Tools for analysing gas treatment

Ralph Weiland and Nathan Hatcher, Optimized Gas Treating Inc., USA, explain why mass transfer rate-based simulation, coupled with thermal imaging, is a suitable tool for design, troubleshooting and plant monitoring.

The most common technology for removing acid gases from gas streams is by absorption into aqueous amine solutions. Although there are numerous variants to the basic processing scheme depending on the amine being used (the desired gas purity, gas pressure, gas composition, and other factors), the basic scheme features an absorber and regenerator coupled together through a lean-rich cross exchanger for energy conservation via heat integration. Absorption is exothermic and solvent regeneration is usually done thermally by elevating the solution temperature and boiling it via a reboiled stripping column. Occasionally, regeneration through a series of pressure let-downs into flash drums is adequate to produce sufficiently stripped solvent for reuse in the absorber.

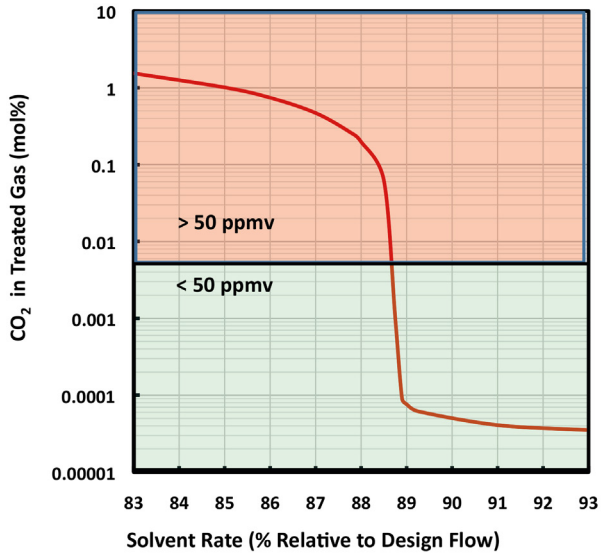


Figure 1. CO_2 leak from a piperazine-methyldiethanolamine (MDEA) absorber.

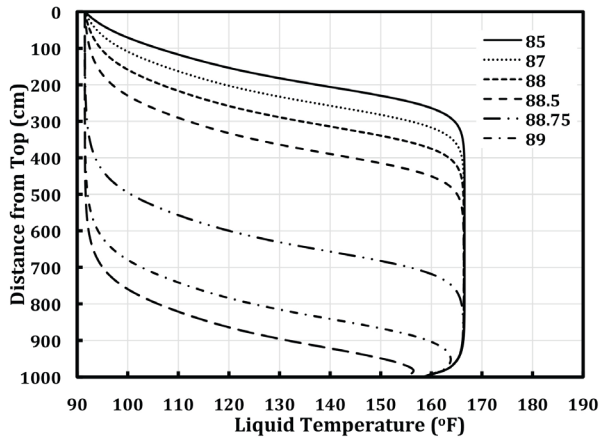


Figure 2. Piperazine activated MDEA absorber temperature profiles.

Superficially, amine treating is simple. On the surface, there are absorption and regeneration columns, with solvent circulating between them in a closed loop through a few pieces of heat transfer equipment, including a cross exchanger and trim cooler, with a reboiler and overhead condenser serving the stripper. However, beneath the surface, the chemistry is complex. The system is reactive; absorption and regeneration produce and consume large amounts of heat; the solvent is a high strength ionic solution, making the thermodynamics not ideal; and the gas phase is often at extreme pressures of more than 100 bar. Modern treating frequently uses a solvent with more than a single amine, which is almost always the case in LNG production. It is extremely difficult to design such facilities reliably without a clear understanding of the physics and chemistry of the system as embodied, for example, in a rigorous mass transfer rate-based simulator. Given the high economic cost of the CO_2 removal section of an LNG plant, it is surprising that antiquated simulators are still used for design when the modern mass transfer rate-based approach is commercially available. Using dated tools results in needless design risk and a lack of reliability, which can cause plants to only reach a fraction of their nameplate capacity, or use oversized equipment.

Falling short

There are numerous reasons that LNG plants fail to meet design throughput, either at start-up or after some time in operation. The focus here is on the CO_2 removal section of the LNG plant, and on some of the factors that can cause design shortfalls and operating problems that limit plant capacity. Apart from using an inadequate simulator and unknowingly generating designs that are too tight, these may include inadequate attention to the following in the design phase:

- Solvent contaminants, such as heat stable salts, hydrate inhibitors (e.g. glycols, methanol), and amine degradation products.
- Changing blend composition because of disparate amine volatilities.
- Liquid and vapour distribution in towers.
- Sensitivity to variation in parameters, such as changing gas and liquid composition and coolant temperatures, all of which can be determined by adequate sensitivity studies.

Due to the presence of high concentrations of acid gases (and to some extent degradation products), amine systems are highly corrosive. This can lead to the following:

- Corroded or missing trays and corroded packing.
- Leaking heat exchangers.
- Plugged instrumentation and equipment from corrosion products.

On the operations side, plants rarely run at steady state. In attempting to win a construction bid, if a contractor has developed a tight design without solid knowledge of how tower internals actually perform from a mass transfer (vs hydraulic) standpoint, normal process fluctuations can throw a plant in and out of compliance with meeting gas treating objectives. This list is by no means exhaustive, but it does contain the majority of the common causes for performance shortfalls. These will be discussed individually in this article.

Tight designs

The expectation that the separation or gas purity achievable by a given volume of packing should depend on the packing type and size ought to be no surprise. Therefore, gas treating process simulators should have a rigorous way to account for the particulars of the tower internals on the separation. Unfortunately, the designer does not have this information and, as such, should not be relied upon to provide this knowledge. It is easy to calculate the number of ideal stages for a specified separation, but it is difficult to take the results of the calculation into an actual volume of specific packing. This has been discussed in detail in a paper presented at the 2016 Laurence Reid Gas Conditioning Conference,[1] where

the performance of a structured packing was compared with three random packings and two types of trays from two internals suppliers in the context of a large LNG facility in Australia.

Tight designs leave little room for error and, unless a thorough sensitivity study is carried out, the likelihood of a failed design is high. As an example,[2] consider the case of treating a raw gas at 16 barg containing 20% CO_2 down to 50 ppm using a 33 wt% methyldiethanolamine (MDEA) with 7 wt% piperazine solvent (an arbitrary, non-optimised composition at this juncture). Figure 1 shows the treating response to changes in solvent circulation rate (reported as a percentage of design flow), and Figure 2 shows contactor temperature profiles.

It only takes a 1% decrease in solvent rate from 89% to 88% of design flow to cause a simulated 1000s-fold increase in CO_2 content from less than 1 ppmv to 2000 ppmv. At 89% of flow, the temperature profile shows a normal bulge a short distance from the bottom of the column (packed to 10 m depth with IMTP-25 random packing). At 88.9% of design flow, this column is operating on the edge of a steep cliff; at 88.8% it has fallen over the edge. There is extraordinary sensitivity because of the fast reaction rate of CO_2 with piperazine. CO_2 reacts so quickly that at adequate solvent rates, most of the CO_2 is removed from gas in the first 2 m of packing. The next 2 m or 3 m polish the gas, and, above the midpoint, the rest of the column does nothing at all. Breakthrough depends on the solvent capacity needed to remove the CO_2 from the gas and, provided there is enough packing in the first place, the breakthrough solvent rate depends relatively weakly on the amount of packing in the column.

This column was over designed. A 10 m deep bed is more than twice what is needed for this particular packing, as would have been shown by a sensitivity study. Indeed, IMTP-50, or even IMTP-70, would have been adequate, and considerably less expensive. A sensitivity study would also show that the design solvent flow has an adequate safety margin to permit reliable operation. But only mass transfer rate-based simulation is capable of providing such information reliably.

Such sharp performance sensitivity is common in LNG absorbers using promoted MDEA solvents. This example is actually a safe design, but without knowing beforehand just how the internals will perform with this solvent composition, it could just as easily have been an unsafe design, or even a design that would not work at all. Mass transfer rate-based simulation will allow tighter designs, but of course, every design must have sufficient margin for contingencies, although optimally no more than necessary. The right tools allow one to achieve the right design while knowing exactly how much margin there really is.

Solvent contamination

In reality and at best, a solvent is truly clean only on the day it is offloaded from the tanker truck into the solvent storage tank. After that, it is contaminated with either of the following:

- Reactive components that entered with the gas or products of their reaction with the amine (heat stable salts).
- Additives (methanol, glycols) injected into the gas at the wellhead to prevent hydrate formation in pipelines.
- Contaminants in the makeup water (Na^+, Ca^{2+}, Mg^{2+}, etc.).
- Amine degradation products (e.g. diethanolamine, methylmonoethanolamine).

In LNG production, unless the gas contains sulfur compounds or oxygen is present, heat stable salts and reactive-amine degradation products of MDEA (such as DEA and MMEA) are not usually present to an appreciable extent. In any case, with an MDEA-based solvent promoted with a highly reactive amine, such as piperazine, these contaminants are only mildly detrimental to treating even if they are present. However, this is not the case with glycols.

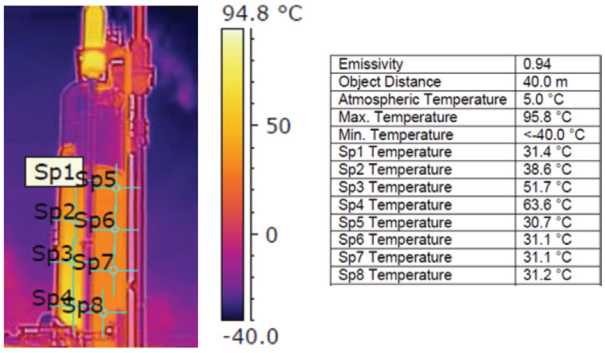
Monoethylene glycol (MEG) and diethylene glycol (DEG) are frequently injected into wellhead gas to inhibit hydrate formation prior to natural gas entering a pipeline. For transportation from offshore wells to land-based process plants, it may be more effective to dehydrate the gas offshore using triethylene glycol (TEG). However, a trace of TEG will inevitably be carried over with the dried gas. Glycols have low volatility and can build to 10 or 15 wt% in the amine treating solution.[3] In effect, any glycol build-up replaces an equal volume of high capacity amine solvent with low CO_2 capacity glycol. The solvent flowrate may remain the same, but it now has a much lower acid gas capacity. It is hard to design for this, but ProTreat® simulation is capable of accounting for this effect, and can be a valuable tool in diagnosing and quantifying this situation.

The hydrate inhibitor, methanol, is another potential contaminant. By treating methanol as a component whose absorption and stripping is controlled by its mass transfer rate, ProTreat allows the residual methanol content of the treated gas to be accurately determined. This may be important if the gas is destined to be used as cracker feedstock to produce ethylene and propylene, because methanol is a serious cracking catalyst poison.

Although not strictly a contaminant, the solvent activator concentration can change over time, because it is considerably more volatile than the MDEA it activates. Thus, the promoter concentration will fall with time-on-stream, and this recommends careful solvent monitoring. One effective way to prevent this problem from occurring is to use a short bed (perhaps only 500 – 1000 mm depth) of random or structured packing in the top of the absorber and run makeup water to the top of this wash section. Similarly, feeding rich amine two or three trays below the reflux return tray (top tray) in the stripper will also capture almost all of the amine leaving in the vapour from the rich solvent feed tray. Both practices should be standard in almost any amine plant to prevent virtually all vaporisation losses.

Liquid and vapour distribution

Uniform liquid distribution (and periodic redistribution) is particularly important in packed columns. By comparison, trays tend to take care of themselves, although multi-pass trays require some care. What is sometimes overlooked is the need to pay careful attention to gas distribution[4] at



Emissivity	0.94
Object Distance	40.0 m
Atmospheric Temperature	5.0 °C
Max. Temperature	95.8 °C
Min. Temperature	<-40.0 °C
Sp1 Temperature	31.4 °C
Sp2 Temperature	38.6 °C
Sp3 Temperature	51.7 °C
Sp4 Temperature	63.6 °C
Sp5 Temperature	30.7 °C
Sp6 Temperature	31.1 °C
Sp7 Temperature	31.1 °C
Sp8 Temperature	31.2 °C

Figure 3. Thermal image of a CO_2 absorber.

the base of columns, particularly packed columns of large diameter, as well as trayed columns. Failure to do so can cause serious maldistribution of gas (and, consequently, liquid) over the column's cross section, which will lead to poor treating performance.

A useful pair of tools for assessing maldistribution, whether gas, liquid, or both, is mass transfer rate-based simulation and thermal imaging of the tower. Figure 3 shows a thermal image of the upper two-thirds of an absorber in an ammonia plant using a piperazine-promoted MDEA-based solvent (the lower third could not be imaged from this position because of the proximity of other equipment). The position of the gas inlet nozzle was behind the column as it is seen in the photograph and towards its left side. As the table in Figure 3 shows, the temperature profile along the height of the absorber exhibited a distinct bulge along its left side (above the gas inlet nozzle) near the bottom of the image, but an almost uniform temperature (and equal to the lean solvent temperature) on the wall opposite the nozzle. This column was suffering from poor gas distribution. It is certainly not normal to see great temperature asymmetries around the periphery of a correctly operating column. Instead of trying to match the plant measured treating performance by tuning an obtuse parameter, such as tray efficiency or residence time per theoretical stage, a true mass transfer rate model would reveal that the wetted interfacial area would need to be derated.

Corrosion

Missing and corroded trays can be hard to diagnose without expensive gamma scans. However, if tray damage is suspected, a thermal scan may show anomalies in longitudinal temperature distribution, especially when compared with mass transfer rate-based simulation. Because a mass transfer rate model uses actual trays, not idealisations, and assumes that all trays are operating properly, simulation of a column with fewer operating trays than it is supposed to contain may allow the simulation to reproduce tower performance data. Similarly, reducing the effective interfacial area in the packed bed will allow the simulation to reproduce performance data if packing is missing or badly damaged. Comparison with thermal scans may also provide further evidence of packing or tray damage.

On the other hand, moderate foaming can actually cause better performance than expected because of the increased interfacial area consequent to the presence of foam. Severe foaming, however, always degrades tower performance. If a mass transfer rate-based simulation needs 20% or 30% more area than physically provided by the packing as simulated, foaming may be indicated.

A leaking heat exchanger, especially a cross exchanger, can result in treating being missed by a wide margin if the leak is from the rich side to the lean side of the exchanger (as it most often is). Treating is usually fairly sensitive to lean solvent loading of acid gas. The simplest diagnosis is rate-based simulation of the regenerator, followed by a comparative measurement of the solvent lean loading as it enters the absorber and, if possible, upstream of the exchanger as well. It should be noted, however, that lean solvents can be hard to assess properly because H_2S tends to oxidise to thiosulfate in the presence of air. Again, simulation will reveal whether the measured lean loading is capable of satisfactorily treating the raw gas. In one instance, mass transfer rate-based simulation pointed an operator to resample around a lean/rich exchanger with bottles pre-purged with nitrogen. The leak was confirmed through sampling only after taking these and other precautions to eliminate oxygen contamination.

Amine units can also fall short because of instrumentation malfunctions caused by equipment fouled not just by corrosion products, but also by materials injected into the system for various reasons. Examples of injected foreign materials include corrosion inhibitors, antifoams, and oxygen scavengers. These materials degrade and form gels and assorted sticky substances that can plug level and flow meter pressure taps, resulting in false readings. Suspended particulates erode orifice plates and also lead to false readings.

Conclusion

The CO_2 absorbers in LNG plants (and other deep CO_2 removal applications, such as syngas) can fail to meet expectations for a wide variety of reasons. The most common ones have been discussed in ths article. The overriding lesson is that genuine mass transfer rate-based simulation, coupled (where appropriate) with thermal imaging, is an excellent tool not just for design, but for troubleshooting and plant monitoring as well. **LNG**

References

1. WEILAND, R., SCHULTES, M., PILLING, M., PORTILLO, J., SUMMERS, D., SHIVELER, G., DUSS, M., STEWART, E., and PRADERIO, A., 'Sensitivity of Treating Plant Performance to Tower Internals', paper presented at the Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, US, (21– 24 February 2016).
2. WEILAND, R. H., and HATCHER, N. A., 'Foundations of Failure', *Hydrocarbon Engineering*, (December, 2011), pp. 57 – 59.
3. SIEDER, G., KATZ, T., and HEARN, J., 'How Glycols Affect the Acid Gas Removal Process', PTQ, Q4, (2013).
4. COOPER, E., and WEILAND, R., 'Reducing CO_2 Slip from the Syngas Unit of an Ammonia Plant', paper presented at Nitrogen + Syngas 2016, Berlin, Germany, (29 February – 3 March 2016).