How Sensitive Is Your Treating Plant to Operating Conditions?*

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Abstract

Normal expectations in operating amine treating plants for acid gas removal is that small changes in operating conditions will result in correspondingly small responses in plant performance. However, such expectations are not always well founded. To establish credibility for the process simulator used in the design of a new LNG plant (ProTreat®), we begin by comparing its mass transfer rate-based simulation results with performance data from an LNG plant operated by Atlantic LNG Company of Trinidad and Tobago (Atlantic LNG).

Attention is then turned to another LNG project currently under study. For this system under consideration, our focus is on the CO_2 removal system which consists of a single, large absorber serviced by two regenerators in parallel. Initially the plant would process about 1,400 MMscfd of gas containing about 16 mol% CO_2. A sensitivity analysis leads to some interesting observations regarding potential susceptibility of treating performance to departures of certain operating conditions from design values, and provides reasons for this sensitivity.

Background

There are a number of well-accepted limits on values of plant operating parameters. Examples are corrosion considerations for carbon steel which usually limit rich amine CO_2 loadings below about 0.4 – 0.45 moles of CO_2 per mole of amine, and upper limits on maximum line velocities to prevent the direct scouring of surfaces and the removal of protective films, particularly sulfide layers. Tower internals have natural limitations on gas and liquid rates beyond which jet flooding or downcomer backup and choke flooding of trays, or packed column flooding, occur. These are natural hydraulic capacity limits. Finally, solvent capacity is itself limited by temperature and acid gas partial pressures.

Corrosion, temperature, and acid gas pressures can all limit rich solvent loadings, i.e., solvent capacity, and limitations on tower hydraulic capacity restrict throughput. These limitations restrict performance but without causing over-sensitivity of performance to small changes in the values of operating parameters. However, the normal small-response-to-a-small-stimulus paradigm changed with the advent of very fast-reacting solvents such as piperazine for CO_2 removal.

The development and availability of highly precise simulation tools, especially tools such as the ProTreat® simulator which is based on the direct calculation of *mass transfer rates*, has encouraged the design and construction of new plants with less and less design margin. It has also allowed engineers to

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assess precisely the effect of operating parameters on performance, and it has revealed the existence of operating cliffs or points of instability on the performance map[1]. Although regions of increased sensitivity have been predicted even for moderately fast-reacting CO_2-MEA absorbers, when piperazine is used to promote MDEA, reactions rates become very large indeed, and unexpectedly high sensitivity of performance has been observed. None of this has been predictable using the more traditional ideal-stage simulation tools even when they have been modified with efficiencies and even with attempts to force reaction kinetic rates into what is fundamentally an equilibrium model. What enables the mass transfer rate model to reveal what has for so long been hidden behind the façade of the ideal stage?

A real absorber contains a certain number of actual trays or a depth of a specific packing intended to promoted contact across the interface between the counter-currently flowing vapor and liquid phases. The flows are always to some extent turbulent, and the turbulence level depends on the tray or packing design, and the fluid properties and flows. Turbulence affects the absorption rate because it affects the mass transfer coefficients that prevail within the phases. In parallel with heat transfer coefficients in various types and designs of heat exchanger, mass transfer coefficients for a wide range of tray and packing types have been well correlated with design details, flow parameters, and properties. In other words, the mass transfer characteristics of tower internals are well understood and well established—there is no guesswork. Of course, absorption rates also depend on concentration *differences* between the phases. The separation actually achieved by a real tray or a certain depth of real packing depends directly on the absorption rate of the component as dictated by the mass transfer characteristics of the internals. The model is completely integrated with the real-world equipment and how it is operated. The ideal stage concept, on the other hand, replaces every important detail with the single, simplifying assumption of equilibrium between the phases. Indeed there are no composition differences at all between phases, and therefore there is really no reason for a separation! Regardless of applying efficiencies or finessing the equilibrium assumption in any other way, the ideal stage assumption eliminates reality from the calculations, leaving a model that is not only unable to perceive critically important process detail, but which is also vulnerable to gross error.

Case Studies

This article consists of two case studies. In the first study, the question, "How closely can one predict the performance of an LNG plant's CO_2 removal section?" is answered by comparing performance predictions with operating data from one of the LNG trains at Atlantic LNG in Port Fortin, Trinidad, the sixth largest LNG facility in the world in annual LNG production. The second case study is an analysis of certain aspects of the CO_2 removal section of a project currently under consideration. The case study examines the sensitivity of the design to operating and design parameters.

Atlantic LNG

Diglycolamine Agent® (DGA®) is used at 41 wt % to treat inlet gas with the composition shown in Table 1. The process flow diagram (Figure 1) is fairly conventional, although mention should be made of the fact that a substantial portion of the reflux water from the stripper overhead condenser is mixed with process makeup water and returned to the top of the absorber rather than to the regenerator. At the top of the absorber, four wash trays recover DGA Agent from the treated gas. There are 20 contacting trays in the absorption section.

The rich amine is flashed to remove hydrocarbons, cross-exchanged with hot lean amine, and sent to the regenerator. The regenerator contains three wash (reflux) trays and 17 stripping trays. The reboiler is energized using hot oil.

Table 1 Composition of Gas to CO_2 Absorber

CO_2 (mole %)	0.34
Methane (mole %)	95.5
C2+ (mole %)	4.1
Nitrogen (mole %)	< 0.1

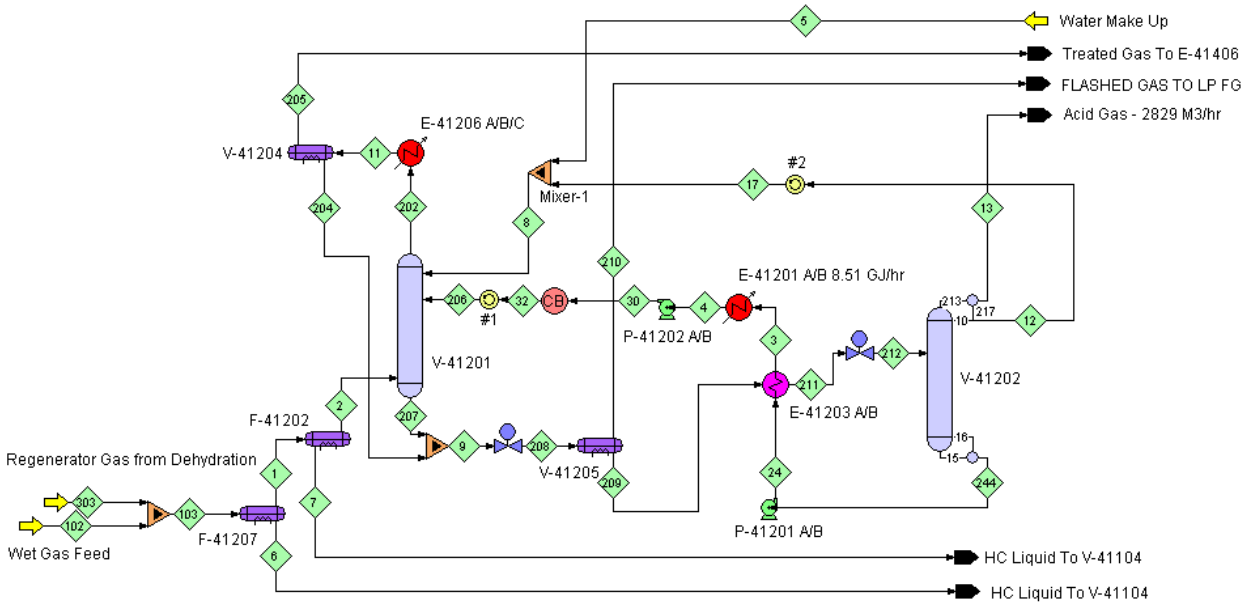


Figure 1 Simplified PFD for the Atlantic LNG Train-4 CO_2 Absorption System

Absorber temperature and composition profiles indicate that the tower is mass transfer rate controlled. Simulated temperatures of various streams throughout the plant are compared with measured data in Table 2. Stream numbers refer to those shown in Figure 1.

Table 2 Actual vs. Simulated Stream Temperatures

Stream	Actual Temp (°C)	ProTreat (°C)	Difference (°C)
103	24.8	24.9	-0.1
202	32.5	33.9	-1.4
206	43.3	44.1	-0.8
207	24.2	23.5	0.7
211	81.8	81.8	0.0
213	111.9	111.8	0.2
13	44.5	44.5	0.0
24	126.7	126.0	0.7

Except for the treated gas temperature, the simulated temperatures of all other streams match plant measurements to better than 1°C; the treated gas differs by only 1.4°C. The measured lean amine loading was 0.04 moles CO_2/mole DGA while the simulated value was 0.036 moles CO_2/mole DGA. These values are almost identical, validating the accuracy of the regenerator simulation. The treated gas CO_2 level was measured at 25 ppmv, whereas, the simulated value was in the range 50–60 ppmv. This is certainly more discrepancy than we are used to seeing. However, the feed gas is known to contain heavy ends, and plant personnel have identified the presence of foaming in the column. Even a small amount of foaming in an otherwise perfectly operating system can increase the vapor-liquid area for mass transfer by 10 or 20%, and this is sufficient to give a predicted value of 25 to 30 ppmv of carbon dioxide.

LNG Project Under Consideration

This plant is in the initial study phases. As such, the name of the project and location will not be disclosed. However, the study phase is the time to perform sensitivity studies and determine (1) that it will be operable over the entire range of expected conditions and (2) whether there are regions in which the operation of the plant might be overly sensitive to one design parameter or another and, if there are, that it operates well away from such regions (or at least has contingencies in place to ensure stable operation can be maintained). Regarding carbon dioxide, the raw gas to the plant under consideration is at the opposite end of the spectrum from the Atlantic LNG facility. The carbon dioxide concentration in the raw gas is about 45 times higher, nominally 16 mole %. Figure 2 shows a simplified PFD. A simplified gas analysis with relevant conditions is provided in Table 2. The absorber has been designed with 3 one-pass valve trays to act as wash trays and assist in the recovery of any vaporized INEOS® GAS/SPEC® CS-1160 solvent from the treated gas. This short wash section swages into the absorption section. The main part of the absorber was designed with two identical 4-metre deep beds of No. 1.5 Raschig Super-Rings®, selected for their excellent hydraulic capacity and very high specific surface area[2,3]. In tests conducted by Fractionation Research, Inc. (FRI), this packing combines high throughput with excellent mass transfer performance. At 60% of flood, the absorber diameter is just over 25 feet, which at 48 barg is a substantial tower shell by any measure.

Table 2 Study Case LNG Feed Gas to the CO_2 Absorber

Temperature (°C)	**46**
Pressure (barg)	54
Volume Flow (kNm3/h)	1 400
Composition (Dry Basis)	
CO_2 (mole %)	16
Methane (mole %)	79
Ethane (mole %)	3
Propane (mole %)	1
Butanes (mole %)	0.5
Other (mole %)	0.5

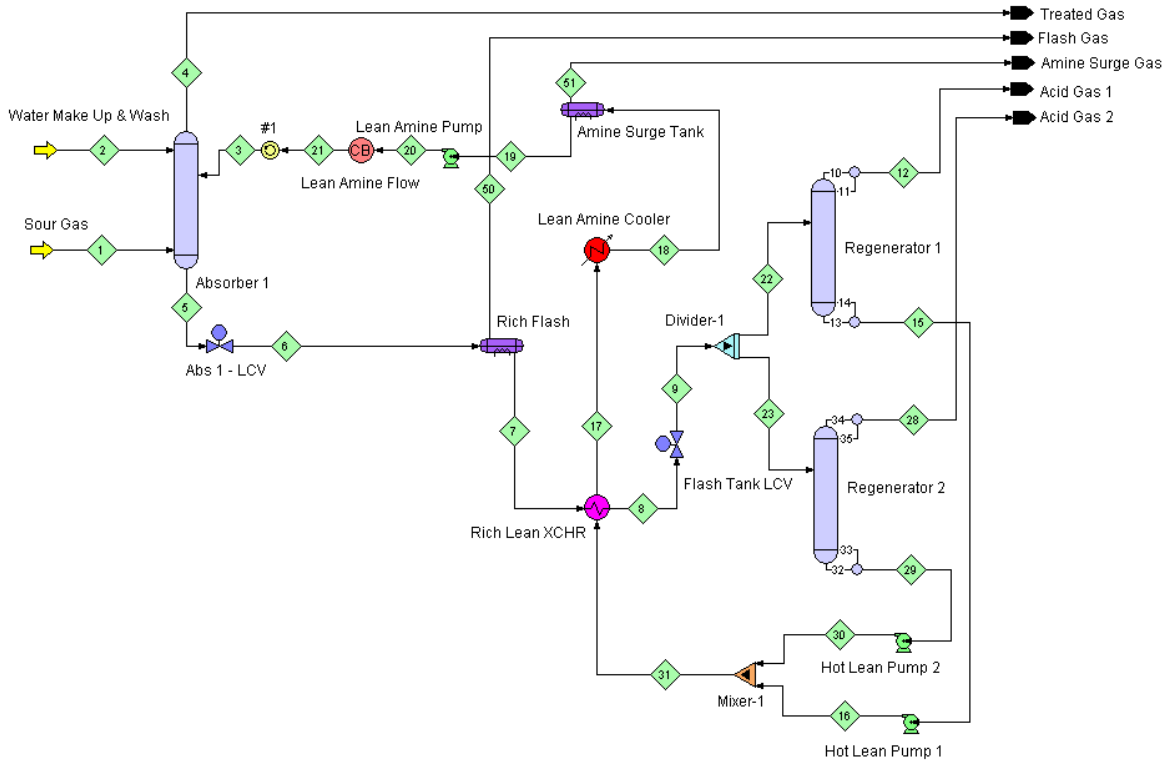


Figure 2 Simplified PFD for the Study Case LNG CO_2 Absorption System

The regenerator's design stripping ratio is 0.8 (stripping ratio is the ratio of water vapor to acid gas in the overhead vapor line going to the condenser). The solvent circulation rate is set to achieve a rich amine loading of 0.5 moles of CO_2 per mole of amine in the solvent. At the design lean amine temperature of 115.8°F into the absorber, the treated gas was simulated to contain 21.4 ppmv of CO_2.

A study of how overall performance might respond to variations in design and operating parameters revealed that, for the most part, the carbon dioxide content of the treated gas was remarkably insensitive, so the design appeared quite solid from an operational standpoint. However, performance was found to be sensitive to (a) the depth of packing in the absorber, and (b) the temperature of the lean amine.

Sensitivity to Absorber Packing Depth

Figure 3 shows the simulated effect of packed bed depth on treating performance as measured by the carbon dioxide level in the treated gas. Note the logarithmic scale on the concentration axis. The design point of an 8-m deep packed bed appears to give a comfortable margin away from the 50 ppmv specified limit for CO_2. However, reducing the bed depth to 7 m, a difference of only a single metre, would result in the treated gas exceeding this specification by at least 20 ppmv versus meeting it with a comfortable 30 ppmv margin. Obviously, for a tight design getting the packing depth right is critical. Indeed, for a truly safe design one must have confidence in the reliability of the simulator. If a simulator that uses ideal stages in any form is used, it must rely on the engineer having high confidence in the accuracy of the HETP value he uses to translate into reality. Unfortunately, even when it exists at all, information on HETP values in amine systems is usually very unreliable. Because the ProTreat® simulator has a real mass and heat transfer rate-basis which allows it to avoid the efficiency and HETP

questions altogether, and because it has been finely tuned to a large amount of commercial plant performance data, it is one of the only commercially available simulators that can reliably get it right. The mass transfer rate model deals directly with the real internals in the tower, not with an idealization needing the band aid of an HETP.

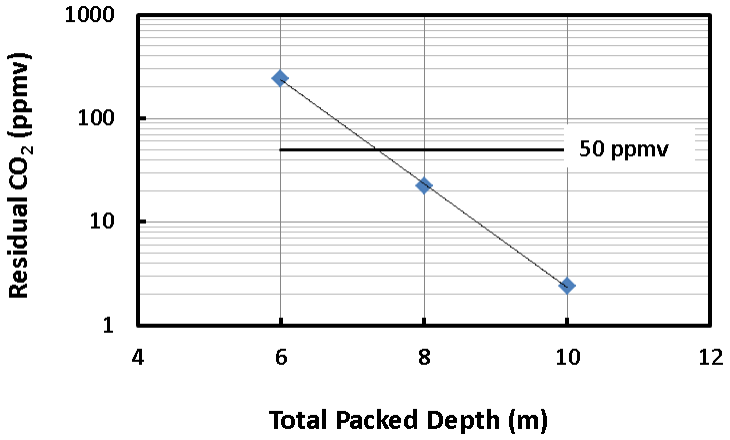


Figure 3 Sensitivity of CO_2 in Treated Gas to Packing Depth in the Absorber

Absorber performance is exponentially sensitive to packed depth, mainly because the absorber's performance in this case is controlled, not by the solvent lean loading, but by the mass transfer itself. The easiest way to understand this is by looking at the CO_2 concentration profile across the absorber, as shown in Figure 4. Detail is made visible by using the logarithm of CO_2 concentration and the temperature profile is shown for reference. The size of the temperature bulge is substantial in the bulge region of the absorber. The carbon dioxide concentration is only slowly changing there because of the high CO_2 backpressure at such temperatures. In other words, the solvent is nearing saturation towards the bottom of the absorber. However, throughout the rest of the absorber the carbon dioxide concentration continues to fall exponentially. Indeed, the CO_2 concentration in equilibrium with the lean amine is less than 1 ppmv so the absorber truly is well away from being lean-end pinched.

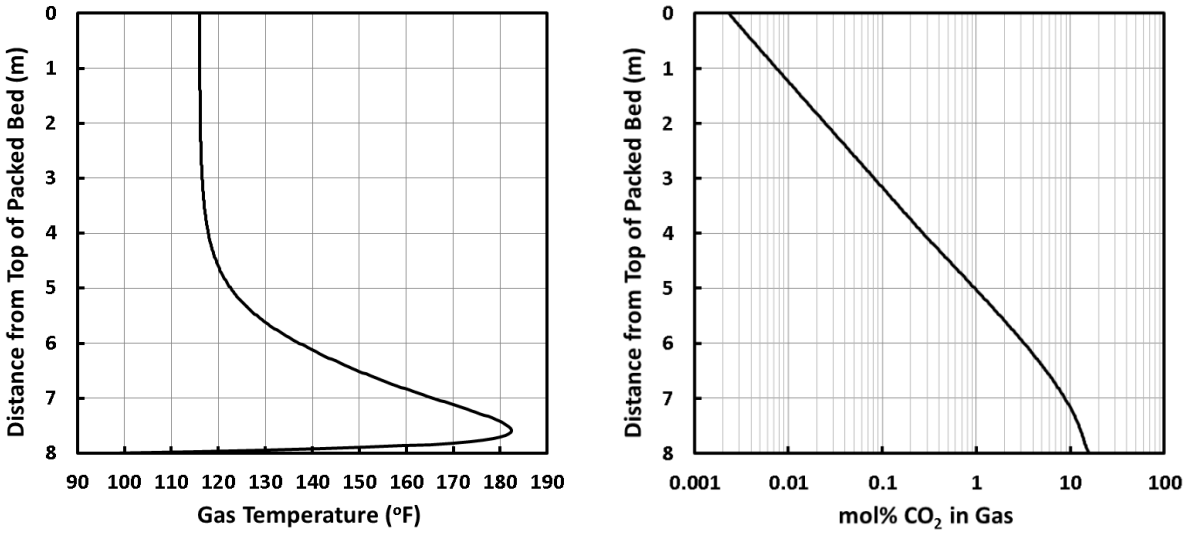


Figure 4 Temperature and CO_2 Concentration Profiles in Gas across the Absorber

Sensitivity to Operating Parameters

If the absorber goes off specification, remedial action must be taken. There are several candidates for control variables, the most obvious being: lean solvent flow rate, lean solvent temperature, regenerator reboiler duty. This absorber is sized for only 60% of flood. Therefore, the solvent rate might be an excellent control variable, at least in terms of tower hydraulic capacity (provided of course that pumps have been adequately sized). The Regenerator reboiler duty, on the other hand, is a poor control variable simply because treating is almost independent of lean loading, (provided only that the loading is low enough). Figure 5 shows the lack of sensitivity of treating to lean loading. As shown in the figure, a 15% increase in reboiler duty results in a lean loading reduction of only 0.0036 loading units and this decreases carbon dioxide in the treated gas by only 2 ppmv.

Lean solvent temperature was the final control variable considered. As the lean amine temperature is increased, one naturally expects to find temperature increases throughout the column in response. A higher temperature solvent is unable to hold as much acid gas as a low temperature one. In other words, it's net loading decreases. This is shown in Figure 6 where the CO_2 level in the treated gas and the net solvent loading are shown side by side. Between 100 and 126°F the rich loading remains constant regardless of the lean amine temperature because the solvent under those conditions is able to absorb virtually all the CO_2 (at least to the 20 ppmv or so level). However, at or above 126°F the rich loading starts to drop with increasing temperature. The ability of the solvent to "load up" with CO_2 is being compromised by it becoming too hot, and what cannot be absorbed must leave in the exiting gas. Thus the treated gas quality starts to suffer very severely. The effect is very noticeable when one is dealing with ppm specifications on the treated gas.

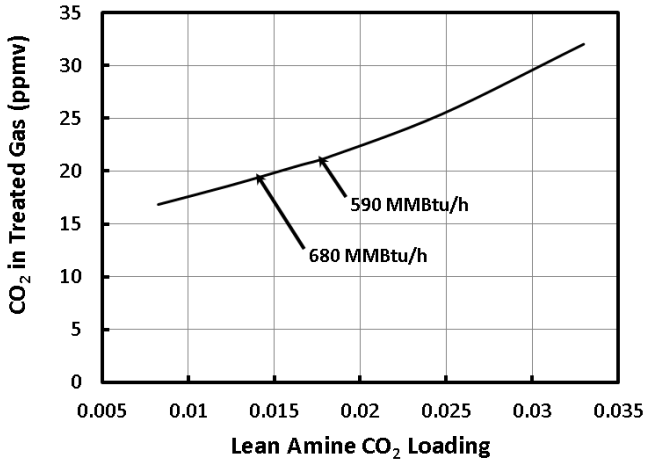
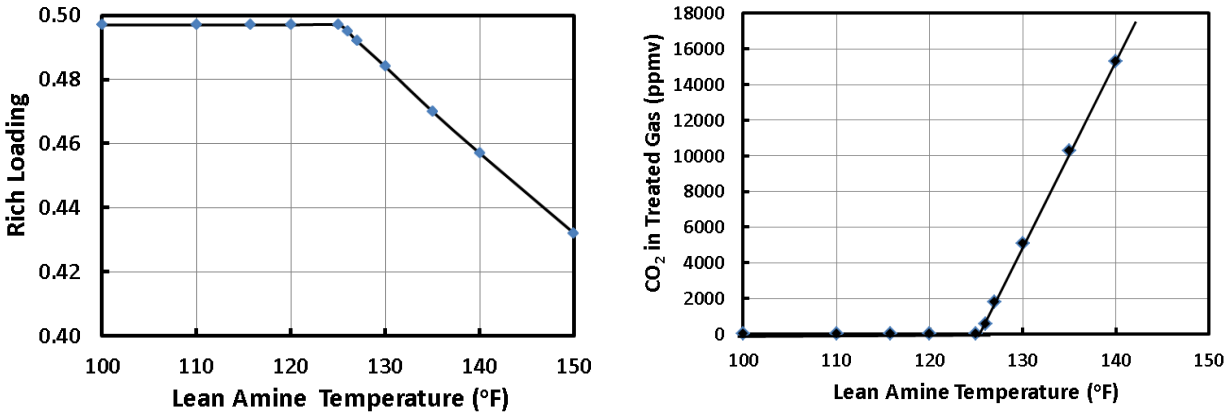


Figure 5 Insensitivity of CO_2 in Treated Gas to Lean Amine Loading (and Reboiler Heat Duty)



(a) How Rich Loading Varies with Lean Amine Temperature

(b) Failure to Make Specification Gas when the Lean Amine is Too Hot

Figure 6 Net Solvent Loading and Response of CO_2 in Treated Gas to Lean Amine Temperature

It is instructive to examine how treated gas composition changes with lean amine temperature in more detail. Figure 7 is a replot of Figure 6(b) on a logarithmic basis to magnify the region where treating fails. The design temperature is 115°F (46°C), and as long as the temperature is kept within 10°F (5°C) of the design point, the plant appears to be very stably operable. However, as Figure 7 shows, once the lean amine temperature approaches 125°F (52°C), the absorber will become extremely unstable; indeed, it will become inoperable. As already discussed, the reason for this apparently remarkable sensitivity to an operating condition has to do with the capacity of the solvent—that part of the CO_2 in the raw gas cannot be absorbed because of a solvent capacity limit passes directly into the treated gas. Continuing to decrease the solvent temperature, however, does not result in continued improvement to treated gas quality. Eventually it starts to have a deleterious effect because the solvent

viscosity is increasing with lowering temperature and mass transfer resistance to CO_2 absorption starts to increase.

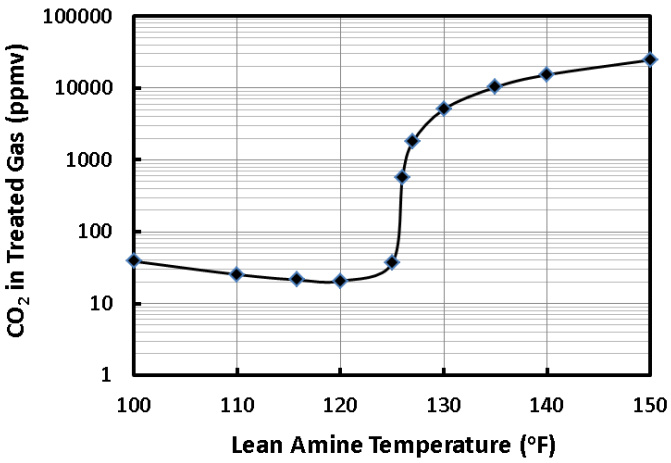


Figure 7 Extreme Sensitivity of CO_2 in Treated Gas to Lean Amine Temperature

The remaining question is: what is the best way to control the absorber if one has to operate with a lean amine that is too warm. The answer is fairly simple: manipulate the variable that will increase the solvent capacity, i.e., its net loading capacity. The choices are limited. Increasing solvent strength is always an option but it is not a control strategy. Producing a leaner solvent would be completely ineffective because lean loading has only a tiny effect on net loading capacity; in no sense is it controlling. Solvent flow rate, on the other hand, directly affects the solvent's capacity for carbon dioxide. This is really the only short-term control variable that would be effective.

Summary

The Atlantic LNG facility is very amenable to simulation using ProTreat's mass transfer rate-based approach. The simulation is truly predictive, requiring no estimates or other input beyond what is available from data sheets, P&IDs, and tower internals vendor drawings and specifications. All temperatures were matched to within better than one might expect from most thermocouple calibrations, and the simulated lean solvent loading was almost identical to measured data. The discrepancy in treated gas CO_2 content was easily explained and accounted for by a small amount of foaming suspected to be occurring in the absorber.

The Study Case LNG unit, which was designed using Raschig Super-Rings®, appears to be quite sound and stably operable, but with the proviso that the lean amine temperature must be kept between about 100 and 125°F. If there is any doubt that this can be achieved throughout the year (which may not always be the case in the region for this study case), then adequate provision must be made for operating at increased solvent flow. This requires adequate design margin in pumps, heat transfer equipment, and the regenerator itself.

The first case study (Atlantic LNG) validated the ability of the well-founded, mass transfer rate-based simulator, ProTreat®, to predict amine unit performance in LNG production with astonishing accuracy. In the second case study we have used the same model to explore the operability of a plant still on the drawing board. Without using such a simulator, it would be fairly non-obvious that there is a

critical operating temperature one simply cannot exceed, and near which the absorber operation will become unstable. There may well be a lower operating temperature as well, although whether the unit will become unstable there is a moot point.

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