Mass Transfer Pinches in Amine Treaters
Part II: Cases of Piperazine-activated MDEA and Generic MDEA

These days, the term piperazine-activated MDEA almost automatically brings to mind carbon dioxide removal in LNG production. However, this solvent is also used in other deep CO_2 removal applications such as purifying ammonia syngas. Mistaken attempts have been made to reduce carbon dioxide to a few tenths of a mole percent using generic MDEA, but most have failed—MDEA is not nearly reactive enough towards CO_2 to achieve normally even such a modest level of treating, so its reactivity must be boosted. Although other amines such as DGA® can be made to work in LNG applications, piperazine is a common promoter for MDEA. This issue of The Contactor™ will look at two case studies: one in LNG production and the other using generic MDEA alone to remove H_2S from a refinery gas.

Case Study 1: CO_2 Removal in an LNG Unit

This case involves removing 20% CO_2 from a gas at only 16 barg using 33 wt% MDEA solvent containing 7 wt% piperazine. The lean loading is 0.005 moles of CO_2 per mole of total amine. ProTreat® simulation gives the temperature profiles shown in Figure 1. The temperature is so constant over almost the entire upper half of the column that there is a strong suggestion the absorber might be lean-end (top-end) pinched. However, the concentration profiles in Figure 2 suggest quite the opposite.

At the top of the absorber the actual and equilibrium carbon dioxide concentrations in the gas are *three orders of magnitude* apart. *There is a very substantial driving force for absorption, especially at the absorber's lean end*. In fact, pinch conditions are being approached more at the location of the temperature bulge, right at the bottom of the absorber. Temperatures are constant across the top because only parts per million of CO_2 are being removed, not because of a pinch.
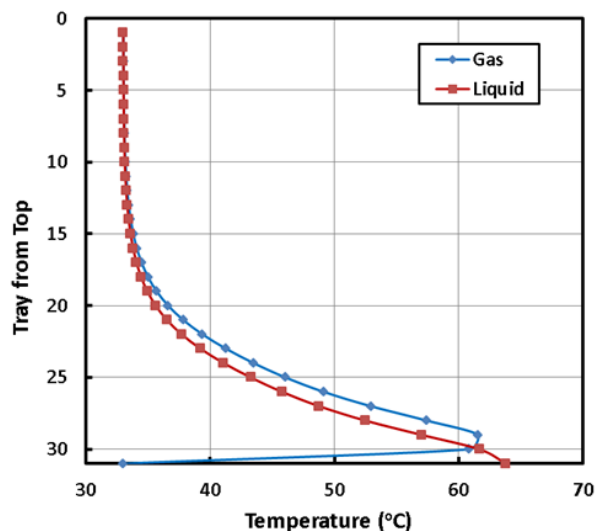

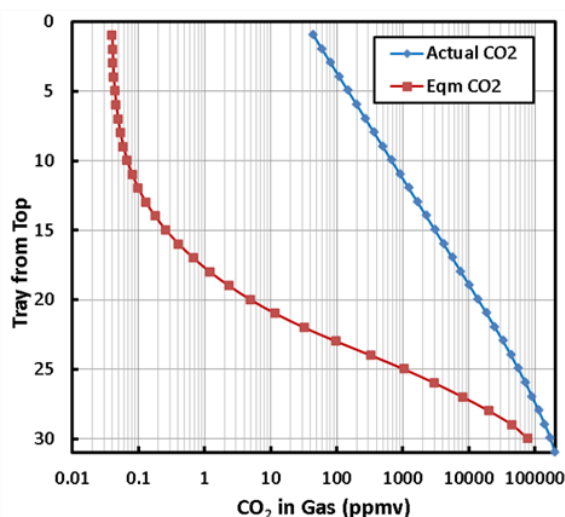**Figure 1   Gas and Liquid Temperatures in the LNG Absorber**

Figure 2   Actual and Equilibrium CO_2 Concentration Profiles in the Gas

Case Study 2: Removing H₂S from Refinery Gas

Raw gas consisting of 3 mole% hydrogen sulfide in predominantly methane and hydrogen with a few percent each of $C_2 - C_5$ hydrocarbons, and nitrogen, flows at 25 kNm³/h. The absorber runs at 7.25 barg and the gas is treated with 41 m³/h of 40 wt% generic MDEA. Figure 3(a) shows the ProTreat® simulated temperature profiles corresponding to these conditions. Temperatures are flat over the upper one third of the absorber, suggesting a lean-end pinch. The pinch is confirmed by the profiles of actual and equilibrium H₂S concentrations shown in Figure 3(b). However, when there is a significant concentration of CO_2 in the gas, the situation is not as clear cut.
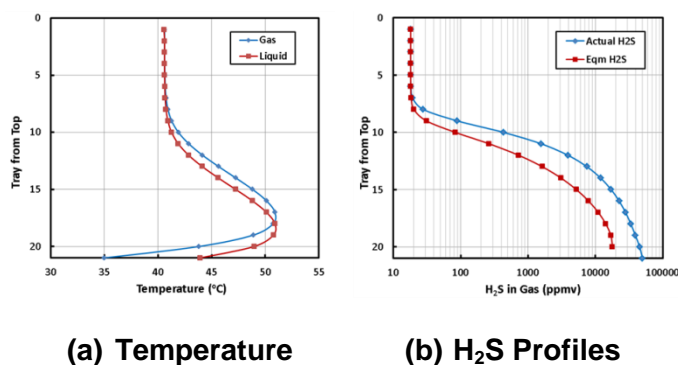

(a) Temperature   (b) H₂S Profiles

Figure 3   Temperatures & Mole Fractions H₂S in an Absorber with H₂S-Only

Figure 4 shows the temperature and H₂S profiles when the gas contains 2 mol% CO_2 in addition to the original 3 mol% H₂S. The temperature bulge is a little hotter because of the additional heat release from CO_2 absorption. But the temperature profile, instead of becoming flat near the top of the absorber, now decreases linearly across the same top six trays.
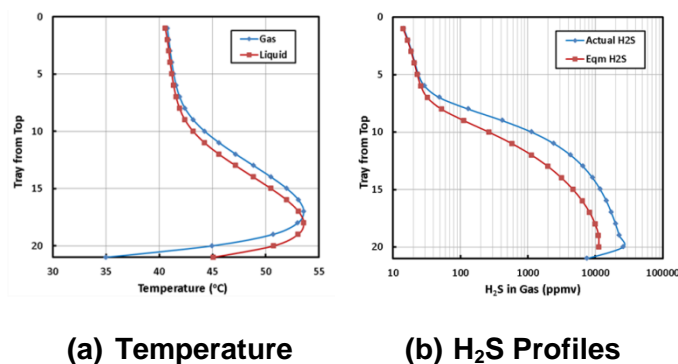

(a) Temperature   (b) H₂S Profiles

Figure 4   Temperatures & Mole Fractions H₂S in an Absorber with Mixed Gases

Across the entire column, CO_2 drops linearly from 2% to 1.74% so heat from this source is being released at much the same rate on every tray in the column. Thus, the steady temperature rise from trays 1 to 6 is only to be expected. The actual H₂S concentration and the equilibrium concentration also show a steady rise across these six trays—higher temperatures mean greater equilibrium partial pressure H₂S. In addition, increasing CO_2 loading of the solvent also causes increased H₂S vapor pressure. Interestingly, however, *hydrogen sulphide is at near equilibrium with the liquid locally on every one of these six trays.* On that basis, its *absorption is still pinched from a driving force standpoint.* The continued absorption of hydrogen sulphide across the top trays results from shifting equilibrium caused by simultaneous carbon dioxide absorption.

Conclusion 1

Temperature profiles alone cannot be relied upon to indicate pinch conditions, at least not for lean-end pinches. To decide, one must compare equilibrium and actual compositions tray-wise across the column before judgment can be passed.

Conclusion 2

If an absorber is lean-end pinched as in Figures 2 and 3a, the pinched component in the treated gas is in equilibrium with the lean solvent. Therefore, treating can be controlled by manipulating the lean solvent loading of that component. Managing the regenerator reboiler duty is often the easiest way to do this.

Conclusion 3

The concentration of a component does not have to remain constant across the top of the column for its absorption to be called lean-end pinched. Its concentration may continue to change as it does in Figure 4b. What is required is that the *gas above a given tray or set of trays in the top of the column be in equilibrium with the solvent on these trays*, i.e., the actual and equilibrium concentrations should coincide on the plot.

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