CO_2 Removal with Piperazine-MDEA Solvents[1]

Ralph H. Weiland

Optimized Gas Treating, Inc.,
12337 Jones Rd., Suite 432
Houston, TX 77070

The most common solvent for removing carbon dioxide in LNG production is based on *N*-methyldiethanolamine (MDEA) combined with modest concentrations of the fast-reacting activator, piperazine. MDEA is nonreactive towards CO_2 and does not form a carbamate. This gives MDEA a significantly lower heat of absorption than primary and secondary amines. This translates into lower solvent regeneration energy costs. However, lack of reaction makes MDEA by itself an unsuitable solvent for CO_2 because absorption is simply too slow. A few weight percent of piperazine (typically 5–16 wt % in the undiluted solvent) greatly accelerates the process. All major solvent vendors offer several formulations of piperazine with MDEA for a variety of carbon dioxide removal applications, and some include such solvents as part of licensed processes.

Pinched mass transfer is a common occurrence in CO_2 removal units for LNG production. In an earlier article[1] a case study was used to discuss the meaning and significance of bulge pinching in the context of LNG. However, the operating conditions were not optimized, and nothing was said about the effect of piperazine concentration and solvent flow rate on treating.

Lean-end pinching is widely recognized in the industry. It simply means that provided the absorber contains enough packing or trays, the final gas purity is determined by the CO_2 loading of the lean solvent at the top of the absorber. Lean solvent loading of course is strictly dependent on the operation of the regenerator, not on the absorber.

Rich-end pinching occurs when the solvent is incapable of coming even close to meeting the treating objective because solvent capacity is too limited. Limited capacity can result from either too low a solvent flow rate, or too low solvent strength.

A third type of pinch, pinching at the temperature bulge (a so-called bulge pinch) is less widely recognized. However it too is also a constraint that can prevent an absorber from treating to a satisfactory level and, when present, can prevent a solvent's full capacity from being utilized. Bulge pinching was described in some detail in an earlier article[1].

The present writing is a case study that looks at the treating response to piperazine concentration and solvent circulation rate. It uses the same absorber and gas conditions as before.

Plant Operating Parameters

The gas pressure, temperature and composition, particularly with respect to CO_2, vary from one application to another. However, a great deal of LNG feed is drawn from pipelines which have a maximum allowable CO_2 concentration of 2%, so this is the value used in the case study. Other gas parameters are shown in Table 1. These parameters, possibly together with the solvent temperature and loading, determine the best solvent flow rate and formulation.

In the case of solvents containing MDEA promoted with piperazine, the total amine concentration and the MDEA-to-piperazine ratio are selectable parameters, as is the lean solvent CO_2

[1] LNG Industry, December, 2018

loading. So there are several parameters that can be adjusted to force the plant to produce specification gas and to optimize its performance.

Table 1 Raw Gas

Temperature (°C)	**20**
Pressure (barg)	60
Composition	
CO_2 (mole %)	2
Methane	85
C_2+	13

Besides ensuring the gas meets treating specifications (usually CO_2 less than 50 ppmv), another design objective is to maximize the solvent's effective capacity, also call the solvent net loading (essentially the difference between the rich and lean solution total CO_2 loading). However, there are also other practical constraints.

Unless special metallurgy is being considered, corrosion avoidance dictates that the rich amine CO_2 loading be kept below about 0.45–0.5 moles CO_2 per mole of total amine. Since the lean amine loading in promoted MDEA is usually fairly low, rich loading and net loading are numerically almost the same. Another constraint that is also related to corrosion issues is the maximum allowable temperature in the absorber. This is at the temperature bulge and is kept below about 85°C (185°F).

Simultaneously meeting all these constraints can place severe restrictions on what operating conditions are even feasible. Meeting constraints also determines possible operating ranges for variables such as solvent circulation rate, temperature, and solvent formulation.

The lean solvent loading is controlled by the steam or hot oil flow rate to the regenerator's reboiler. Sometimes (but not always) this can be used with great effect to control treating. However, if the absorber is bulge or rich-end pinched such is not the case and treating can be completely insensitive to reboiler duty. The often ignored but critical factor in much of this is the heat of absorption because it plays a large role in determining whether there are mass transfer pinch limitations, and if there are, then the type of pinching and what operating parameters control the operation.

Case Study

The case study has three objectives: the first is to show how various constraints can conspire to rule out use of a particular solvent strength regardless of its formulation. The second is to show how the formulation itself (specifically the piperazine-to-MDEA ratio) can be used to improve ease of operability of the absorber. The third is to show how moving a process parameter in what seems to be an instinctively obvious direction can actually be a move in the *wrong* direction. The solvent parameters considered are flow rate, strength, formulation, and temperature. The case study uses the ProTreat® simulator.

The real physical absorber that is used as the basis for the study contains Mellapak M-250X structured packing; in the actual plant, the regenerator contains trays. The packing specific (dry physical) area is nominally 250 m^2/m^3.

Operating Parameters

Conventionally, solvent formulations are usually referred to the *neat solvent*, i.e., as received by rail car or tanker, or in drums, undiluted with water. In this study, performance parameters and operating windows were obtained from two sets of simulations using 40 and 50 wt% solvent at 35°C and a third set using 50 wt% total amine at 45°C. Six solvent formulations were used: 5, 7.5, 10, 12, 14, and 16 wt% piperazine with the balance MDEA. Performance was assessed on the basis of the treated gas purity achieved, whether the bulge temperature was below or above 85°C, and how solvent net loading responded to these solvent parameters. Lean solvent loading was kept at 0.02 moles of CO_2 per mole of total amine (0.02 mol/mol). In the interest of conserving space, only the case with 50 wt% solvent is described in any detail; the other two cases are simply referenced.

It should be noted that treating may or may not be much improved by more thorough regeneration of the solvent, i.e., by generating a leaner solvent, depending on whether the absorber is lean end pinched. Simulated CO_2 profiles in the absorber is most useful for determining pinch conditions.

50 wt% Total Amine

Figure 1 shows how absorber performance as measured by treated gas CO_2 content responds to solvent rate for various formulations. The line separating satisfactory from unsatisfactory values of the bulge temperature is also shown. Given enough piperazine in the solvent, there is a large operating range of solvent flows to the left of the 85°C boundary that will produce gas meeting the < 50 ppmv CO_2 specification. There is an optimal solvent flow for each solvent formulation. It should be noted that only formulations with more than 10 wt% piperazine are capable of reaching 50 ppmv CO_2 in the treated gas.

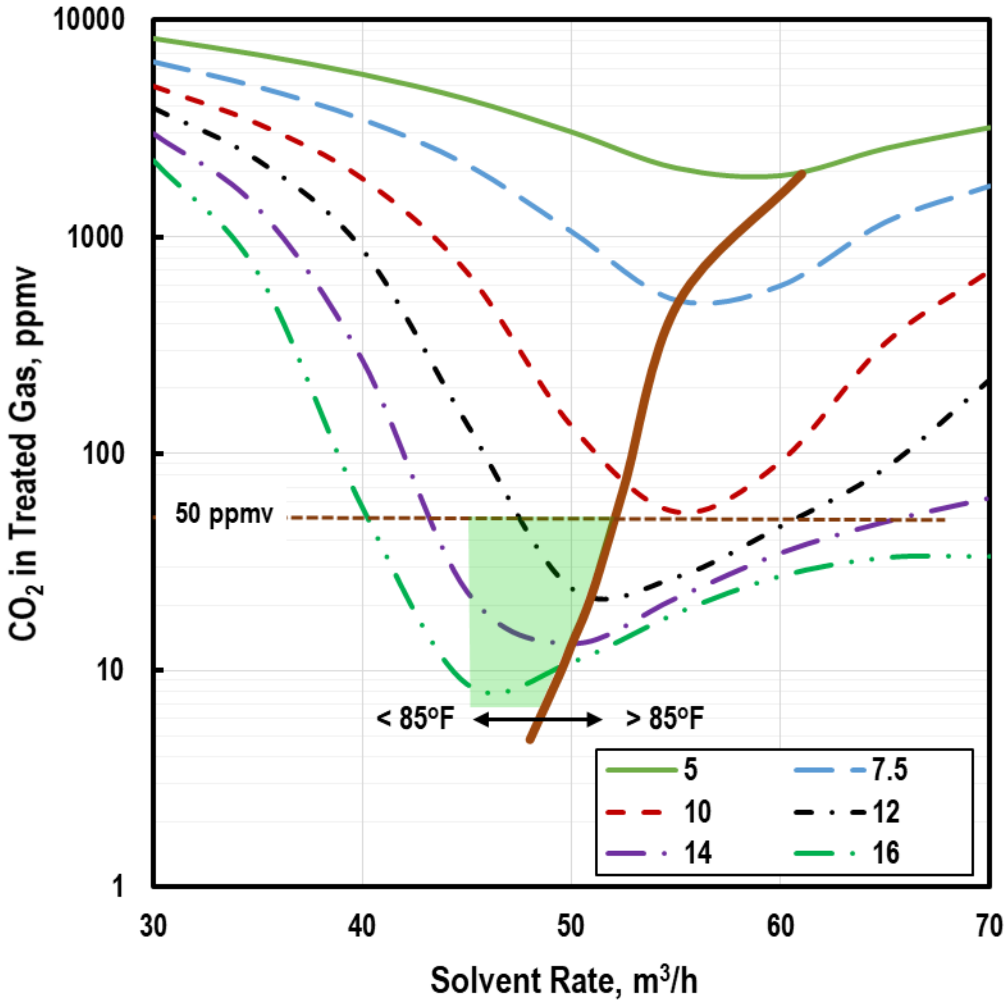

Figure 1 Treating Response using 50 wt% Total Amine

Solvent net loading is the difference between the rich and lean solvent loading values. It is a useful measure of how effectively the solvent's actual capacity is being used. In the present case, the lean loading is only 0.02 mol/mol, which is numerically small compared to the rich loading so net loading and rich loading are nearly the same number. Figure 2 shows how solvent net loading responds to the same solvent parameters as in Figure 1. The important observation here is that for solvents able to produce 50 ppmv treated gas, only solvent rates greater than about 45 m^3/h can do so while keeping the rich loading below about 0.5 mol/mol. This eliminates a sizeable portion of the potential operating area in Figure 1. Thus, controlling corrosion by requiring the rich solvent loading to be below 50 ppmv CO_2 squeezes the operating range into the pale green area shown in Figure 1.

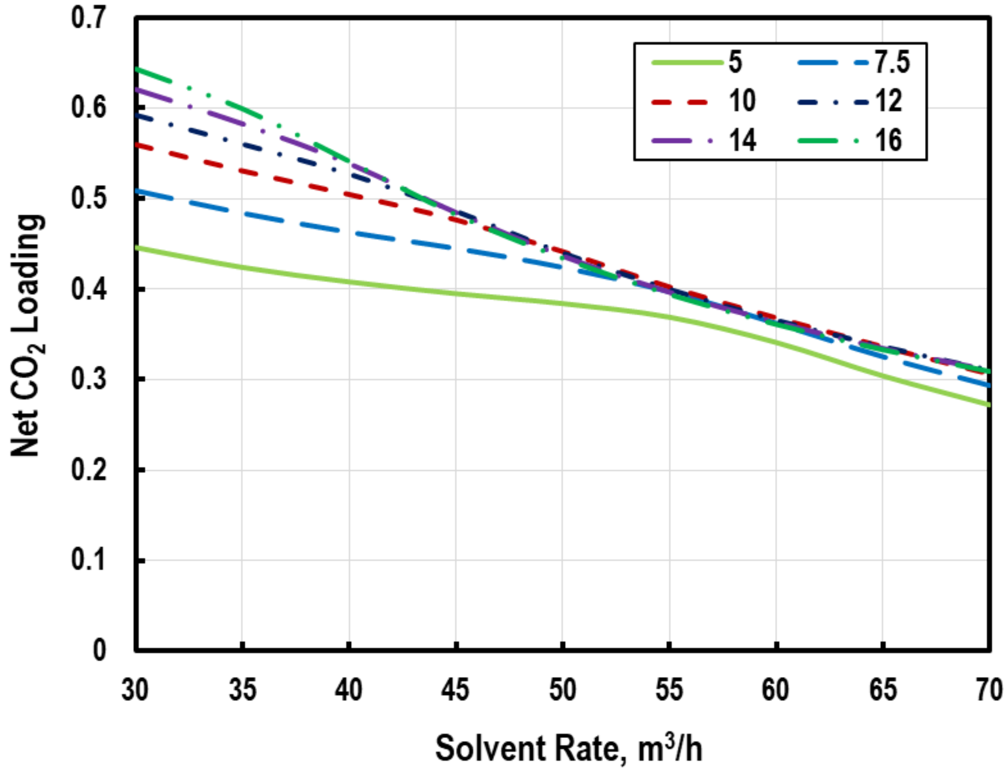

Figure 2 Plots of CO_2 Partial Pressure Showing Pinched and Non-pinched Operation

The shape of the curves in Figure 1 deserves some explanation if only because normally one would expect that higher solvent rates would lower the residual CO_2 in the gas, even if that means the solvent is less effectively used. However, Figure 1 shows the opposite.

All the solvent flow rates in Figure 1 (even including the upper end) have relatively low values because one of the objectives is to remove 2% CO_2, a small amount, with the highest effective solvent utilization (net loading) as possible, and therefore *using minimal solvent flow rate*. The relatively high gas flow forces the temperature bulge to lie near the top of the column. There just isn't enough liquid flow to drive it downwards into the bottom of the column where it is usually found in most gas treating applications.

The gas flow conveys heat up the column where it meets a small flow of cool entering lean solvent. The cool solvent then absorbs some of the heat and redirects it downward. If the upward and downward convection are in rough balance, the released heat of absorption keeps getting redirected towards the centre of the absorber where it becomes trapped and creates a very hot temperature bulge before it can escape. If gas flow dominates, the bulge ends up at the top. If liquid flow dominates, it locates at the bottom. It's all a matter of which phase conveys the most heat along the column[2].

In the present context, when an already low liquid flow is reduced further, the heat of absorption is convected by the gas out the top of the column even more easily, temperatures are cooler, and equilibrium favours better absorption. Thus, treating improves. However, when reduced below a certain value, treating then starts to worsen because of inadequate solvent capacity for the gas.

Effect of Other Parameters

A full set of ProTreat® simulations equivalent to what is shown in Figures 1 and 2 but for 40 wt% solvent was performed to determine whether higher loading values could be obtained by using less amine. The results showed instead that there was no operating window for any solvent formulation at all that met all criteria for treating, namely, < 50 ppmv CO_2 with bulge temperature less than 85°C, and maximum solvent utilization as indicated by a highly loaded rich solvent. Rich solvent loadings between 0.35 and 0.5 mol/mol could be obtained only at the expense of bulge temperatures well in excess of 85°C regardless of solvent formulation. Of course, at very high solvent rates (> 100 m^3/h) treating to a few ppmv CO_2, far better than necessary, could be easily achieved but only with the economic penalty associated with high pumping and energy costs, and poor solvent utilization.

Higher lean solvent temperatures can potentially drive treating in either direction. Hotter solvents have faster reaction kinetics and lower viscosity which both encourage faster absorption rates. Colder solvents have more favourable CO_2 solubility. However, a third set of simulations run with the solvent temperature increased from 35°C to 45°C showed virtually no effect of solvent temperature on absorber performance itself, or on the extent of the feasible operating ranges with regard to solvent formulation and flow rate. Treating performance was completely insensitive to lean solvent temperature, at least at these two levels.

Summary

The results discussed in this article are quantitatively valid only for the precise conditions of the study; however, the results are qualitatively applicable to many LNG production situations. The very fast kinetics of the reaction of CO_2 with piperazine has a tendency to generate sharp high temperature peaks within the absorption column which exaggerates behaviours seen when less aggressive amine solvents are used.

Bulge pinching is not limited to piperazine promoted MDEA solvents. However, the rapid reaction kinetics this type of solvent shows with CO_2 makes bulge pinching more likely. The kind of operating map discussed here can be generated using ProTreat's true mass transfer rate basis for any combination of solvent formulation and gas composition and flow. It may not always be possible to operate with full solvent utilization at optimally low flow rates, but if it is, a concise visual picture is very easy to obtain of just how large the operating window is and how much leeway there is from a process control standpoint.

References

1. Weiland, R.H., *Title?*, pp. X – Y, LNG Industry, August, 2018.
2. Weiland, Ralph H., Hatcher, Nathan A., *Understanding Temperature Profiles*, Hydrocarbon Engineering, February, 2017.