STABLE OPERATING LIMITS IN AMINE TREATING UNITS

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Abstract

Common guidelines for amine-based acid gas recovery (AGR) unit designs include the maximum loading (thermodynamic) limit, hydraulic limits, and limitations imposed by anticipated degradation and corrosion. Our concern in this paper is with operability limitations.

Operability limits encompass performance barriers imposed by the size and location of temperature bulges, as well as high treated gas and rich solvent temperatures. These are commonly known as bulge, lean-end and rich-end pinch conditions. Temperature bulges, in particular, pose serious albeit sometime subtle problems that prevent achieving design treating rates. In a similar vein, regenerators are often very forgiving over wide ranges of operating conditions yet they can fail precipitously with only a small change in an operating parameter. This paper analyzes a series of design cases from the standpoint of operating stability.

Introduction

Amine unit performance is directly affected by solvent and equipment limitations. For example, rich amine CO_2 loadings are usually recommended to be kept below about 0.5 moles of CO_2 per mole of amine because of accelerated corrosion on hot surfaces. There are general rules of thumb for maximum line velocities to prevent scouring of metal surfaces and removal of protective films. Tower internals have natural limitations on gas and liquid rates above which jet flooding or downcomer backup and choke flooding become more likely. Towers have capacity limits. The capacity of a solvent is affected by its temperature and the partial pressures of the acid gases over it. So, corrosion can limit rich solvent loadings, tower hydraulic capacity limits throughput, and operating conditions affect the solvent's capacity to absorb and hold acid gas. However, none of these limitations usually lead to any form of operational instability; they just restrict performance.

Over the years plant designs and operations have become increasingly lean, with operating expenses (OPEX) cut to the bone. This sometimes pushes plant operations very close to operational limits where only a small excursion in a parameter can cause a plant to miss its treating goal by a very wide margin. Pushed to the limit, plants can become unstable and very hard to operate.

The other reflection of cost conscious operations is the need to process higher and higher gas volumes with the same equipment, forcing operating process plants significantly above their original design capacity. Eventually the plant will be pushed to its limit where it will be unable to handle any but the smallest excursions without going wildly off specification.

A comprehensive sensitivity and operability study should be part of any plant design. A properly conducted study using a reliable and realistic simulation tool will reveal the edges of operating cliffs and regions where operability may be compromised. These unstable regions are determined not by phase equilibrium limitations, hydraulic limits, or such factors as corrosion and solvent degradation that limit capacity or performance. They are determined by the very nature of the process itself.

Amine plants can be quite forgiving of upsets and often run unattended for long periods of time, so the notion that such plants are highly stable is well founded. However, unlimited stability cannot always be taken as a given. When operators try to cut solvent rates and reboiler duties too far or try to push gas rates too high there can be very sudden failures of absorbers to treat properly, and regenerators to strip adequately. This paper shows several instances wherein (a) an absorber suddenly fails to treat by a wide margin in response to a very small change in solvent circulation rate and (b) the flow of stripping steam through a regeneration column suddenly collapses and the lean solvent loading rises to unmanageable levels.

Amine Absorbers

The most economical way to operate an absorber is with the minimum solvent rate necessary to absorb the requisite amount of acid gases and meet the specifications on the treated gas. This is predicated on the solvent rate being high enough to keep the rich amine loading below some predetermined maximum value. We will look at three cases of absorber performance as the solvent rate is turned down. The three cases are a selective treater using MDEA, removal of CO_2 from a 5% gas using MEA, and removal of CO_2 from a 20% gas using piperazine-activated MDEA.

Selective Treating Using MDEA

The 20-tray absorber is to remove H_2S to below 4 ppmv from sour methane containing 2.5% H_2S and 2.0% CO_2 at 340 psia and 115°F. The solvent is 40 wt% MDEA at 120°F with H_2S and CO_2 mole loadings of 0.001 and 0.003, respectively. The contactor was simulated using ProTreat™, a mass and heat transfer rate-based process simulator. Figure 1 is a plot of temperature profiles simulated at a series of solvent circulation rates. When the temperature profile bulges near the column's bottom, as it does at
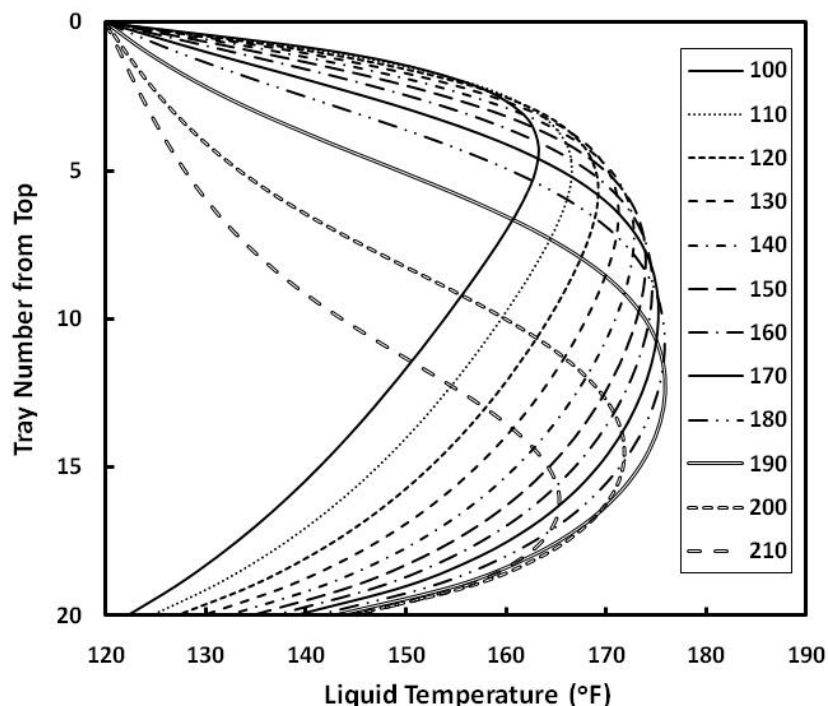

Figure 1   MDEA Absorber Temperature Profiles at Various Solvent Rates (USgpm)

solvent rates of 200 and 210 gpm, the absorber is being fed with more than more than enough solvent to keep the contactor lean-end pinched. This is confirmed by the results shown in Figure 2 where it can be seen that as the solvent circulation rate is increased above about 205 gpm, there is no further improvement in H_2S removal. The treated gas H_2S level is determined by the lean amine quality, which is determined in turn by the regeneration side of the process. However, as the solvent rate is turned down below 205 gpm, the absorber begins to lose treat and this occurs fairly rapidly. Only a 2.5% drop in solvent rate from 200 to 195 gpm results in the H_2S leak going from 4 ppmv to 15 ppmv, and a further 2.5% drop pushes the H_2S leak to 50 ppmv. In other words, a 5% decrease in solvent flow results in an order-of-magnitude increase in H_2S leak.

At around 200 gpm, the solvent barely has sufficient capacity to absorb the requisite amounts of the acid gases and below that flow rate the solvent falls increasingly short on capacity. Consequently, the acid gases it cannot absorb simply pass through the column and exit with the treated gas. This is what causes the transition from <4 ppmv H_2S gas to a gas containing 10s and 100s of ppm. Another term for this is acid gas breakthrough. In the vicinity of breakthrough, the column will become harder to control because small fluctuations in such process parameters as solvent flow rate, raw gas flow or raw gas composition will cause changes in treating that might be several 10s of times greater than the original fluctuation. Nevertheless, temperature profiles change quite smoothly from lean-end to rich-end pinched conditions as solvent rate is decreased.

This particular absorber could probably still be operated satisfactorily at 200 gpm with an override on circulation rate triggered by a high temperature reading (>150°F) from a thermocouple installed on tray 6 or 7. The operation becomes more sensitive to circulation rate around 200 gpm but the treating response to reasonable changes in circulation rate is moderate: the column could not be called unstable.
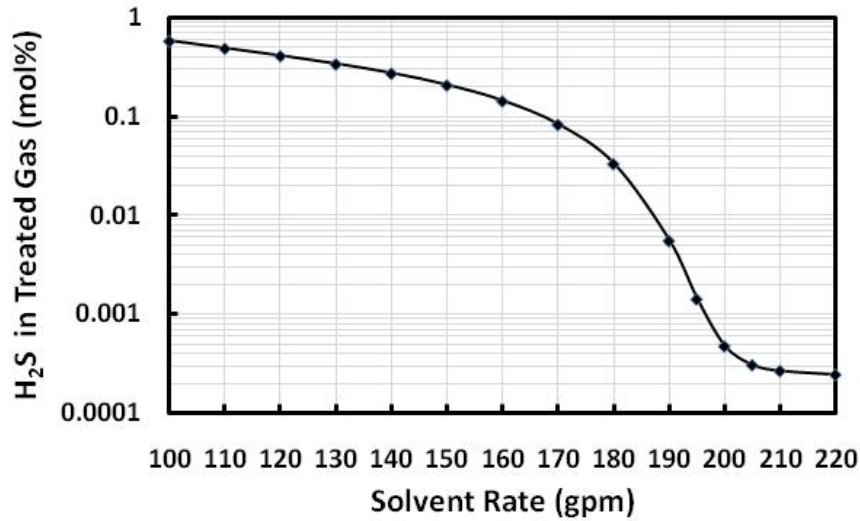

Figure 2   H₂S Leak from an MDEA Absorber at Various Solvent Rates

Deep CO₂ Removal using MEA
This case involves the removal of 5% CO_2 to <10 ppmv using 30 wt% MEA using a 20-tray contactor. Solvent lean loading is assumed to be 0.1 mol/mol. As Figure 3 shows, at solvent flow rates above about 240 gpm, the 10 ppmv specification can be met; however, there is a precipitous rise in CO_2 leak in the treated gas when the solvent rate falls below this value. A 4% decrease in solvent flow from 240 to 230 gpm causes the CO_2 content of the treated gas to rise from 10 ppmv to 300 ppmv. If this were an LNG plant, for example, this increase would be a disaster.
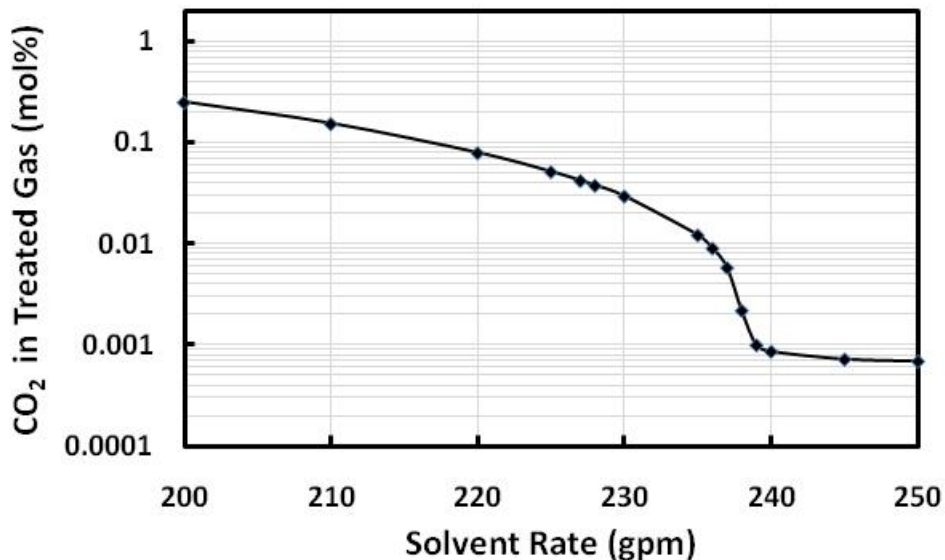

Figure 3   CO₂ Leak from an MEA Absorber at Various Solvent Rates

The temperature profiles shown in Figure 4 reveal a much more sudden transition from lean-end (bulge at the bottom) to rich-end (bulge at the top) pinch conditions than displayed by MDEA (Figure 2). The rapidity of transition is caused by the fast chemical reaction in a liquid-phase controlled process.
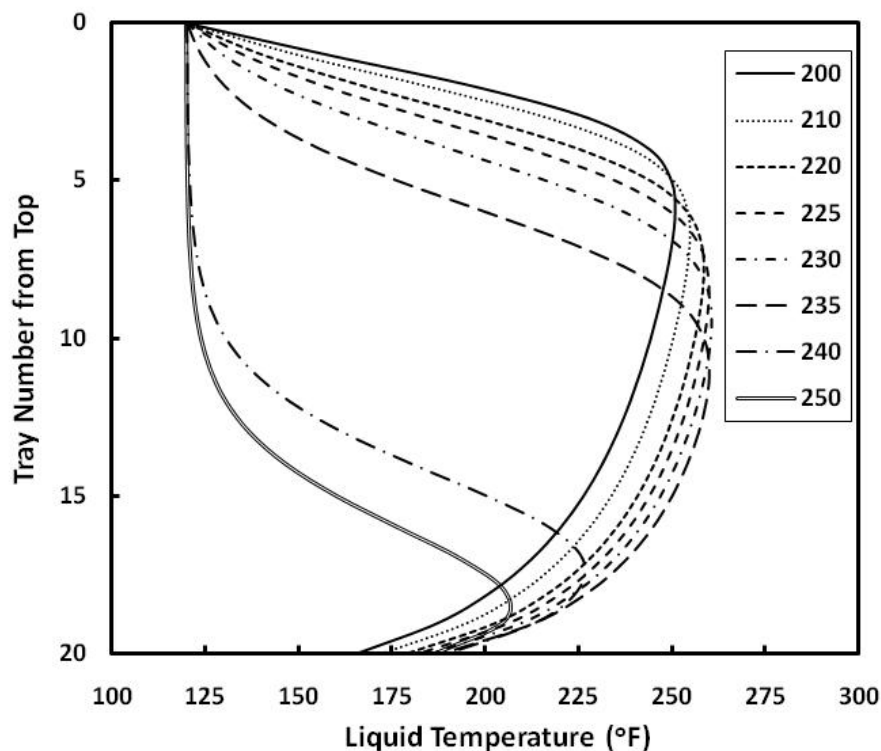

Figure 4   MEA Absorber Temperature Profiles at Various Solvent Rates (USgpm)

Piperazine-promoted MDEA

Piperazine promotion of MDEA has been used for over 25 years to remove CO_2 from synthesis gases down to < 1,000 ppmv levels and, more recently, for very deep CO_2 removal preparatory to natural gas liquefaction. This example uses a 33 wt% MDEA with 7 wt% piperazine solvent to remove CO_2 from a dehydrated raw gas containing 20% CO_2 down to a few parts per million. Gas pressure is 16 bar(g). Figure 5 shows the treating response to changes in solvent circulation rate (reported as percent of design flow), and Figure 6 shows how contactor temperature profiles change.

A 1% decrease in solvent rate from 89 to 88% of design flow is simulated to cause a three-orders-of-magnitude (1000 fold) increase in CO_2 content from below 1 ppmv to 2,000 ppmv! The temperature profile goes from being bulged only a short way from the bottom of the column to a temperature bulge occupying nearly the lower two-thirds of the column (the column is packed with IMTP-25 random packing). At 88.9% of design flow this column is operating right on the edge of a very steep cliff; at 88.8% it has fallen over the edge. The reason for the now extraordinary sensitivity (instability) is the rapidity of the reaction rate of CO_2 with piperazine. Carbon dioxide reacts so quickly that at adequate solvent rate most of it is removed from gas in the first couple of meters of packing that the gas encounters. The next two or three meters do polishing, and above the midpoint the rest of the column does nothing at all. Because breakthrough depends on the solvent capacity relative to the CO_2 to be removed from the gas, the breakthrough solvent rate is relatively independent of the amount of packing in the column (provided, of course, there is enough to treat the gas at some solvent rate).
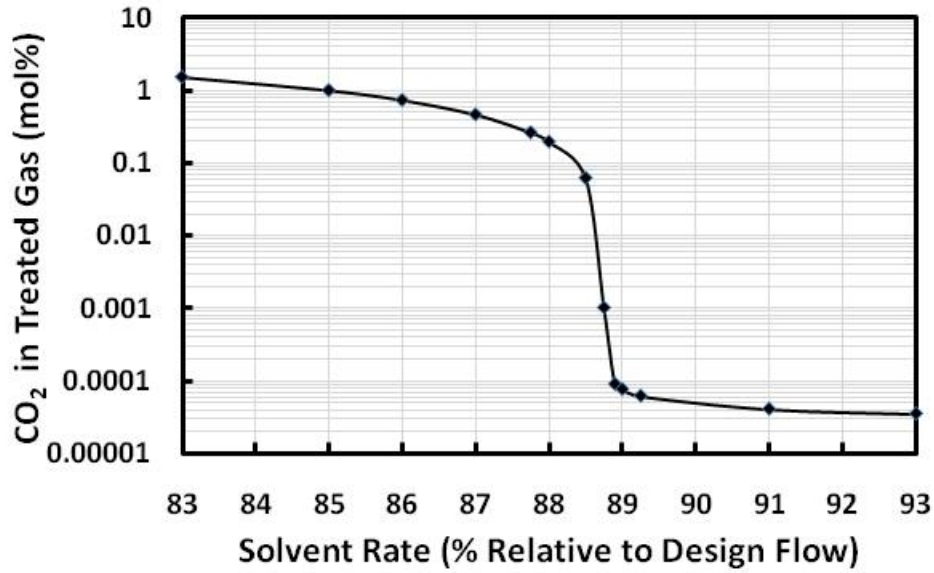
Figure 5   CO$_2$ Leak from a Piperazine-MDEA Absorber
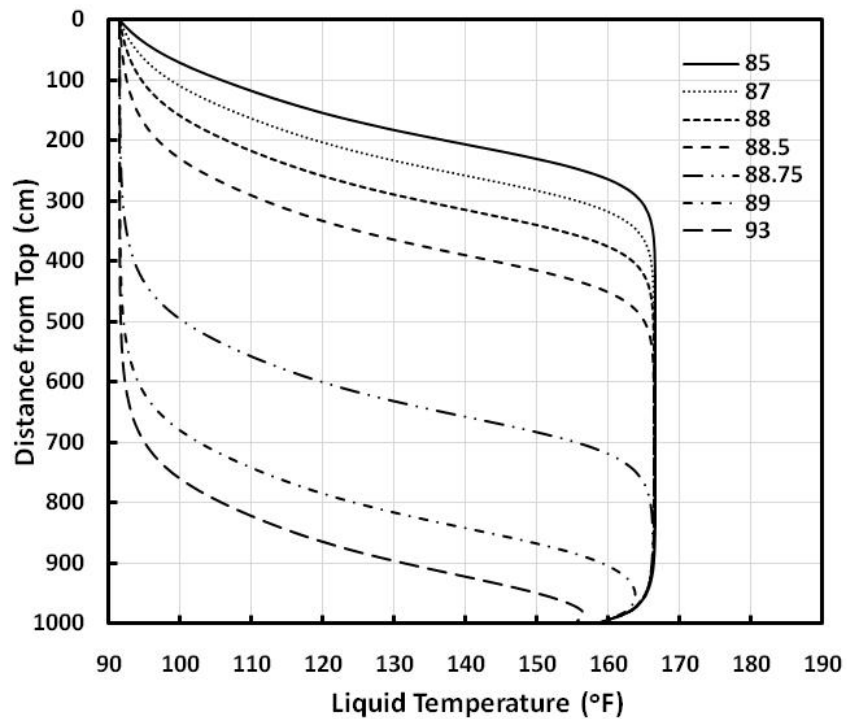

Figure 6   Piperazine Activated MDEA Absorber Temperature Profiles

Figure 7 shows profiles of CO$_2$ concentration in the gas at various solvent flow rates. The bulk of the CO$_2$ is removed in a fairly narrow band of packing about four meters high and the band moves up and down the column as the solvent rate is decreased and increased. The same behavior will occur as the gas rate increases or decreases, and as the CO$_2$ content of the raw gas rises and falls.
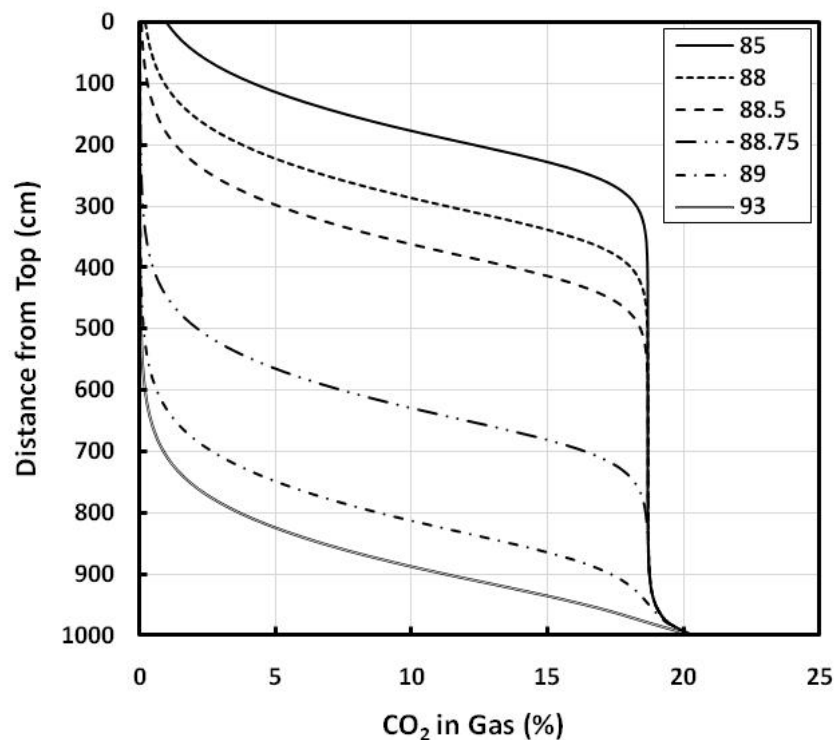
Figure 7   Piperazine Activated MDEA Gas-phase CO_2 Profiles

It appears that for solvents with very fast CO_2 reaction kinetics, absorbers can become quite unstable when conditions are such that the solvent is about to reach its maximum capacity for absorbing one or other of the acid gases. The instability is more severe as the reaction kinetics increase, i.e., the narrower the absorption/reaction zone, because a very narrow zone is too localized to give any warning of impending failure until it is about to occur. In some cases it may be possible to operate fairly close to the point of instability but special precautions may have to be taken to override a controller should the column temperature at some specified position in the column rise past a threshold or trigger value.

Amine Regenerators

Most amine regenerators are operated with enough boilup to provide a reasonable flow of condensable[1] stripping steam to every tray or all the packing in the column. 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[2]. The transition does not result solely from

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[1] As long as there is a vapor flow to all the trays, each tray will see a nonzero water concentration; however, the water content may not be adequate to transfer any heat to the liquid via condensation. Normally, regenerator vapors have high water content and stripping energy is provided by steam condensation.

[2] Here instability does not imply inoperability. It means an unexpectedly large change in a performance variable caused by a change in a control variable.

throttling reboiler energy (steam, hot oil) flow. It can equally well be caused, for example, 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. We will explore the instability by referring to an example.

Case Study

The example is 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 head pressure of 0.95 $kg/cm^2(g)$ (13.5 psig).

Effect of Rich Amine Feed Temperature

With the reboiler duty set at 2.25 MMBtu/hr, the temperature of the rich amine feeding the column was varied from 185 to 215°F in 5°F increments in the simulations. Figure 8 illustrates the simulated effect of feed temperature on the solvent lean loadings produced by the regenerator. Figure 9 shows vapor-phase temperature profiles from which it can be seen that 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.
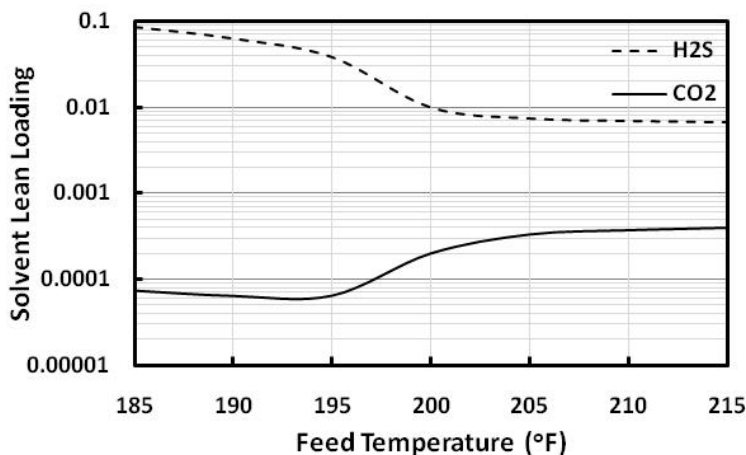

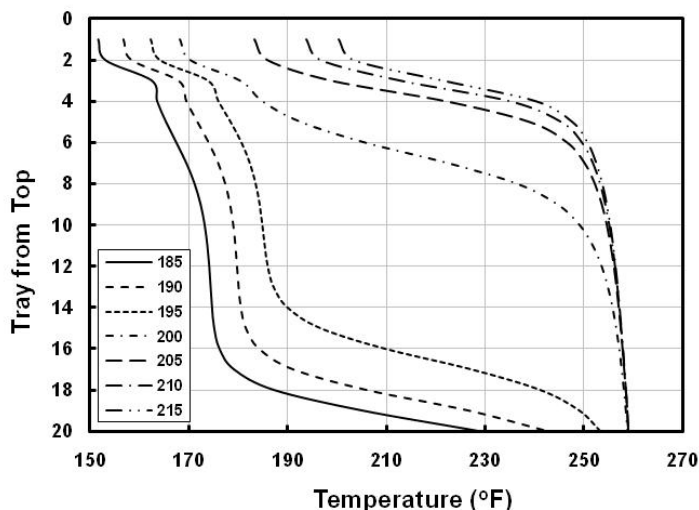**Figure 8   Effect of Feed Temperature on Lean Loadings**

Figure 9   Effect of Feed Temperature (Parameter) on Profiles in an MDEA Regenerator

But 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 10). In Figure 10(a) we see that with a 195°F feed the top part of the column is so cold it is actually behaving 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. Figures 10(a) and (b) show that the hotter rich feed allows more of both gases to flash on the feed tray; however, Figure 10(b) 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 10(b) towards the bottom of the column where a leaner lean loading is reached at lower temperature.
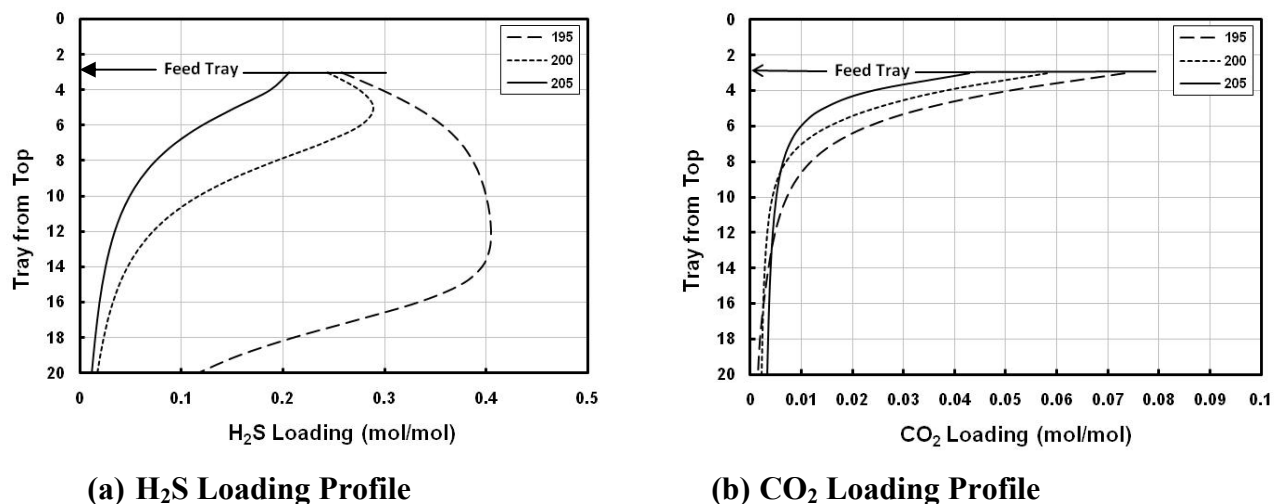

(a) H₂S Loading Profile   (b) CO₂ Loading Profile

Figure 10   Effect of Feed Temperature (Parameter) on Loading Profiles in MDEA Regenerator

It is also interesting to note how reflux ratio and stripping ratio depend on the rich amine feed temperature as shown in Table 1. Obviously the more the rich feed is sub-cooled below its bubble point the more steam will be condensed to heat it and therefore the less water vapor 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, its value is certainly questionable.

Table 1   Reflux and Stripping Ratio[3] 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

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[3] 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 vapor and is more nearly independent of how the condenser operates.

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 11 shows, there are simulated to be sharp changes in acid gas loadings for this example between 2.5 and 2.8 MMBtu/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 11, 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 and 2.75 MMBtu/hr. It should be noted that in the absence of H_2S, an improvement to CO_2 lean loading will not occur at low reboiler duties. The improvement seen in Figure 11 is strictly the result of H_2S absorption in the stripper pushing CO_2 out, just as the vapor-liquid equilibrium says it must.
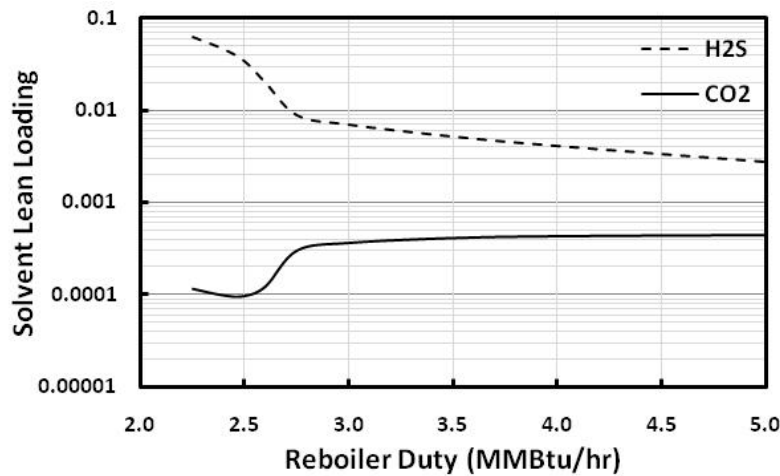

Figure 11   Effect of Reboiler Duty on Lean Loadings

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.
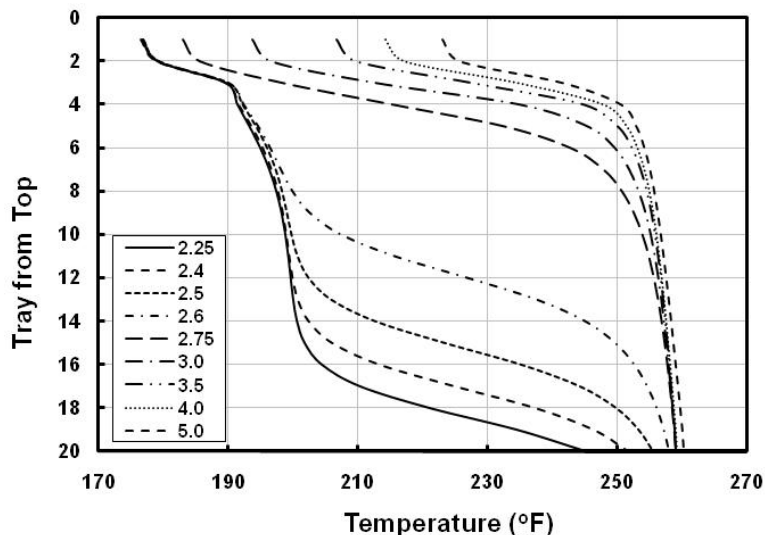

Figure 12   Effect of Reboiler Duty on Regenerator Temperature Profiles

Table 2   Reflux and Stripping Ratio Dependence on Reboiler Duty

Reboiler Duty (MMBtu/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

Summary

Operating regions in which unexpectedly large changes in performance occur as a consequence of normal changes in operating parameters can be highly unstable because they mark conditions in the vicinity of which controllers might not have been tuned to operate. For example, in the regenerator example described here, the response of H_2S lean loading to reboiler duty is some 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 (which may be exactly where one wants to run them to minimize energy consumption) may be hard to control, especially if the reboiler duty is cascaded to a temperature (feed tray, for example) within the tower for energy optimization.

Absorbers near the point where their operation changes from lean-end to rich-end pinched can also exhibit instability whose degree may be dependent upon reaction kinetics. For a very fast reacting system exemplified by deep CO_2 removal using piperazine-promoted MDEA, failure to treat can be catastrophic and arrive virtually unannounced. Systems such as these would benefit from internal tray temperature measurement to provide a warning means for plant operators. A plant producing gas with a few ppm of CO_2 suddenly starts to produce 4,000 ppmv gas. Performance has gone over the edge of a cliff and crashed onto the rocks below, and the cause might be a small fluctuation in gas composition or flow rate or a solvent flow rate controller overshoot in response to a fluctuation caused by some other parameter.

The performance of amine plants can be limited not only 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.