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Overcome challenges in treating shale gases

Manipulating process plant parameters helps meet pipeline specifications

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Shale represents an astonishingly large, new source of natural gas and natural gas liquids (NGLs). However, a common misconception seems to be that, for the most part, shale gases are sweet and do not need to be treated.

Although not highly sour in the traditional sense of having high H_2S content, and with considerable variation from play to play and even from well to well within the same play, shale gas often contains tens or hundreds of parts per million of H_2S, with wide variability in CO_2. Gas in the Barnett shale play of North Texas, for example, contains several hundred parts per million by volume (ppmv) of H_2S and several percentages of CO_2—far from pipeline quality.

In other shales, such as Haynesville and the Eagleville field of the Eagle Ford play, H_2S is known to be present. In other cases, such as the Antrim and New Albany plays, underlying sour Devonian formations may communicate with and contaminate the shale formations.[1] Some plays in Western Canada have low CO_2 but enough H_2S to require treating. Thus, after removing the NGLs, there are many situations in which the shale gas may still need to be treated to pipeline specifications, at least for sulfur content.

Difficulties posed by shale gases. The challenge in treating such gases is the very low H_2S-to-CO_2 ratio and the desire to meet, but not exceed, pipeline specifications on CO_2 content. In terms of cost and effectiveness, the solvent of choice for H_2S removal and CO_2 slip is *N*-methyldiethanolamine (MDEA) used in a traditional gas treating plant. But how does one go about taking the H_2S content from, for example, 100 ppmv down to 4 ppm without taking out excessive CO_2 at the same time? Another related issue is what to do with the acid gas from the amine unit, since it will likely be of substandard quality for a Claus plant.

This article uses specific examples to show, quantitatively, how various process plant parameters affect selectivity and, in particular, the ability to treat a variety of shale gases to pipeline specifications. Solvent selection, strength, temperature and circulation rate, as well as the type and quantity of internals used in the contactor, are some of the process parameters and design variables considered.

Problem-solving with trays. A new tactic is to use multi-pass trays even when, hydraulically, a single-pass tray is more than adequate to handle the flows. The key is to understand that trays operating in the froth vs. spray regimes have radically different mass-transfer performance characteristics. A critical element in the underlying analysis is the availability of a real-mass and heat-transfer rate-based simulation capability, because the selectivity issue is intimately tied to the separation taking place from a mass-transfer *rate* perspective. Ideal stages are incapable of dealing with this properly because, no matter how embellished by efficiencies and residence times, an ideal or equilibrium stage is completely oblivious to the effect of hydraulics on mass transfer.

Rather than devoting column space to discussing what a mass-transfer rate model is and how it works, we will instead present a set of case studies and simply refer interested readers to a previous *Hydrocarbon Processing* article[2] for model details. However, it will be important in what follows to understand this fact: H_2S absorption is a process controlled by resistance to mass transfer in the gas phase, whereas CO_2 absorption is liquid-phase-resistance controlled. Therefore, whatever can be done to lower gas-phase resistance and increase liquid-phase resistance will improve H_2S pickup and increase CO_2 slip.

The reaction between CO_2 and MDEA is so slow that reaction kinetics play a very minor role in determining CO_2 absorption rates. Carbon dioxide and hydrogen sulfide absorption are controlled strictly by the mass-transfer characteristics of the specific trays or packing under the hydraulic conditions being used.

TRAYS OPERATING AT LOW LIQUID RATES

During 2007 and 2008, several plants were found to be producing gases with unbelievably low concentrations of H_2S and astonishingly high CO_2 slip values. These values were far outside the range suggested by any simulator, whether mass transfer rate-based or ideal-stage. In each case, the absorber contained trays. More importantly, the weir liquid load (volumetric flow rate of solvent per unit length of weir) was always quite small.[3] Later, performance data was found for six more plants also operating at low weir liquid loads and, as Fig. 1 shows, the data from all nine plants show remarkable quantitative consistency with, and support for, the spray-regime explanation.[4]

Froth vs. spray regime. The experimental data from which the fundamental mass-transfer coefficient correlations are drawn in a mass transfer rate-based model all corresponded to trays operating in the *froth* regime, in which the biphase on the trays is a frothy liquid containing a dispersed gas. However, the trays

in these nine low-weir-load instances were all operating in the *spray* regime, with some operating with essentially pure sprays (left side of Fig. 1) and others with mostly froths but with a modicum of spray (right side).

In froths, the liquid is continuous and the gas is dispersed as large and small gas bubbles and jets; in sprays, the liquid is dispersed as droplets (about 1 mm in diameter in aqueous systems) bouncing across the tray and finding their way into the downcomer through a continuous gas phase.

Hydraulically, the flows are radically different, and so is the mass transfer. The spray regime has much higher liquid-phase resistance (to mass transfer) because, internally, the liquid drops are almost stagnant. The lack of mixing produces lower CO_2 absorption rates (remember: CO_2 absorption is liquid-phase controlled)—i.e., increased CO_2 slip.

On the other hand, gas-side mass transfer is much improved because of the highly turbulent flow of gas around the drops—hence, better H_2S absorption. This scenario is completely consistent with what was seen in the performances of all nine plants. Thus, to improve H_2S removal and to slip more CO_2, trays should be operated in the spray regime if possible.

Spray regime challenges. It is unfortunate that, in the distillation community, tray operation in the spray regime has a bad rap. However, the poor reputation is the fault of many tray designers who repeatedly fail to use a seal pan to ensure that downcomer bottoms are positively, hydrostatically sealed (vs. dynamically sealed).
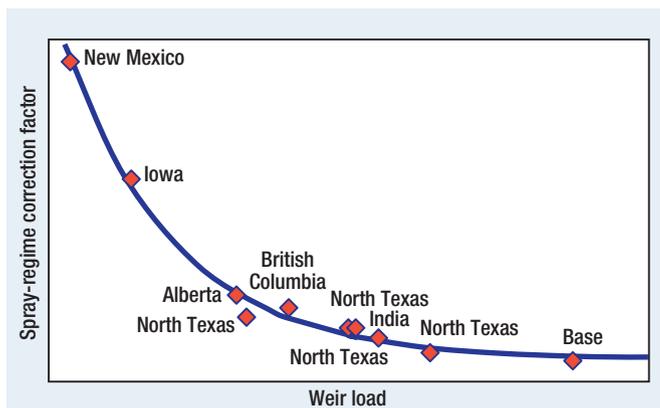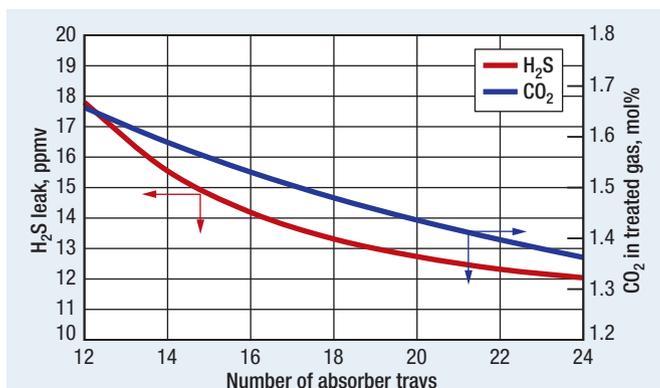
A good seal prevents gas from blowing up the downcomers (rather than through the tray deck), causing massive entrainment of liquid and an undeserved bad reputation. In fact, in the spray regime, trays having positively sealed downcomers actually have *higher* jet flood capacity than conventionally operated trays. Attempting to seal downcomers dynamically, at very low liquid rates, is an invitation to failure.

The gas-treating benefit of the spray regime was the subject of a 1981 patented tray design.[5, 6] However, the patented design failed to gain popularity, perhaps because of the limited area of application 30 years ago. Nonetheless, the spray-regime operation of trays has promising application in shale gas treating today.

TREATING A GAS FROM THE BARNETT SHALE

The gas plant in question is one of three units in Texas between Dallas and Houston intended to process gas from fields in the Barnett shale. As built, this particular plant was intended to treat 330 million standard cubic feet (MMscfd) of gas containing 750 ppm H_2S and 2.5% CO_2 at 960 pounds per square inch absolute (psia) to pipeline quality—i.e., 4 ppmv H_2S and < 2% CO_2.

The absorber was designed with 12 single-pass valve trays using an equilibrium-stage simulator and assumed tray efficiencies. From startup in mid-2009, the plant has consistently failed to produce on-specification gas at more than 60% of the nameplate production capacity, even with reboiler and circulation pumps running at full capacity. The generic MDEA solvent was gradually spiked with a stripping promoter, allowing it to treat 240 MMscfd, or 73% of capacity. However, the internals were inadequate to move beyond this limit, and a revamp of the tower—perhaps even a new and taller column—was required.

Literally hundreds of cases were run using a mass transfer rate-based amine simulator to determine the right course of action. Focusing on the absorber, the tray count was varied from 12 to 26, and solvent rates, amine strength, gas temperature and solvent temperature were varied. Consideration was given to tray type and design, the use of structured packing and even a combination of packing and trays in the same column to achieve the nameplate rate with on-specification gas. The results were somewhat surprising and very educational.

Simulation results. Traditional thinking would suggest that, if a plant is not meeting treating specification, a higher solvent circulation rate and a more aggressively reboiled regenerator should improve treating. However, in the present case, the oil

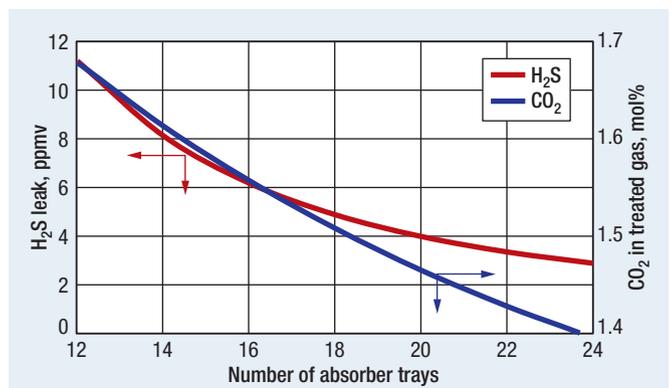**FIG. 1**   The correction factor for spray-regime operation varies with weir liquid load.

FIG. 2   Adding trays does not meet the treating specification with MDEA at design rates.

FIG. 3   The use of a stripping promoter meets treat but removes too much CO_2.

flow to the regenerator reboiler and the circulation rate through the unit were already at equipment limits. Furthermore, the solvent was already at 50 wt% MDEA and contained a stripping promoter, so only a small increase was possible by raising the MDEA strength by 5 wt% or 10 wt%—certainly not enough to increase performance significantly.

One of the most influential parameters was simulated to be the raw gas temperature. (Solvent temperature had a much smaller effect because the gas-to-liquid ratio was high in this plant.) However, significantly reducing the gas temperature would have required a large gas heat exchanger, and any achievable lower temperature was found to be insufficient to allow treating at the design rate. Thus, the focus shifted to the tower internals.

Using the right tray design. The preference was to use generic MDEA rather than a specialty amine. Fig. 2 shows that, with generic MDEA, adding trays will indeed lower the H_2S leak into the treated gas, but not nearly enough to meet the H_2S specification. Note that the weir load in this case is 65 gallons per minute per foot (gpm/ft), requiring application of a small correction for a small amount of spray.

However, the problem with the absorber is that, the more trays there are, the more CO_2 is removed. Already twice as much CO_2 as necessary is being removed from the gas. Solvent capacity is being used to remove the wrong component (CO_2) instead of the noncompliant component (H_2S). No matter how many trays are used in this absorber, generic MDEA will not allow the gas specification to be met at design rates.

Using a stripping additive would permit the originally intended gas rate to be processed to pipeline specifications, as Fig. 3 shows. However, mass transfer rate-based simulation shows that at least 20 absorber trays would be needed, and even if 20 trays could be shoehorned into the existing shell, twice the necessary amount of CO_2 would be removed. It turns out that a moderate crimp structured packing could be used effectively in this particular column, achieving less than 1 ppmv H_2S and 1.95% CO_2 in a 35-ft bed, but only with an amine solvent containing a stripping promoter. With generic MDEA, simulation showed that 6–7 ppmv H_2S was the best that could be achieved, albeit with 1.9–2.0% CO_2.

Hydraulically speaking, one-pass trays are perfectly adequate for handling the gas and liquid flows in the absorber. However, if two-pass trays were installed, the 65-gpm/ft weir load would drop to about 40 gpm/ft, and a significant benefit to both H_2S removal and CO_2 slip would result. Furthermore, rich-solution loadings are quite modest, so the solvent has more capacity than is being used. This situation suggests that, if the solvent rate were reduced to below the plant limit, even lower weir load and better H_2S removal and CO_2 slip would result. Fig. 4 shows simulated treating results for a 20-tray absorber containing two-pass trays as a function of solvent rate.

This absorber is simulated to handle the full-design gas flow (330 MMscfd) using only generic MDEA at just 70% of the nameplate solvent rate. The keys are using mass transfer rate-based simulation, and knowing how tower internal details (e.g., tray passes) affect the absorption process. This kind of technical sophistication allows a simulation model to be converted into a "virtual plant." An absorber that was completely unable to meet design criteria—no matter how many trays or how much packing it contains—has been transformed into a success.

■ **Contrary to urban legend, entrainment rates and tray capacity do not have to be negatively affected by the sprays that accompany low weir liquid loads.**

As a backup plan, the danger of a small margin for error in meeting the H_2S specification can be mitigated by using a specialty amine to achieve < 0.5 ppmv quite easily. Shale gas can be very challenging to treat. However, mass transfer rate-based simulation and appropriately specified and designed tower internals can make shale gas treating no harder than treating any other gas. Without both ingredients, though, treating shale gas can be a guessing game.

TREATING SHALE GAS FROM BRITISH COLUMBIA

This particular example has 26 ppmv H_2S and about 1.1% CO_2, so the gas needs to be treated for H_2S while allowing as much CO_2 slip as possible, since CO_2 is already below pipeline specifications. Due to the very small amount of acid gas needing to be removed, the absorber has only 12 trays, and plant data indicate that the rich solvent is lightly loaded. The treated gas is below 4 ppmv (no measurement is available), and the unit is slipping about 80% of the CO_2. The weir load is about 30 gpm/ft, so the amount of spray is a significant fraction of the total biphase on the tray. Simulation with no adjustment for low-weir-load (spray-regime) operation suggests a CO_2 slip of 54% with 1 ppmv of H_2S slip.

However, when proper account is taken of the hydraulic operating region in which the trays are operating (spray regime), the simulated CO_2 slip is 78% vs. 80% measured. The H_2S treat is 1.3 ppmv, well below the 4-ppmv specification. Obviously, the tray hydraulic operating region has a profound effect on treating. In particular, selectivity is a very strong function of a tray's hydraulic operating region. The simulations are truly out-of-the-box predictions because no input was used beyond tray construction details and basic plant flows. Nothing was tweaked to force a match to performance data.

OPTIONS

With the wrong modeling tools, shale gas treating units can be very challenging to simulate and, therefore, challenging to build with any reasonable assurance of performance. The difficulty lies in the very low H_2S content of shale gases, which leads to low liquid-to-gas flowrate ratios in amine contactors. A critical and essential element in reliable tower design for shale gas treating is a solid mass transfer rate-based simulator, because tray hydraulics profoundly affect not just pressure drop; they also impact mass transfer and the very separation process itself. Ideal stage calculations are oblivious to what is actually in the column, let alone the mode of operation.

Under conditions that are common in shale gas treating, trays will often have to be operated in the spray regime, where care must be taken on the part of tray designers and design engineers to ensure that downcomers remain positively sealed against massive bypassing of gas. However, even when trays operate with froths, there is great potential advantage to be gained from contriving methods to force operation into the spray region, and the more spray-like the biphase, the greater the potential
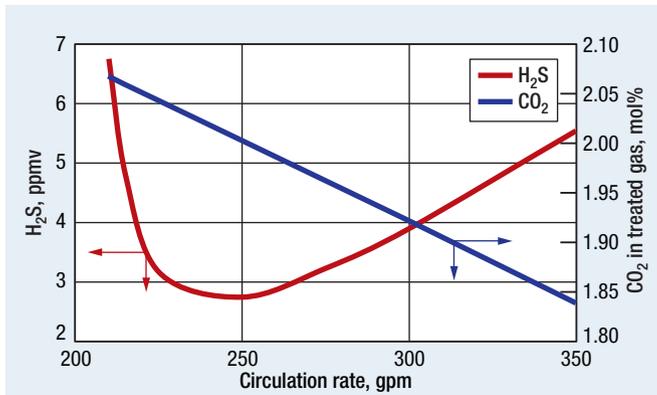
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FIG. 4 Processing 330 MMscfd at reduced circulation rate using 20 two-pass trays with 50 wt% generic MDEA.

Ralph Weiland founded Optimized Gas Treating Inc. 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 and MASc degrees and a PhD degree in chemical engineering from the University of Toronto.

advantage in terms of enhanced selectivity.

Contrary to urban legend, entrainment rates and tray capacity do *not* have to be negatively affected by the sprays that accompany low weir liquid loads. However, tray designers must be attentive to the need for positive downcomer seals, preferably through the use of recessed seal pans beneath the downcomers. Multi-pass trays are an under-appreciated but powerful weapon that can be brought to bear in amine unit design to meet the unique treating challenges offered by shale gases and other gases requiring small liquid flows to treat large volumes. **HP**

Nate Hatcher joined Optimized Gas Treating Inc. as vice president of Technology Development in 2009. He is responsible for making improvements and adding functionality to the ProTreat gas treating process simulator. Mr. Hatcher has spent most of his 16-year career involved with sour-gas treating and sulfur recovery, first in design and startup and later in plant troubleshooting, technical support and process simulation development. He is a member of the Amine Best Practices Group and serves on the Laurance Reid Gas Conditioning Conference advisory board. Mr. Hatcher received a BS degree in chemical engineering from the University of Kansas and is a registered professional engineer in the state of Kansas.
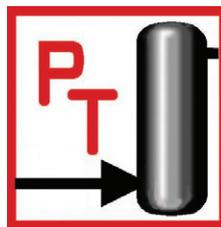
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