Amine regenerator instabilities

Ralph H. Weiland and Nathan A. Hatcher, Optimized Gas Treating, Inc., USA, examine the stable operating limits in amine regenerators.

Solvent and equipment limitations restrict amine unit performance. For example, there are recommended limits on maximum solvent loading, maximum line velocities (especially in piping carrying hot rich amine), and the approach to flooding limits in towers. None of these limitations usually lead to operational instability; they just restrict performance.

Modern designs and operations are often very tight, with operating expenses (OPEX) cut to the bone. Sometimes this can push plant operations close to an operational cliff where even a small excursion in a parameter will result in a very large drop in performance. One or more process parameters can become sensitive to upset, making the plant as a whole very hard to operate.

An earlier article described unstable operation of absorbers, in which treating performance became incredibly responsive to small changes in process parameters.[1] In this case, the article will focus on what might cause regenerators to overreact to changes in reboiler duty or rich amine feed temperature. Gas treating performance is lost when regenerators suddenly begin to produce grossly under stripped amine following this overreaction.

Most amine regenerators are operated with enough boil up to provide a reasonable flow of condensable stripping steam to every tray or all of the packing in the column. It is not enough for each tray to have vapour flowing through it; the water content of the vapour must be high enough to transfer heat to the liquid via condensation. Normally, regenerator vapours have high water content and stripping energy is provided by steam condensation. Sometimes, however, regenerators are purposefully operated with such a low flow of energy to the reboiler that only the lowermost trays receive condensable stripping steam. This seems to be the norm for post combustion carbon capture plant designs, and it occurs frequently when the CO_2 section of an ammonia plant is retrofitted with activated (piperazine promoted) MDEA.

The transition from over boiled to under boiled can be rather sudden, leading to unexpected plant instability. In this

context, instability does not imply inoperability; it means an unexpectedly large change in a performance variable caused by a relative change in a control variable. The transition does not result solely from throttling reboiler energy (steam, hot oil) flow. It can equally well be caused by increased solvent load on the regenerator or by gradual loss of heat transfer efficiency in the cross exchanger, perhaps as a result of fouling, leading to colder than intended rich amine entering the regenerator.

Case study: amine regenerator

This example centres on a 20 tray regenerator with kettle reboiler stripping a 50 wt% MDEA solvent loaded with H_2S and CO_2 to 0.28 and 0.23 mol/mol, respectively. This 2 ft diameter column is fed on the third tray from the top and operates at a top pressure of 13.5 psig. The study was carried out using a genuine mass transfer rate based column model embedded within the ProTreat®

Table 1. Reflux and stripping ratio dependence on feed temperature

Feed temperature (°F)	Reflux ratio	Stripping ratio
185	0.128	0.163
190	0.153	0.189
195	0.185	0.221
200	0.226	0.262
205	0.375	0.411
210	0.529	0.565
215	0.681	0.717

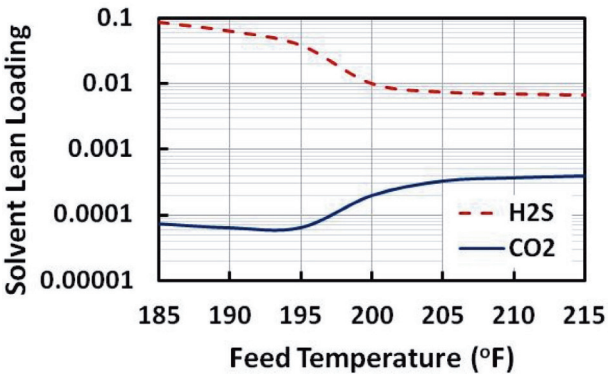

Figure 1. Effect of feed temperature on lean loadings.

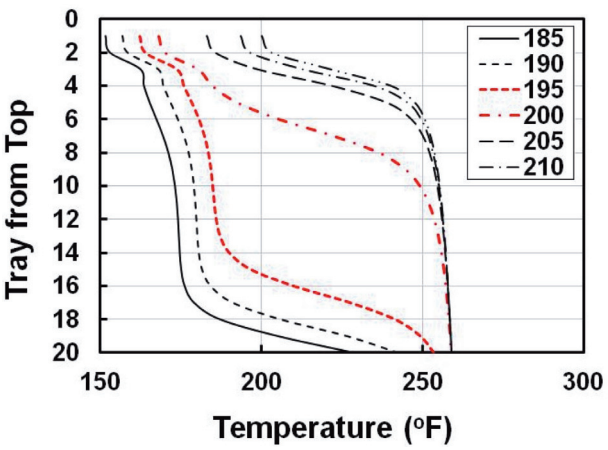

Figure 2. Effect of feed temperature (parameter) on profiles in an MDEA regenerator.

simulator. This kind of simulation creates a close computational approximation to a real plant, and allows the impact of changing process parameters to be predicted with extremely high reliability because the model itself contains all the pertinent physics, chemistry and engineering.

Effect of rich amine feed temperature

With the reboiler duty set at 3.0 million Btu/hr, the temperature of the rich amine feeding the column was varied from 185 – 215 °F in 5 °F increments in the simulations. Figure 1 illustrates the simulated effect of feed temperature on the solvent lean loadings produced by the regenerator. Figure 2 shows vapour phase temperature profiles. When the feed temperature is dropped from 200 °F to 195 °F, there is a sudden collapse in the temperatures throughout most of the column. This is the same temperature range over which the lean loadings experience a sizeable change. Interestingly, the H_2S and CO_2 loadings move in opposite directions. A glance at the loading profiles at 195 °F and 200 °F shows why (Figure 3).

Figure 3 (top) shows that a 195 °F feed makes the top part of the column so cold that it actually behaves as an absorber for H_2S. The H_2S stripped from the solvent on the bottom few trays and in the reboiler gets reabsorbed in the rest of the column. Both graphs in Figure 3 show that a hotter rich feed allows more of both gases to flash on the feed tray; however, Figure 3 (bottom) shows that CO_2 is stripped throughout the regenerator, regardless of the lower feed temperature. The higher H_2S loadings at lower temperatures actually assist CO_2 stripping because higher H_2S loading forces a higher CO_2 partial pressure at equilibrium. This can be seen in

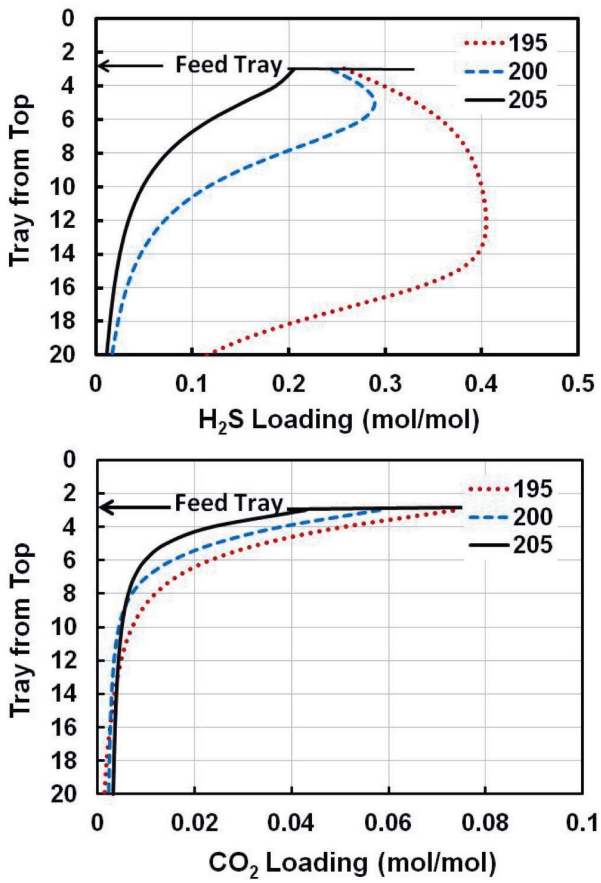

Figure 3. Effect of feed temperature (parameter) on loading profiles in MDEA regenerator. H_2S loading profile (top) and CO_2 loading profile (bottom).

Figure 3 (bottom), where towards the bottom of the column a leaner lean loading is reached at lower temperature.

Table 1 shows how reflux ratio and stripping ratio depend on the rich amine feed temperature. (Reflux ratio is the molar flow of water returned to the column as reflux divided by the molar flow rate of acid gases overhead. Stripping ratio is the ratio of water to acid gases in the column overhead vapour and is more nearly independent of how the condenser operates.) Obviously the more sub cooled below its bubble point the rich feed is, the more steam must be condensed to heat it and therefore the less water vapour there is to condense from the acid gas going overhead to the condenser.

It is common in gas treating to see rules of thumb for what are reasonable reflux ratios for the regeneration of various amines as though reflux ratio were an indication of the reboiler energy needed; however, given the dependence of this parameter on feed temperature, it should not be applied blindly. Its use must be tempered with good judgment.

Table 2. Reflux and stripping ratio dependence on reboiler duty

Reboiler duty (million Btu/hr)	Reflux ratio	Stripping ratio
2.25	0.299	0.334
2.40	0.300	0.336
2.50	0.301	0.337
2.60	0.303	0.339
2.75	0.364	0.400
3.00	0.529	0.565
3.50	0.866	0.901
4.00	1.198	1.234
5.00	1.858	1.893

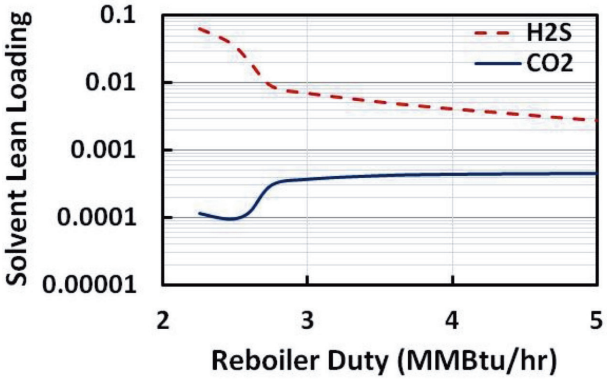

Figure 4. Effect of reboiler duty on lean loadings.

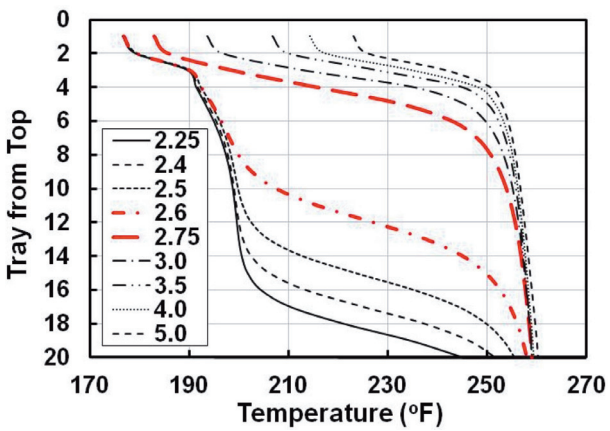

Figure 5. Effect of reboiler duty on regenerator temperature profiles.

Effect of reboiler duty

Most of what has already been written about the effect of rich amine feed temperature also applies to reboiler duty. As Figure 4 shows, sharp changes in acid gas loadings result in between 2.5 – 2.8 million Btu/hr reboiler duty with a rich amine temperature of 210 °F. For the reason already discussed, the response of H_2S and CO_2 loading are in opposite directions. And, as shown in Figure 4, the sudden changes in lean loadings occur right where the temperature profiles indicate the collapse of steam flow through the tower, at reboiler duties between 2.6 – 2.75 million Btu/hr. It should be noted that in the absence of H_2S, an improvement to CO_2 lean loading would not occur at low reboiler duties. The improvement seen in Figure 4 is strictly the result of H_2S absorption in the stripper pushing CO_2 out, just as the vapour to liquid equilibrium says it must.

Table 2 shows how reflux ratio and stripping ratio depend on reboiler duty, and it should be noted that values of reflux and stripping ratio at low duties are quite similar to values at low feed temperatures. Once again, these results suggest that rules of thumb based on reflux and stripping ratio are not as credible as one might be led to believe. Good judgment is required for successful application.

Conclusion

Operating regions in which unexpectedly large changes in performance occur as a consequence of normal changes in operating parameters can be highly unstable, and controllers might not have been tuned to operate in such regions. In this case, the response of H_2S lean loading to reboiler duty is approximately 50 times greater near the point of steam flow collapse than it is at twice the duty. CO_2 lean loading is nearly 100 times more sensitive, and in the opposite direction. This suggests that regenerators operating near the point of incipient steam flow collapse may be hard to control, especially if the reboiler duty is cascaded to a temperature (feed tray, for example) within the tower for energy optimisation. To minimise energy consumption, this region may be the precise area where control is desired. However, attempting to control performance on a cliff may not be advisable.

When tightly run regenerators are coupled to absorbers operating near the point where their operation changes from lean end to rich end pinched, the instabilities in both can be exacerbated. This is especially true when very fast reacting systems such as piperazine promoted MDEA are involved. In such cases, failure to treat can be catastrophic and arrive virtually unannounced.

The performance of amine plants can not only be limited by thermodynamics, hydraulics and corrosion. When plants are pushed too far above their design capacity or an attempt is made to cut operating costs below what is prudent, it is quite possible for the plant to be pushed into an unstable operating region and the ability to control the plant will ultimately become the real operating limit.

References

1. WEILAND, R.H. and HATCHER, N.A.; 'Foundations of failure', Hydrocarbon Engineering, December 2011.