The CONTACTOR™

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Mass Transfer Pinches in Amine Treaters

Part III: Bulge Pinches in Deep CO_2 Removal—LNG

Deep CO_2 removal applications include LNG production and the treating of ammonia synthesis gas. The most commonly used solvent is piperazine-activated MDEA although DGA® is also used in these processes. MDEA alone is not nearly reactive enough towards CO_2 to meet typical LNG and syngas specifications—its reactivity must be boosted, and the high reactivity of piperazine makes it an ideal reaction rate promoter. This issue of The Contactor™ continues the analysis of CO_2 removal in LNG production.

Case Study: CO_2 Removal in an LNG Unit

The case involves removing 20% CO_2 from a gas at 17.1 barg using 33 wt% MDEA solvent promoted with 7 wt% piperazine. The lean loading is 0.005 moles of CO_2 per mole of total amine (MDEA + piperazine). ProTreat® simulation at a solvent flow of 350 m^3/h showed a very flat temperature profile across the top half of the absorber, suggesting a lean end pinch. However, the profiles of actual and equilibrium carbon dioxide concentrations above each tray (Figure 1) show that there is a very substantial driving force for absorption, *especially at the absorber's lean end*. In fact, pinch conditions are being approached more closely in the vicinity of the temperature bulge right near the bottom of the absorber.

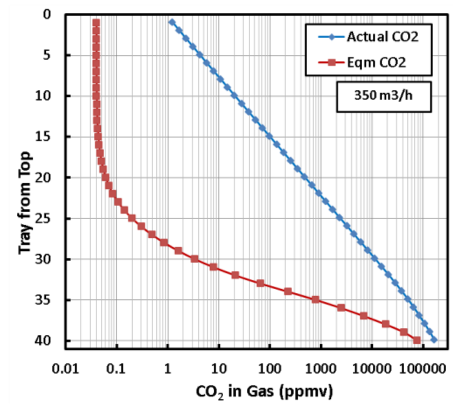
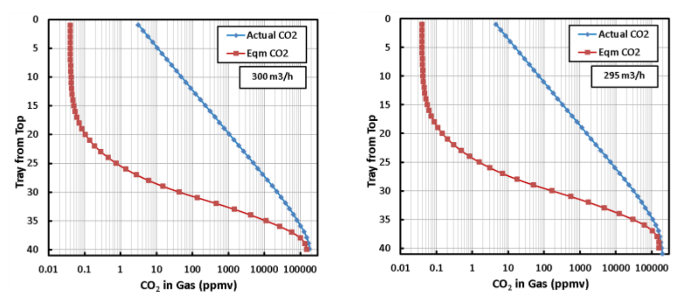


Figure 1 Actual and Equilibrium CO_2 Concentration Profiles in the Gas



(a) 300 m^3/h **(b) 295 m^3/h**

Figure 2 Profiles at Lower Solvent Rates

When the solvent flow is dropped to 300 m^3/h and then to 295 m^3/h, the concentration profiles start to show a serious approach to being pinched near the very bottom of the absorber (Figure 2). Figure 3 shows an enlarged view of Figure 2b near the absorber bottom. From this it can be seen that the absorber is not quite pinched yet. However, a further reduction of only 5 m^3/h in solvent flow rate sends the absorber into a very broad *bulge* pinch as shown in Figure 4. There appears to be virtually no absorption taking place in the lower half of the column, although an expanded view indicates only trays 25 through 36 are truly at equilibrium. It is perhaps interesting to note that between 350 and 295 m^3/h solvent flow the CO2 in the treated gas increases from 1 ppmv to 15 ppmv but at 290 m^3/h the gas has risen to 1,500 ppmv. Treating has failed precipitously and without warning. Anyone operating this particular absorber using the bare minimum of solvent flow would possibly be completely shocked to find the plant going in and out of control this way.

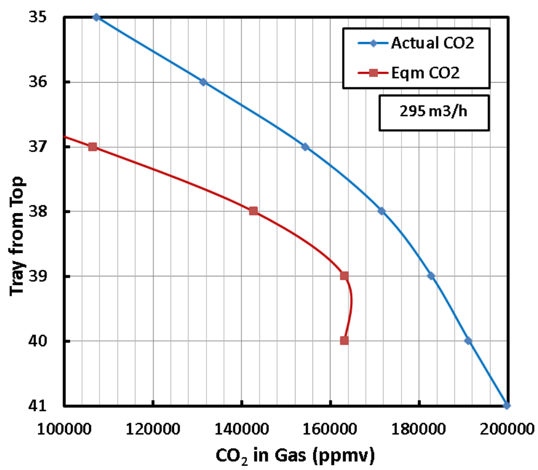


Figure 3 Magnified View of Concentration Profiles at 295 m^3/h Solvent Flow

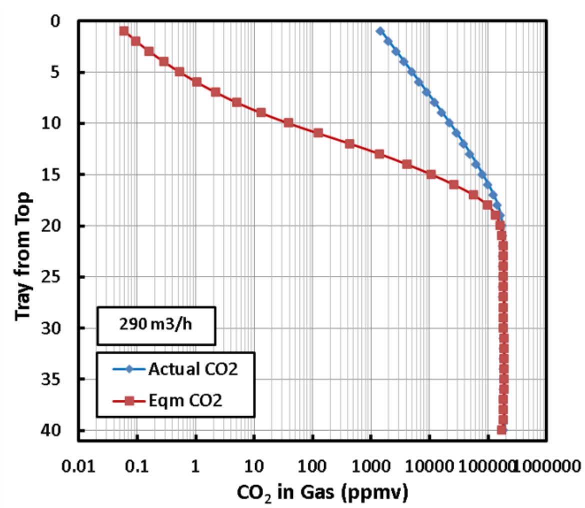


Figure 4 A Bulge Pinch — Concentration Profiles at 290 m^3/h Solvent Flow

Process licensors and designers are aware of this kind of behavior and they make operating recommendations intended to keep the plant a safe distance away from such operating conditions. Nevertheless, if only to cope with changing feed gas conditions, it would certainly be useful to know just how close the precipice really is.

Just before the normal, sharp temperature bulge morphs into an enormously broad, flat one, the driving force for absorption at the top of the sharp bulge becomes essentially zero. Any attempt to load the solvent any higher (in this case, by lowering its flow rate ever so slightly) forces the bulge to propagate across a considerable number of trays. The bulge cannot grow in magnitude; all it can do is spread until it meets sufficiently cold solvent to lower its temperature and allow absorption to resume. Incidentally, slightly increasing the lean solvent loading has the same effect as slightly decreasing the solvent flow.

Bulge pinches are not limited to piperazine-promoted MDEA. They can occur with almost any reactive solvent and are related to solvent capacity. In the present case, the temperature profile in normal operation exhibits a sharp bulge which at first moves slowly up the column (and becomes slightly hotter) with decreasing solvent flow. When the bulge pinch occurs, it does so simultaneously with what might be called CO_2 breakthrough and the formation of a broad temperature bulge rather than a sharp one, but with a temperature only two or three degrees hotter.

Conclusion 1

Bulge pinches tend to be associated with unstable operating regions and with designs that are inadvertently too tightly optimised. The cure is simple: recognise the problem and stay away from operating too close to the edge, where columns become harder, if not impossible, to control.

Conclusion 2

With a bulge pinch, significant driving force for absorption is apparent at both ends of the column, but in the middle section accompanying the temperature bulge, the driving force becomes quite small.

Conclusion 3

During design and optimisation, if a small change in a variable causes an unexpectedly large change in a simulated performance parameter, your simulator may really not have gone crazy: you may have hit upon an inherently unstable (uncontrollable) region of operation!

The only way to detect the possibility of a bulge pinch and to pinpoint the absorber's operating envelope reliably is by mass transfer rate-based simulation. That's the ProTreat® way.

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

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