on theoretical stages is past. So what does the term "mass transfer rate-based" really mean and what distinguishes it from other approaches?

Instead of efficiencies and heights equivalent to theoretical plates (HETPs), mass transfer rate models use mass (and heat) transfer coefficients, gas-liquid contact areas (equivalent to heat transfer surface areas), and concentration difference driving forces (just like temperature differences in heat transfer). Fig. 1 illustrates a magnified view of the gas-liquid interfacial region of the liquid film flowing on the surface of structured packing. Just as temperature differences drive heat flow, concentration differences drive the diffusion of material species.

Mass-transfer coefficients play the role of heat-transfer coefficients, but now the interface across which chemical components transfer is a flexible moving boundary rather than the fixed boundary of a heat-exchanger tube or plate. The advantage in heat transfer is individual shell and tube-side coefficients for heat transfer that are readily correlated with thermal transport properties (density, heat capacity, thermal conductivity) and equipment geometry (tube diameter, plate spacing, baffle placement). This allows heat-transfer calculations to be generalized and fully predictive. If there are good correlations for individual heat transfer coefficients and the equipment geometry has been characterized by physical measurement, the performance of a given heat exchanger can be predicted. This is also true for mass transfer. Good correlations for film coefficients and measured equipment geometries (weir heights, passes, open area on trays, random packing size and brand, or crimp angle and crimp height of a structured packing) allow the performance of a real tray or a given depth of real packing to be *predicted*. The mass transfer rate model does not use artificial parameters such as residence time per theoretical stage, or HETP, and it does not rely on engineer-supplied estimates of efficiency any more than heat-transfer calculations do.

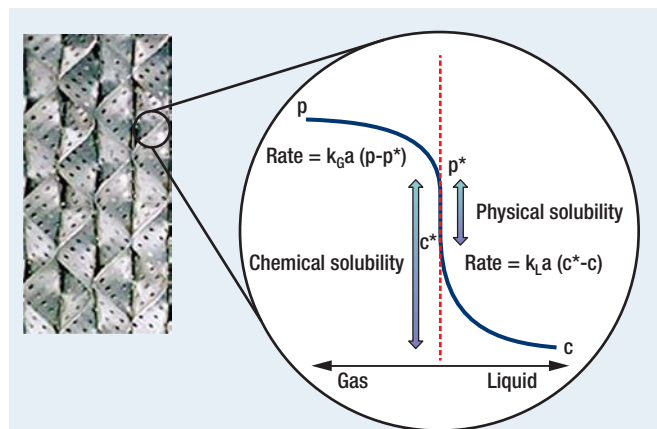


FIG. 1 Region around the gas-liquid interface of liquid film flowing over packing.

A mass transfer rate-based model should not be confused with “rate-based” or one that estimates tray efficiency and then applies it to a few equilibrium stages. There seems to be disinformation, at least in the gas-treating arena, as to what constitutes a rate model. Any column simulation based on equilibrium-stage calculations, no matter how modified, is patently not a rate model. The need for a mass-transfer-rate basis is most evident when selectivity for hydrogen sulfide (H_2S) over carbon dioxide (CO_2) is a concern, commonly when aqueous methyl diethanolamine (MDEA) is the solvent. MDEA absorbs CO_2 slowly because the main reaction, CO_2 hydrolysis to bicarbonate, is slow. Nevertheless, MDEA is capable of absorbing a lot of CO_2 , so CO_2 absorption cannot

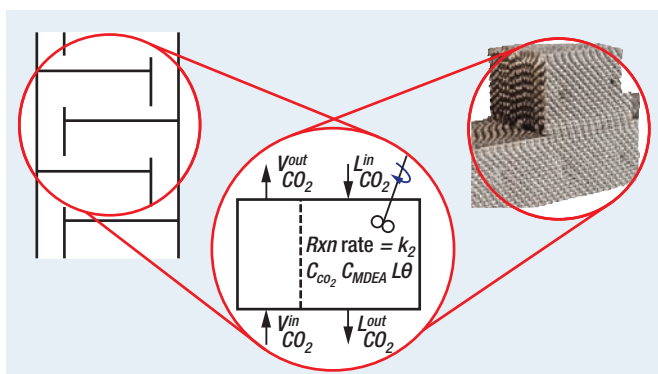


FIG. 2 Ideal stage with chemical reaction as the rate-limiting step.

be ignored. In fact, it determines the CO_2 slip through the absorber, influences the equilibrium pressure of H_2S and the H_2S -treated gas content. Getting the CO_2 slip right is critically important to getting the treating right.

One approach to modeling CO_2 absorption by MDEA which retains the equilibrium stage concept while attempting to account for reaction rates, is to conceptualize the liquid volume held up on a theoretical stage as a stirred tank reactor. This conceptualization is illustrated in Fig. 2, where several trays or a large volume of random or structured packing is represented by a single ideal contact stage. Dissolved molecular CO_2 reacts with MDEA at a rate dictated by the reaction kinetics. For an ideal stage whose liquid holdup volume is V (equal to volumetric liquid flowrate, L , multiplied by the ideal-stage residence time, θ), CO_2 disappears by reaction on the stage at the rate (mol/s) shown in Fig. 2. Physically, an ideal stage is unrelated to anything that is inside the column. Since this is an idealization, the meaning of ideal-stage residence time defies reason.

In principle, the calculated reaction rate (Fig. 2) can be used to compute the increase in total flowrate of dissolved CO_2 between the liquid inlet and outlet (i.e., separation). This allows the outlet liquid *not* to be in equilibrium with the outlet gas (equilibrium is the primary approximation of the equilibrium stage model). Is the problem solved? Not quite. There are two issues with this approach. The first is how to assign a value to the ethereal residence time on a theoretical stage. The second is there is no way of knowing the concentration of dissolved but unreacted CO_2 in the bulk liquid phase, C_{CO_2} . If the reaction was fast, C_{CO_2} could be zero; if it's slow, it could be the value in equilibrium with the gas.

Absorption is a two-step process:

- Dissolve, then diffuse through the liquid
- React.

The simplest assumption is that the reaction is slow enough and the mass transfer is fast enough for C_{CO_2} always to have its equilibrium value (i.e., no mass transfer resistance and the rate-limiting step is reaction). The reactor model focuses on the wrong process as the rate-limiting step. In fact, CO_2 absorption is never reaction-rate controlled—it is always mass-transfer-rate controlled. Disregarding this fact may result in the highest calculated absorption amount. Although simulation can be matched to plant performance data through the adjustable parameter, θ , the residence time per theoretical stage is disconnected from anything physical. The right value for a new situation is just as unknown as stage efficiency. If too small a value is guessed, then there is too little CO_2 removed; too large, then too much is removed. There is an element of “rate” through reaction kinetics, but to call it rate-based is disingenuous—it is still an equilibrium stage model, but now containing an adjustable parameter.

Recently, Nagpal concluded that accurate “rate-based” process simulators are required for optimal design of sulfur removal units (SRUs) and tail-gas-treating units (TGTUs), but there is considerable variability among commercial simulators.¹ Unfortunately, the simulators compared by Nagpal were not mass transfer rate based. His conclusion—that reliable operating data from existing units are required to validate the simulator results deserves applause. It is futile to compare results between simulators and vendor runs because all are simply simulations. Traditionally, the focus of most ideal stage-based simulation has been trays. Equilibrium stage models cannot confidently determine the bed height needed and the separation to be expected in packed tower. A mass-transfer rate-based simulator is compulsory.

A simulation tool is truly rate-based only if it:

- Does not use equilibrium stages in any way
- Asks for no data that cannot be directly measured in the plant
- Reliably predicts performance without knowing the answers first
- Predicts tray performance and random and structured packing.

Not meeting capacity in a shale-gas-treating plant. Shale gas is usually low in H_2S but high enough

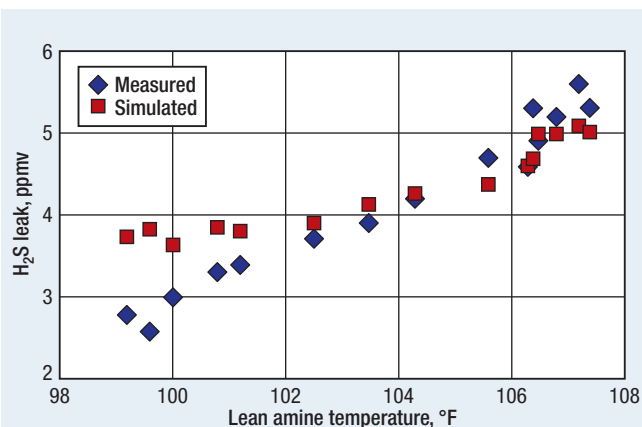


FIG. 3 Measured vs. simulated H_2S leak for June 28, 2009 data.

TABLE 1. Plant performance data for 60% capacity operation compared with simulation

Time	Gas rate, MMscfd	Amine rate, gpm	Lean amine, °F	Raw gas, °F	Inlet H ₂ S, ppm	Outlet H ₂ S, ppm	Inlet, CO ₂ %	Outlet, CO ₂ %	Calc H ₂ S, ppm	Calc CO ₂ , mol %
7:30 a.m.	200	240	100	84.0	400	3.0	2.4	1.8	3.64	1.67
8:00 a.m.	202	240	99.2	85.2	400	2.8	2.4	1.8	3.73	1.68
8:30 a.m.	202	240	99.6	86.6	400	2.6	2.4	1.7	3.82	1.69
9:00 a.m.	199	240	100.8	87.8	400	3.3	2.4	1.7	3.85	1.69
9:30 a.m.	199	240	101.2	89.2	380	3.4	2.4	1.7	3.80	1.70
10:00 a.m.	198	240	102.5	91.0	380	3.7	2.4	1.7	3.90	1.70
10:30 a.m.	202	240	103.5	93.3	380	3.9	2.4	1.7	4.14	1.72
11:30 a.m.	203	240	104.3	94.8	380	4.2	2.4	1.7	4.27	1.72
12:00 p.m.	203	240	105.6	96.0	380	4.7	2.4	1.6	4.38	1.73
12:30 p.m.	207	245	106.3	95.5	380	4.6	2.4	1.6	4.60	1.73
1:00 p.m.	207	245	106.4	96.5	380	5.3	2.4	1.6	4.68	1.73
1:30 p.m.	209	250	106.8	96.8	390	5.2	2.4	1.6	4.99	1.74
2:30 p.m.	209	255	107.4	95.9	380	5.3	2.4	1.6	5.02	1.73
3:00 p.m.	209	255	107.2	96.8	380	5.6	2.4	1.6	5.09	1.73
4:00 p.m.	209	255	106.5	95.2	380	4.9	2.4	1.6	4.98	1.72

in CO₂, where it's difficult to treat. A particular plant was intended to use 50 wt% MDEA to treat, to pipeline quality, 330 million standard cubic feet per day (MMscfd) of a high-pressure gas having 700 ppmv H₂S and 2.5% CO₂. The plant was designed using an equilibrium-stage based simulation tool, and, from the day it started up there was a major problem. Beyond 60% of the design gas rate, the 12-tray contactor could not meet the 4-ppmv H₂S specification, and the CO₂ level was already well below the targeted 2% even with maximum solvent circulation rate, maximum reboiler duty and only 400 ppmv H₂S in the raw gas. Startup was during the relatively cool month of June, but with August approaching, the situation was likely to get worse. Mass transfer rate-based simulation showed that missing the H₂S treat was caused by absorbing far more CO₂ than suggested by the original design tool. In essence, the predicted CO₂ slip was wrong.

With a mass-transfer rate-based amine simulator in their hands, the engineers first tried to predict the performance of the plant as measured shortly after startup. Data for an 8-hr period are compared with simulation in Table 1, and the data provide confidence in the simulation tool. The calculated results were obtained "out of the box" using no adjustable parameters whatsoever—absolutely none. As Fig. 3 illustrates, the H₂S leak from the absorber tracked extremely well with the temperature of the lean amine. However, it did not provide even a hint at what the cause was or what the best "fix" might be.

As an interim measure, the solvent vendor proposed a formulated MDEA containing an acidic stripping agent to reduce the H₂S loading in the lean amine so that at least the 60% production level could be maintained over the summer.² Using the mass transfer rate-based simulator, the plant's engineers showed that this solvent would allow < 4 ppmv H₂S leak, and with the treating rate improved to 73% of capacity. As a result, the existing 50 wt% MDEA solvent was gradually converted to the formulated solvent, and plant capacity also increased despite the high summer temperatures. The longer-term remedy for the plant was retraying the absorber.

Twelve trays were sufficient to reach 4 ppmv H₂S only at

**FIG. 4** Two-pass tray with recessed seal pan and anti-jump baffle.

reduced rates. Mass transfer rate-based simulation showed that adding more trays would remove more CO₂ but not allow 4 ppmv H₂S gas to be produced at design rates. However, it is known that if trays can be forced into the spray regime of operation, much improved selectivity can result.³ Tray weir liquid loads below 60 gpm/ft of weir length result in spray formation. Also, the lower the weir load, the more the biphasic on the tray becomes a spray of fine droplets (approximately 1 mm). Even though a single pass tray was hydraulically adequate, the new trays were built with two passes, i.e., double the weir length or half the weir load (Fig. 4). Within the existing shell constraint, the tower could accommodate 18 trays on closer spacing. Simulation suggested the gas would be 2.5 ppmv H₂S using 50 wt% generic MDEA. This was too close for surety and the backup plan was to reintroduce formulated solvent that would guarantee just below 2% CO₂ and < 0.2 ppmv H₂S.

Another valuable result from the mass transfer rate-based simulations was the discovery that a solvent rate considerably less than maximum solvent rate was necessary to meet the treating objective with generic MDEA. The reason is that low solvent rates significantly reduce weir liquid loads, improving selectivity by generating a greater proportion of spray vs. froth, i.e., higher CO₂ slip and better H₂S removal.

Correcting poor treating of refinery fuel gas. Refinery amine systems are notoriously contaminated with heat-stable salts (HSSs) generated in cracking and

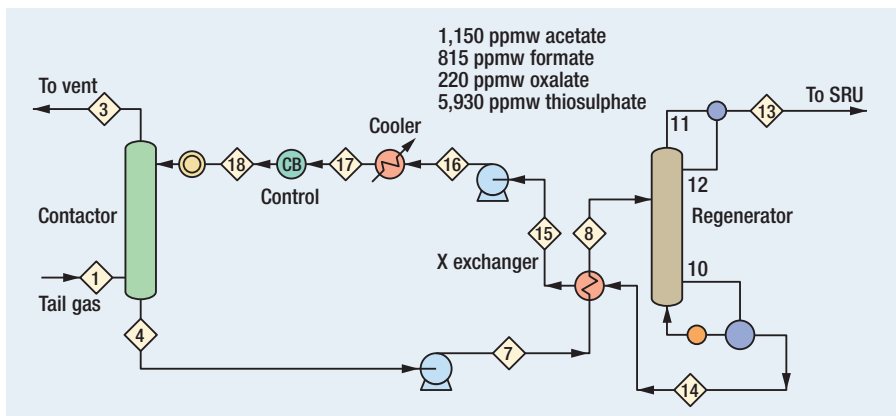


FIG. 5 Refinery tail-gas treating unit.

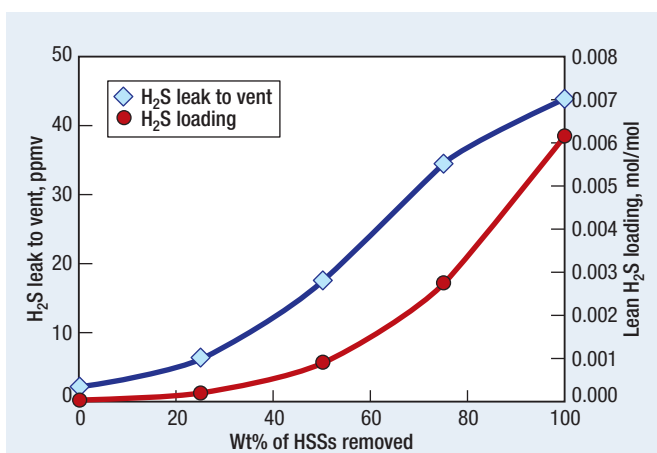


FIG. 6 Solvent reclaiming effect on TGTU performance.

TABLE 2. Analysis of solvent used in fuel-gas treater

MDEA, wt%	38	Formate, ppmw	14,305
CO ₂ , loading	0.00014	Sulfate, ppmw	230
H ₂ S, loading	0.0009	Thiocyanate, ppmw	3,225
Acetate, ppmw	2,580	Chloride, ppmw	1,675

hydrotreating operations. In this example, to reduce operating expenses, a refinery switched from monoethanolamine (MEA) to MDEA during a turnaround. At the same time, they revamped the fuel-gas treater from trays to random packing.

Before the revamp, the high-pressure treater was satisfactorily sweetening a 200-psig fuel-gas stream from 0.5% H₂S to below 4 ppmv. Following the revamp, the column failed to achieve satisfactory treating. The solvent vendor's simulation suggested the contactor should be capable of reaching 2 ppmv H₂S in the treated gas, but H₂S leaks in the range from 20 ppmv–30 ppmv were measured regularly. In agreement with the solvent vendor's expectations, a popular commercial simulation tool also suggested that the treated gas should contain 1 ppmv–2 ppmv H₂S. The simulation basis was a clean solvent and both sets of simulations used measured acid gas loadings in the lean solvent. Neither was capable of simulating a regenerator. The presence of HSSs was not considered, nor could this factor be accounted for by either simulator. With clean-solvent

simulation results, a consultant blamed the trays-to-packing revamp for the failure under the flawed premise that the liquid residence time on the packing was too short to allow sufficient H₂S absorption. (This is surprising when CO₂, not H₂S, absorption into MDEA is suggested to be residence-time dependent.) On the consultant's recommendation, the tower was revamped back to trays. However, the results were extremely disappointing—performance was essentially unchanged from packing. This was a consequence of ignoring the effect of HSSs. However, in the absence of accurate lean loading values, reliable regenerator simulation is critical to assessing HSS effects and mass

transfer rate-based simulation is the best way to do this.

When the solvent analysis shown in Table 2 was used in mass-transfer rate-based simulations, packing was predicted to produce 26.5 ppmv H₂S and 26.0 ppmv for the 17 trays. A performance test on the trayed column showed a treating level of 26 ppmv H₂S, in perfect agreement with the mass transfer rate-based simulation. If the correct simulation tool is used in the first place, the embarrassment of a failed, expensive revamp can sometimes be avoided, and the right corrective action taken instead—in this case, reclaiming the solvent.

Making the right solvent-reclaiming decision. The Gulf Coast refinery TGTU shown in Fig. 4 is a conventional scheme using 34 wt% MDEA solvent. It treats tail gas having 1.7% H₂S and 3.4% CO₂ and the contactor is packed with 20 ft of structured packing. TGTUs are normally run on a separate amine circuit from the rest of the refinery to avoid problems caused by HSS-laden solvents. In this case, the TGTU used the refinery amine system. Despite the HSS analysis shown in Fig. 5, the unit was treating the tail gas to a remarkably low 3 ppmv H₂S. A mass-transfer rate-based simulation of this system, including the full solvent composition per the analysis, predicted 2.3 ppmv H₂S leak, in notable agreement with measured performance.

The solvent was quite contaminated—0.8115 wt% HSSs. Plant personnel were considering reclaiming, but before making that recommendation, they ran several mass transfer rate-based simulations to determine if TGTU treating would be affected. Fig. 6 shows that, with increasing degrees of reclaiming, the TGTU would rapidly lose its ability to treat to really low H₂S residuals. Although not shown, reclaiming was simulated to have a negligible effect on CO₂ slip, which would remain at 65%. The reason for such outstanding H₂S treating is the HSS's effect on solvent regeneration—they are acting as stripping promoters, reducing the solvent lean loadings of H₂S and CO₂ by a factor of between 10 and 100! This translates into lower H₂S leak. If thorough reclaiming had been done without first trying to assess its effect on treating, the TGTU was predicted to slip nearly 20 times as much H₂S to vent—well above the permit level. Using a mass transfer rate-based simulation tool with HSS capabilities prevented a potentially catastrophic outcome. No reclaiming was done in this case.

A good place to start the reclaiming decision-making process is an assessment using a process simulation tool that has

high accuracy and reliability. Mass and heat transfer rate-based simulations meet these criteria. One must be able to model the actual system under study, not just the detailed solution chemistry but also the mass-transfer behavior of the real column internals being used. Accurate regenerator modeling is crucial because this is where HSSs and stripping promoters have their real effect, so one cannot just assign values to acid-gas loadings in the lean solvent.

Bulk CO₂ removal with MDEA. Knowledge grows and technology advances, so what does one do if double checking an original design late in the construction phase shows the design is inadequate? A plant for treating 9.5% CO₂ in a methane stream with 50 wt% generic MDEA to a target level of 0.5% was initially designed according to a commercial, reaction-modified equilibrium-stage-based simulator. This simulator suggested that 22 actual trays would be adequate. The treated gas was to be blended with other streams to meet a pipeline specification of 2% CO₂. Equipment was being installed and the plant was scheduled for startup when the solvent vendor was asked to validate the MDEA design. Using a mass transfer rate-based simulator showed the plant could not meet even the 2% CO₂ specification required for the final blended gas, much less the 0.5% CO₂ target for the treated gas. Indeed, 50 trays were needed to reach 0.5% CO₂ in the outlet gas using MDEA! This was certainly not what the engineering team expected, and they were left scrambling for a solution. Fortunately, the initial gas rate and its CO₂ content were expected to be lower than in the design, and another low CO₂ gas stream was available for blending. As a precaution, contactor weir heights were raised from 2 in. to 5 in.

The original design tool suggested that at design conditions the 2-in. and 5-in. weirs would produce gas with 0.68% and 0.20% CO₂, respectively. The mass transfer rate-based tool predicted 2.08% and 1.72% CO₂. It's not known which was correct since the plant never operated at design rates with generic MDEA. However, the initial operating data (taken at 6.4 MMscfd vs. 10 MMscfd with 7.95% CO₂ vs. 9.5% CO₂) validated the mass transfer rate-based simulation that predicted 0.7% CO₂ vs. 0.8% measured in the plant. After operating for two years with the solvent circulation pump's capacity limiting processing to 9 MMscfd, the outlet gas was measured at 1.7% CO₂ compared with 1.34% CO₂ by mass transfer rate-based simulation. Under no circumstances was anything like 0.5% CO₂ ever produced with generic MDEA. Eventually, the situation took on greater urgency when corrosion in another unit caused the source of low-CO₂ gas to be shut off. Without blend-gas to dilute the CO₂, the facility was forced to cut production.

The consequences of the poor original design were mitigated in part by a last-minute tray modification, and by the fact that the actual gas flow and composition when taken together amounted to over 30% lower load than the design was supposed to accommodate. After two years of operation, when the original design conditions needed to be met, the consequence of using an equilibrium-stage-centered model for this application came to a head. A sensible solution was a solvent change-out to a specialty amine. Fortunately, the availability of

a mass transfer rate-based simulation tool allowed the operators of this facility to anticipate and plan for corrective action well in advance. With a mass transfer rate-based simulation tool, this wouldn't have happened—conversion to a specialty solvent could have been avoided.

Summary. Mass transfer rate-based simulation has been used with great success for 25 years in the design and analysis of high-purity, azeotropic, extractive, catalytically reactive, three-phase distillations, and in gas treating with amines. Mass transfer rate-based models are highly detailed and completely predictive. They require the user to provide details of tray type, weir height and length; the number of passes; and packing types by brand name, size and material. They require parameters that are physically meaningful and which can be measured. Such details are necessary for mass transfer rate calculations, not just for estimating flooding and pressure drop.

Theoretical stages, efficiencies, HETPs and ideal-stage residence times never come up in mass transfer rate-based simulation. The only input data is information that can be measured or read from a drawing. Practitioners can be as confident with mass transfer rate-based simulation as they are in heat-exchanger design software. The cases presented are real-world, and show the power of the methodology and the benefits that engineering and operating personnel can reap by using mass transfer rate-based simulation to tackle the very problems once shelved as "can't-be-solved." **HP**

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ACKNOWLEDGMENT

All photos courtesy of Sulzer Chemtech.



Ralph Weiland founded Optimized Gas Treating in 1992 and has been active in Canada, Australia and the US in basic and applied research in gas treating since 1965. He developed the first mass transfer rate-based model for amine columns for Dow Chemical and is responsible for the development of the Windows-based ProTreat process simulation package. Dr. Weiland also spent 10 years in tray research and development with Koch-Glitsch LP, Dallas, Texas. He earned BASc, MASc and PhD degrees in chemical engineering from the University of Toronto.



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