

The CONTACTOR™

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Confidence in Design — Got the CO₂ Slip Right?

In selective treating, a great deal hinges on CO₂ slip if only because it sets the proportion of solvent capacity available for H₂S removal. If the expected CO₂ slip is too high, selectivity will be overstated and the result will probably be an optimistic assessment of the expected level of H₂S treating. If simulated CO₂ slip is too low, then the design solvent rate, for example, may be a lot higher than what's really needed: overdesign can be expensive. CO₂ slip and H₂S removal are very closely tied physico-chemically. The combination of CO₂ slip and H₂S removal is called the selectivity.

To understand selectivity at a mechanistic level requires us to

- conceptualize the absorption of these gases in terms of mass transfer rates, and
- understand what the factors are that determine these rates.

Mass and heat transfer rates are quite analogous in that both can be calculated from the rate equations for the two phases. For the liquid phase, for example, the respective heat and mass transfer rates (for a particular species, *i*, such as CO₂) are:

$$Q = h_L a (T_{Wall} - T_{Bulk})$$

$$N_i = E_i k_{i,L}^o a (C_{i,Interface} - C_{i,Bulk})$$

In a nutshell, transfer rates are calculated from transfer coefficients (for heat or mass), the area for transfer, and temperature or concentration differences. These differences are the driving forces. The quantities h_L and $k_{i,L}^o$ are called film coefficients because they pertain to the layer of resistance close to the interface in the liquid. In heat transfer there is a huge database of coefficients for flow through and around tubes, between parallel walls, and around various shapes immersed in flows. For mass transfer the database is not as extensive but it contains enough information to make the calculation of mass transfer rates quite reliable and accurate. There are correlations for various types of trays and for a host of random

and structured packings. The superscript on the $k_{i,L}^o$ term indicates the coefficient is for the component when there is *no* chemical reaction. The effect of reaction is found in the enhancement factor, E_i ; if there is no reaction, E_i is 1.0, and if the reaction is fast, it is large. But the actual value depends on the reaction kinetics, and it can be calculated from the known solutions of equations describing diffusion with chemical reactions of various orders and types. But how does this impact selectivity?

The solubility of H₂S in a given amine is not enormously different from the solubility of CO₂ in the same amine. Solubility is *not* what makes one amine selective and another not. There are two main factors that control selectivity:

- *How fast CO₂ reacts* with the amine, or indeed, whether it reacts at all or not, i.e., the value of the enhancement factor E_i , and
- *The mass transfer characteristics of the contacting device*, i.e., values of the gas- and liquid-side mass transfer coefficients.

At the head of the list is reaction kinetics. H₂S forms H⁺ and HS⁻ ions instantly when it dissolves into water, and water is plentiful. Its kinetics are infinitely fast, putting all the resistance to mass transfer into the gas phase. But CO₂ reacts at finite (albeit sometimes fast) rates with amine, leaving 95% or more of the resistance to CO₂ absorption in the liquid phase. It's the opposite nature of these resistances that results in selectivity. The degree of selectivity can be controlled via CO₂ kinetics (E_i), selection of column internals (which alters the relative values of $k_{i,L}^o$ and $k_{i,G}$), and choice of optimal process conditions, which affect VLE, E_i , $k_{i,L}^o$ and $k_{i,G}$.

Selectivity is superficially a simple term and a simple concept, but it has a somewhat complex explanation at the physical and chemical level needed for the *prediction* of treating column performance. Simulation of amine contactors and

regenerators using ProTreat's® mass transfer rate approach provides a model so firmly grounded in engineering science that it truly builds a virtual plant. It does this by applying phase and reaction equilibria, reaction kinetics, mass transfer characteristics of tower internals, and physical and transport properties such as solvent viscosity and diffusion coefficients into the model.

Getting the CO₂ slip right is critical to predicting absorber performance. One of the most challenging situations for most simulators is posed by packing, especially structured packing because gas treating experience is mostly lacking. It's tough to know how to convert ideal stages into packed height in design, and it's nigh impossible to figure out the selectivity. For the remainder of this issue of The Contactor™, we will look at a specific case.

The absorber in question is treating 966 psia gas containing about 1% CO₂ and 1.6% H₂S with a 12-m bed of Mellapak M252Y structured packing. The solvent is generic 45 wt% MDEA. A solvent analysis was available which showed HSSs at a few 100s of ppmw sodium, potassium, formate and acetate. The lean amine analysis showed an unusually low H₂S loading, but it also showed sulfate and thiosulfate in the sample. Our experience is that these components, especially in a gas plant, are really oxidized lean loading, i.e., H₂S that has been oxidized by air during transport in the sample bottle and during analysis[†]. A charge balance on the sample failed to close, indicative of analysis errors, too. So before the simulations even got underway, we had detected questionable data, in particular the all-important H₂S lean loading. Sulfate and thiosulfate were converted to equivalent H₂S loading and added to the measured loading. Simulations included all other ions.

The H₂S and CO₂ in the treated gas were measured at 2 ppmv and 0.42 mol%, respectively. A straight out-of-the-box ProTreat® simulation predicted 0.7 ppmv H₂S and 0.417 mol% CO₂. Bound amine was not included in the solvent analysis but the ion balance showed unequivocally that some *had* to be present. Just a trace (0.1 wt%) of bound amine matched the performance data at 1.9 ppmv H₂S and 0.421 mol% CO₂.

It may be interesting to look at the H₂S profile in the absorber to see if the column was lean end pinched which would indicate an equilibrium

limit. ProTreat® calculates both the actual and local equilibrium H₂S composition in the gas at all points in the column. Figure 1 shows such a plot.

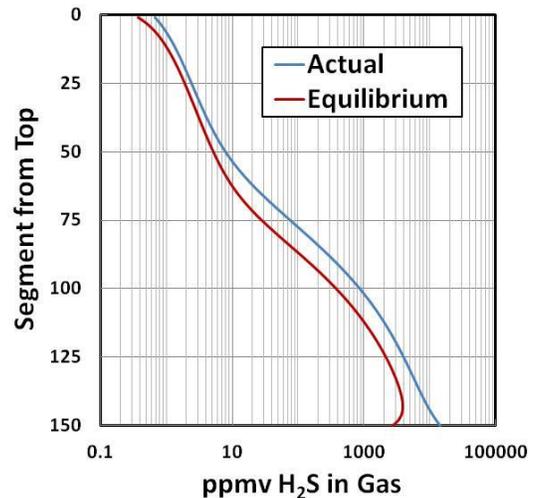


Figure 1 H₂S Profiles in the Absorber

Figure 2 shows the difference between the actual and equilibrium values, in other words, the concentration driving force. Clearly there is a driving force of roughly the same size as the local concentrations themselves.

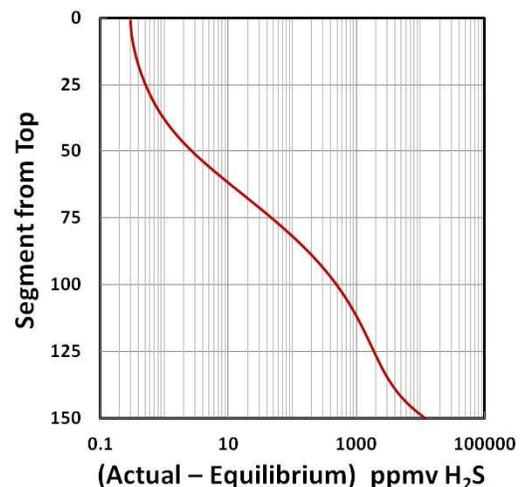


Figure 2 H₂S Driving Force for Absorption

This column is effectively mass transfer rate limited, thus providing a valid test of the efficacy of ProTreat's® ability to predict the performance of structured packing reliably.

To learn more about this and other aspects of gas treating, plan to attend one of our seminars. Visit www.ogtr.com/seminars for details.

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[†] See The Contactor™, Vol. 2, No. 2 for further information on H₂S oxidation and the benefits of charge balancing analyses.