FOUNDATIONS OF FAILURE

RALPH H. WEILAND AND NATHAN A. HATCHER, OPTIMIZED GAS TREATING INC, USA, ANALYSE INSTABILITIES IN AMINE UNITS, HIGHLIGHTING THE CAUSES OF FAILURE THROUGH A SERIES OF CASE STUDIES.

Solvent and equipment limitations directly affect amine unit performance. For example, rich amine CO_2 and H_2S loadings are usually kept below approximately 0.5 mol. of CO_2 and H_2S /mol. of amine because of accelerated corrosion on hot surfaces. There are several guidelines 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. Thus, 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 merely restrict performance.

Over the years, plant designs and operations have become ever tighter, with operating expenses substantially cut to only the bare necessities. 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.

Another challenge of cost conscious operation is the need to process increasingly higher gas volumes with dated 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

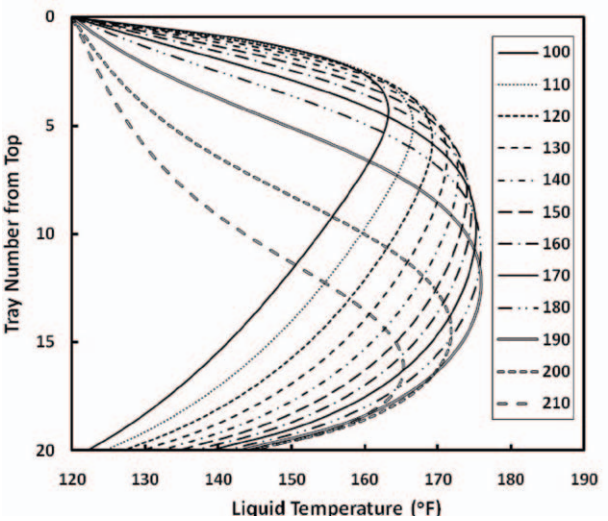


Figure 1. MDEA absorber temperature profiles at various solvent rates (gal. /min).

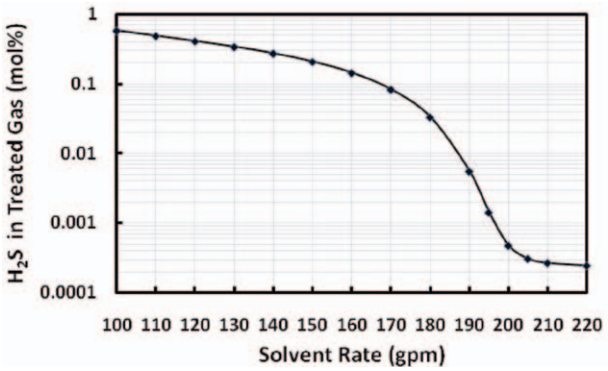


Figure 2. H_2S leak from an MDEA absorber at various solvent rates.

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 relatively 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. Using the ProTreat™ mass transfer rate based simulator, several instances can be demonstrated wherein:

- An absorber suddenly fails to treat by a wide margin in response to a very small change in solvent circulation rate.
- 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. Absorber performance as the solvent rate is turned down will be examined in three cases:

- A selective treater using methyl diethanolamine (MDEA).
- Removal of CO_2 from a 5% gas using monoethanolamine (MEA)
- Removal of CO_2 from a 20% gas using piperazine activated MDEA.

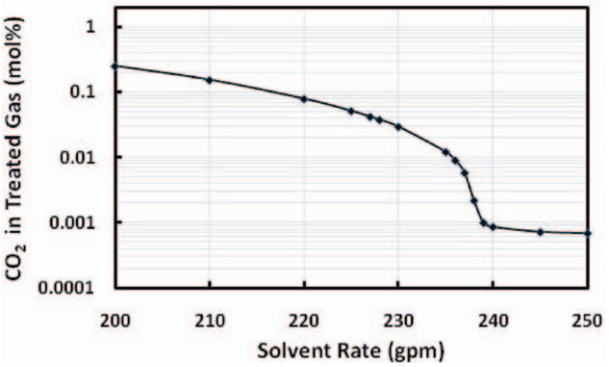


Figure 3. CO_2 leak from an MEA absorber at various solvent rates.

Selective treating using MDEA

The 20 tray absorber is to remove H_2S to below 4 ppm 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 mol. 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 solvent rates of 200 and 210 gal. /min, the absorber is being fed with 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 approximately 205 gal. /min, 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 gal. /min, the absorber begins to lose treat and this occurs relatively rapidly. Only a 2.5% drop in solvent rate from 200 down to 195 gal. /min results in the H_2S leak going from 4 ppm to 15 ppm, and a further 2.5% drop pushes the H_2S leak to 50 ppm. In other words, a 5% decrease in solvent flow results in an order of magnitude increase in H_2S leak.

At approximately 200 gal. /min, the solvent has barely sufficient capacity to absorb the requisite amounts of the acid gases. Below this 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 less than 4 ppm H_2S gas to a gas containing tens and hundreds of ppm.

Another term for this is acid gas breakthrough. In the vicinity of breakthrough, the column becomes harder to control because small fluctuations in such process parameters as solvent flow rate, raw gas flow or raw gas composition cause changes in treating that might be several factors of 10 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 gal. /min with an over ride on circulation rate triggered by a high temperature reading (over 150 °F) from a thermocouple installed on tray 6 or 7. The operation becomes more sensitive to circulation rate at approximately 200 gal. /min but the treating responds moderately to reasonable changes in circulation rate: the column cannot be called unstable.

Deep CO_2 removal using MEA

This case involves the removal of 5% CO_2 to less than 10 ppm using 30 wt% MEA and a 20 tray contactor. Solvent lean loading is assumed to be 0.1 mol. /mol. At solvent flow rates above approximately 240 gal. /min, the 10 ppm 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 gal. /min causes the CO_2

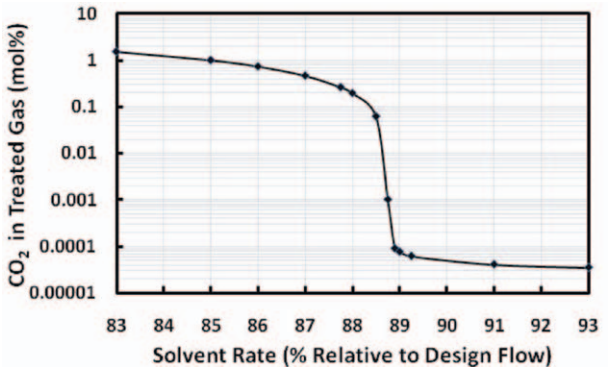


Figure 4. CO_2 leak from a piperazine MDEA absorber.

content of the treated gas to rise from 10 ppm to 300 ppm. If this were an LNG plant, for example, the increase would be a disaster.

The response curve shown in Figure 3 reveals a much more sudden transition from lean end (bulge at the bottom) to rich end (bulge at the top) pinch conditions than shown by MDEA (Figure 2). The suddenness of transition is caused by the fast chemical reaction in a liquid phase controlled process.

Piperazine promoted MDEA

Piperazine promotion of MDEA has been used for over 25 years to remove CO_2 from synthesis gases down to less than 1000 ppm 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 raw gas containing 20% CO_2 down to a few ppm. Gas pressure is 16 bar (g). Figure 4 shows the treating response to changes in solvent circulation rate (reported as percent of design flow), and Figure 5 shows how contactor temperature profiles change.

A 1% decrease in solvent rate from 89% to 88% of design flow is simulated to cause a thousand fold increase in CO_2 content from below 1 ppm to 2000 ppm. The temperature profile goes from being bulged only a short way from the bottom of the column to a 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 fast reaction rate of CO_2 with piperazine. CO_2 reacts so quickly that at adequate solvent rates most of it is removed from gas in the first couple of metres of packing that the gas encounters. The next two or three metres do polishing, and above the midpoint the rest of the column does nothing at all. Due to the fact that breakthrough depends on the solvent capacity needed to remove the CO_2 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 6 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 approximately four metres high and the band moves up and down the column as the solvent rate is decreased and increased. The same behaviour will also occur as the gas rate increases or decreases, and as the CO_2 content of the raw gas rises and falls.

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. Instability is more severe as the reaction becomes faster, i.e. the narrower the absorption/reaction zone, because a very narrow zone is too localised to give any warning of impending failure until it is too late. 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

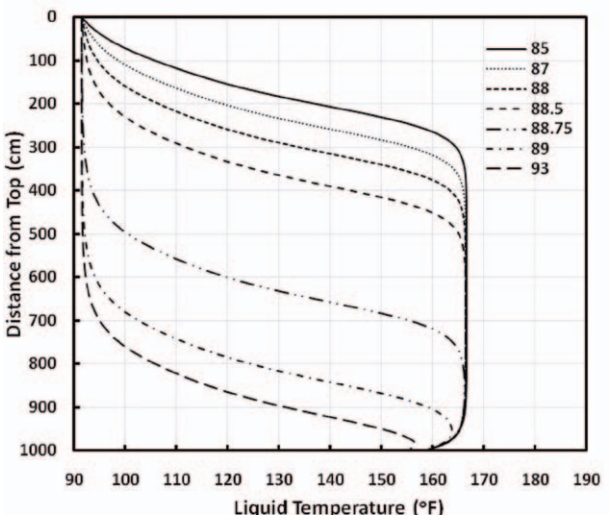


Figure 5. Piperazine activated MDEA absorber temperature profiles.

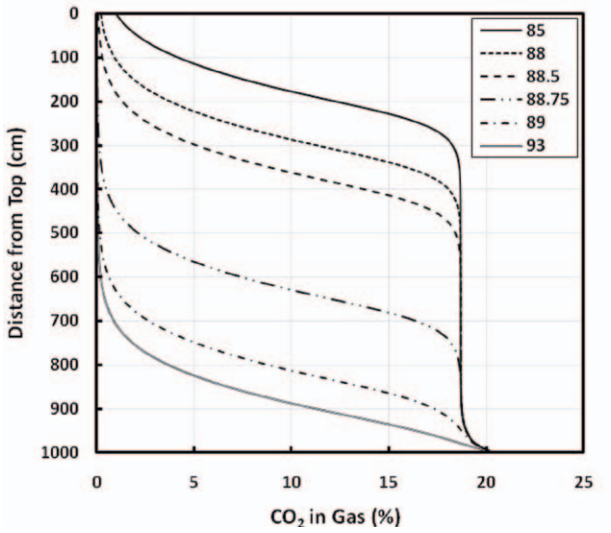


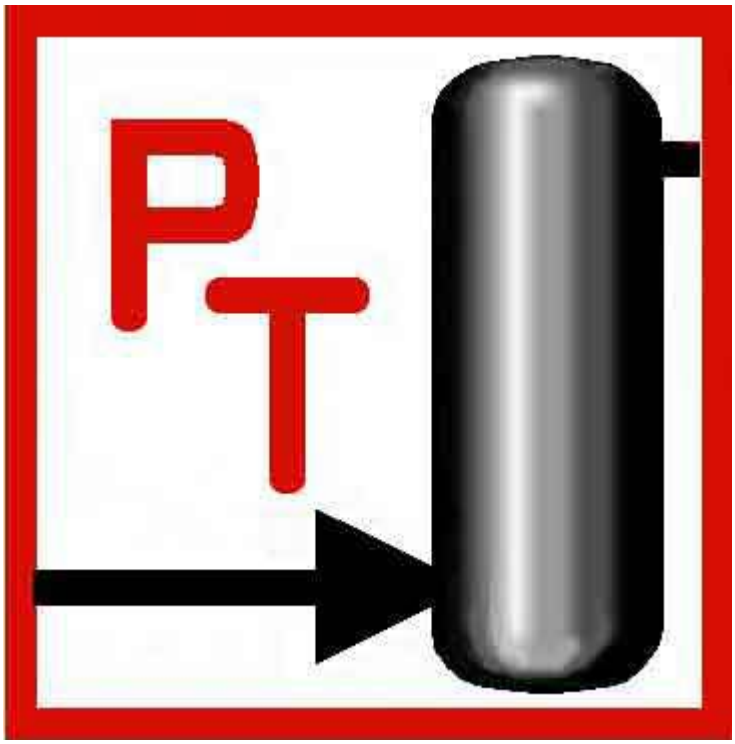
Figure 6. Piperazine activated MDEA gas phase CO_2 profiles.

override a controller should the column temperature at some specified position in the column rise past a threshold or trigger value.

Conclusion

Absorbers near the point where their operation changes from lean end to rich end pinched can 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 4000 ppm 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 becomes the real operating limit.



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