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Extreme Sensitivity to Solvent Temperature in the CO_2 Removal Section of an Ammonia Plant

Removing CO_2 in ammonia plants is an operation with a lot of room for process innovation and the development of clever flowsheeting schemes to minimize energy consumption. An example is the two-stage CO_2 absorber shown in Figure 1 and used in an ammonia plant in the Middle East. Because the heat exchange equipment were designed too tightly, the semi-lean stream of piperazine-promoted MDEA was operating too hot and the plant could not treat below a few thousands of ppm CO_2 in the syngas.

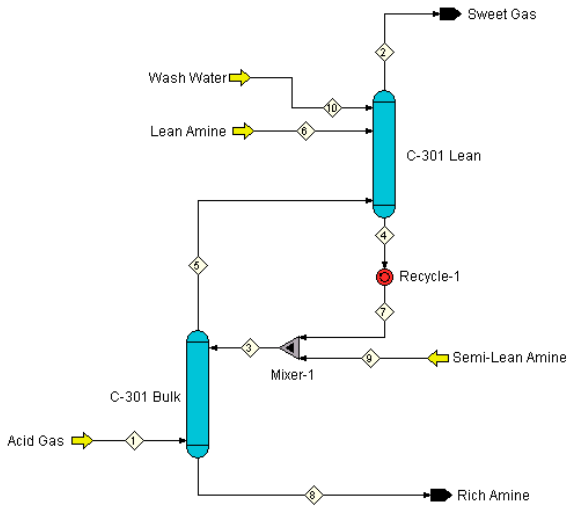

Figure 1 Two-Stage Absorber for CO_2 Removal in an Ammonia Syngas Plant

It has already been established[1,2] that there is a boundary that marks the edge of a stable operating region when using piperazine-MDEA blends. In the two-stage syngas absorber shown in the figure, operating the unit at higher and higher *semi*-lean temperatures leads to the performance curve shown in Figure 2.

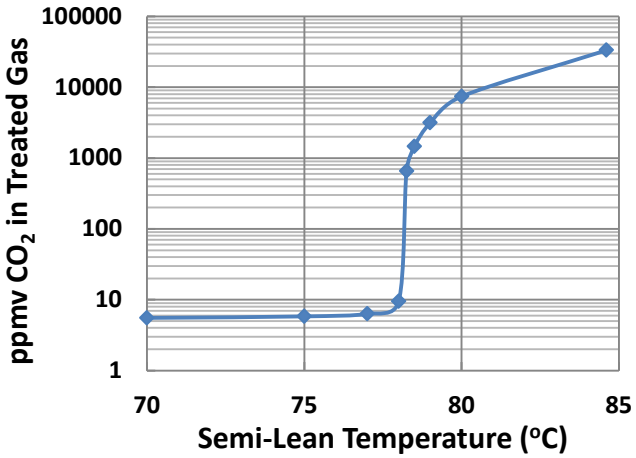

Figure 2 Effect of Semi-lean Temperature on Performance of 2-Stage Absorber

As long as the semi-lean temperature is kept below about 78°C, the treated gas will more than meet a 500 ppmv CO_2 treating specification, and by quite a wide margin. But it is not possible to operate this unit with a semi-lean feed much above 78°C stably because the packed lean absorber (C-301 Lean) goes immediately from being lean-end to rich-end pinched. This can be seen in the two temperature profiles shown in Figures 3 and 4 where the semi-lean temperatures are separated by only 0.25°C. When the semi-lean temperature is slightly too high, the packed *bulk* absorber (C-301 Bulk) cannot adequately handle the CO_2 load and the excess CO_2 spills over into the Lean absorber. It immediately overwhelms it into a rich-end pinch condition. This sends the CO_2 in the final treated gas from 10 ppmv to some 700 ppmv: a huge performance drop for only a very small temperature change! Operation with semi-lean at 78°C is completely unstable—*even the slightest*

[1] Weiland, R.H. and Hatcher, N.A., *Foundations of Failure*, Hydrocarbon Engineering, December (2011)
[2] Weiland, R.H. and Hatcher, N.A., *Stable Operating Limits in Amine Treating Units*, Proceedings of the Lawrence Reid Gas Conditioning Conference, Norman, Oklahoma, February, 2011.

variation of inlet CO_2 content, solvent rate, gas rate, or temperature in the wrong direction will cause the outlet gas to go wildly off spec.

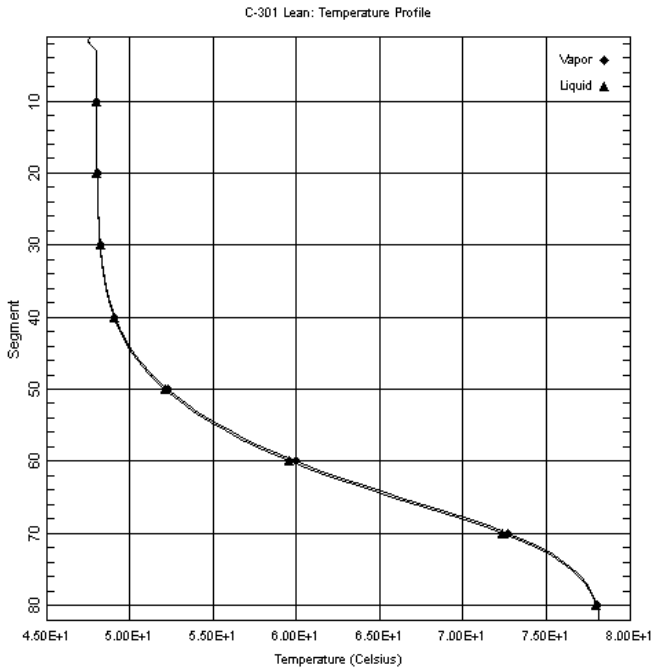

Figure 3 "C-301 Lean" Temperature Profile with Semi-lean at 78.0ºC

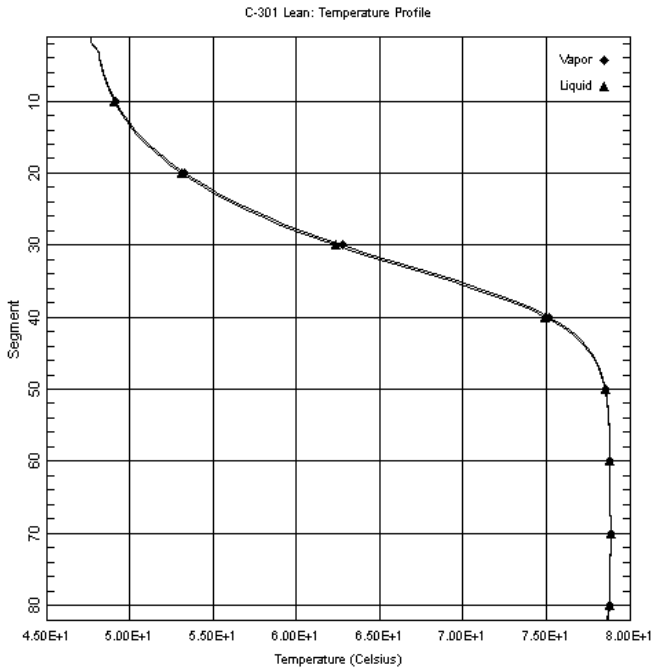

Figure 4 "C-301 Lean" Temperature Profile with Semi-lean at 78.25ºC

The transition from lean-end to rich end pinch[3] is sudden because the slightly higher temperature of the large-flow *semi*-lean amine lowers the CO_2 absorption capacity of the *bulk* column (C-301 Bulk) just enough that it spills an unmanageable amount of CO_2 over into the trace-removal column "C-301 Lean". Because the flow rate of fully lean solvent is relatively small, the CO_2 spillover starts to swamp the small-flow, fully-lean amine running through this part of the column.

As shown in the cited references, sudden failures-to-treat can also occur in LNG applications using piperazine promoted MDEA, where a slight reduction in solvent flow too close to the stable operating limit can send the treated gas from a few ppmv CO2 to well over 1,000 ppmv. A discussion of some interesting behavior in an LNG application and performance comparison between packing and trays will appear in the November, 2012 issue of The Contactor™.

This failure-to-treat behavior is apparently well-known, at least to the more astute solvent vendors and process licensors. However, some engineering contractors continue to provide designs that are too tight. The result is that plants are still being designed and commissioned with built-in instabilities.

This is not the only kind of seemingly unusual plant performance behavior that can be found with piperazine activation. Indeed, unexpected performance is not limited to piperazine-promoted solvents. In the January, 2013 issue of The Contactor™ we will look at the performance map of another fast reacting amine: MEA in a post-combustion, carbon-capture situation.

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To learn more about this and other aspects of gas treating, plan to attend one of our free seminars. Visit www.ogtrt.com/seminars for details on free one-day seminars in Calgary, Denver, Tulsa, and Houston being presented in 2012.

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[3] The telltale characteristic of a lean-end pinched absorber is a temperature (or composition) profile that is fairly flat near the top of the column. A rich-end pinch is characterized by a flat temperature (or composition) profile in the bottom of the absorber. However, when H_2S and CO_2 are present together, the absorber may be pinched with respect to H_2S at the top while CO_2 continues to absorb. Thus, if H_2S drops by only a few ppm over the top several trays, the absorber is lean-pinched in H_2S even though temperature may be changing.