Piperazine Promoted MDEA in LNG Service[1]

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Piperazine-promoted MDEA has proven to be one of the most effective solvents for CO_2 removal in LNG production. Its use was first disclosed in U.S. Patent 4,336,233 issued June 22, 1982. Between 1982 and 2002, BASF's aMDEA® (activated MDEA) solvent captured the lion's share of the market in ammonia synthesis gas purification and several applications where deep CO_2 removal was the primary concern. In recent years, CO_2 removal from gas in LNG production has become a primary application area. Following the original patent's expiry, most solvent suppliers now offer a version of piperazine-activated MDEA solvent under a variety of trade names.

The main advantage of piperazine as a promoter is its extreme reactivity towards CO_2. The second-order reaction rate constants for a number of amines with CO_2 are listed in Table 1 at 25°C. Piperazine is almost 10 times more reactive with CO_2 than any of the other common amines, making it an excellent promoter for the reactions that occur when CO_2 absorbs into aqueous MDEA. For many deep CO_2 removal applications, piperazine promoted MDEA is a superior solvent because of its high reactivity, low heat of absorption, and high capacity for CO_2. Primary and some secondary amines have high reactivity, too, but their heats of absorption for CO_2 are much higher, and because they are not generally used at concentrations as high as MDEA, their capacity tends to be lower[2]. Primary and secondary amines also consume two amine molecules per molecule of CO_2 absorbed, versus a one-to-one ratio for MDEA, which again lowers their capacity[3]. Significantly lower energy consumption is a primary driver for making piperazine promoted MDEA the solvent of choice. Another consideration is the availability of a process guarantee, which may not be offered if a generic amine is used in a non-licensed process.

Table 1   Reaction Rate Constants of CO_2 with Common Gas Treating Amines

Amine	Reaction Rate Constant (L·mol^{-1}s^{-1})
MEA	6,000
DGA	4,500
DEA	1,300
DIPA	100
Piperazine	59,000
MMEA	7,100
MDEA	4

MDEA does not react with CO_2 at all. Nevertheless, it has high capacity for CO_2 because the tertiary amino group is sink for the hydrogen ions produced by CO_2 hydrolysis and the reaction of CO_2

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[2] Because we are dealing with chemical reactions, molar amine concentrations are more meaningful than mass concentrations. Diglycolamine (DGA®) and MDEA at 50 wt% are 14.6 and 13.1 mol% amine, respectively, which gives DGA a slight capacity advantage. At 65 wt%, DGA's theoretical capacity advantage is nearly a factor of two.
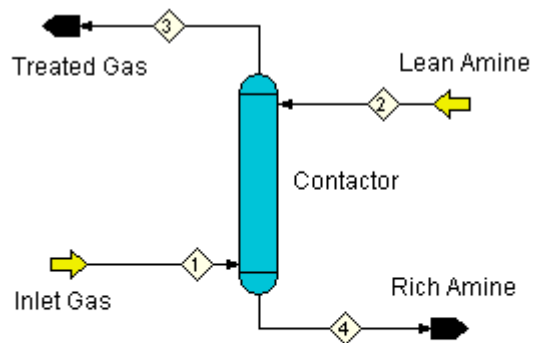
[3] Corrosion considerations limit CO_2 absorption to a rich amine loading of roughly 0.45 in any case, so very little of the theoretical 1:1 versus 1:2 ratio of CO_2 to amine capacity advantage can really be enjoyed unless metallurgy is upgraded.

with piperazine. This factor gives MDEA an enormously higher capacity than water alone—the MDEA is able to be protonated. In contrast, Piperazine reacts rapidly and it very strongly binds with CO_2. In a mixture with MDEA however, piperazine carbamate will revert some of its CO_2 to bicarbonate and uses the MDEA to accept the accompanying hydrogen ion. The reactivity of piperazine with CO_2 lowers the equilibrium backpressure of CO_2 over the solution, and this is especially important at the top of an absorber where the final treated gas is being produced. In addition, at the very top of the absorber, CO_2 is exposed to a lot of free reactive piperazine, it reacts quickly with it and is held in solution by it—this is what allows very low (parts per million) treated gas CO_2 specifications to be achieved that could not be done with MDEA alone. But towards the middle and bottom of the contactor, the piperazine is consumed to a considerable extent by CO_2. Nevertheless, carbon dioxide absorption rates are enhanced by the presence of free piperazine throughout the column.

The rest of this article demonstrates (a) how much changing the piperazine concentration matters to treating when all other parameters such as circulation rate and reboiler duty are kept fixed, and (b) how changing circulation rate can result in what, at first glance, appear to be very strange performance curves.

Case Study 1

In the following example, a 22-tray contactor is used to treat 1,160 psia, 77°F gas containing 30% CO_2. We will compare 50 wt% generic MDEA with MDEA containing 5%, 7% and 9% piperazine in a total amine mixture of 50 wt%, all at 1,150 gpm and 120°F. Although not shown in Figure 1, the simulation *using the ProTreat® simulator* is of the entire plant including regeneration and heat exchange. Reboiler duty and all other process conditions were kept constant for all four cases. Key simulation results are shown in Table 2.

Lean Amine Temp. = 120 F.
Amine Circulation = 940 GPM, 50wt% MDEA
Feed Gas Flow = 60 MMSCFD, 30% CO2
Column ID= 6.0 feet, 22 Nutter Float Valve Trays

Figure 1   PFD and Process Conditions

Table 2   Effect of Piperazine on Treating

Wt% Piperazine	Treated Gas (ppm CO_2)	Lean CO_2 Load (mol/mol)
0 (22 trays)	85,300	0.0015
0 (50 trays)	48,300	0.0015
0 (100 trays)	48,000	0.0015
5 (22 trays)	51	0.016
7 (22 trays)	39	0.021
9 (22 trays)	10	0.026

The effect of piperazine on CO_2 treat is nothing short of spectacular—it allows *promoted* MDEA to reach a few tens of ppmv while MDEA alone cannot do better than 8.5% in the same equipment, and it cannot get below 4.8 mol% CO_2 *even with 100s of trays in the column* under otherwise identical conditions.

MDEA was originally developed as a solvent for *selectively removing H_2S* from gas streams down to parts per million, while *slipping* as much CO_2 as possible. *MDEA was never intended for CO_2 removal*. While it can be useful for <u>bulk</u> removal, *it certainly cannot be used by itself for deep removal*.

The commercial and economic advantages of using piperazine promoted MDEA for CO_2 removal, especially deep removal, are twofold. Firstly, this type of solvent needs considerably lower circulation rates compared with conventional reactive amines such as MEA and DEA because it can be used at much higher concentrations. The implication is smaller pumps, lower pumping costs, and smaller towers and other auxiliary equipment. Second, as a result of the reduced circulation rate and the smaller heat of reaction, the reboiler energy requirements are also significantly lower than conventional single amines and so is the size of the equipment.

Turning to another case study, piperazine promoted MDEA (and probably other highly reactive solvents as well) can show quite counterintuitive behaviour, too. Sometimes, if knowledge of the behaviour is missing, process movements away from a set-point can receive control responses in the completely wrong direction and destabilize the process. The following case study is an example.

Case Study 2

This case reports on a design study for a CO_2 absorption system in a proposed LNG plant, with some quite surprising findings. The gas to be treated is nominally 84% methane, 10% ethane, and 4% propane containing 2% carbon dioxide all on a dry basis. The treating specification is < 50 ppmv CO_2. The column is intended to contain 30-ft (9-m) of IMTP®-50 random packing with the tower diameter sized for 80% of flood. Inlet gas is at 850 psig (60 bara) and 110ºF (43ºC), and it is being treated using a blend of 32 wt% MDEA + 8 wt% piperazine.

Three sets of simulations were run at a series of solvent rates, but with each set having a constant value of CO_2 lean loading, as shown in the legend of Figure 2. At each lean loading, the absorber fails to treat adequately if the solvent rate was too low. This is just as one should expect, because at too low solvent flows the solvent just doesn't have enough capacity to remove CO_2 to the desired level. It's solvent capacity limited, and inadequate capacity, i.e., a saturated rich solvent, is what makes the column rich-end pinched. The surprise though is the apparent presence of a "sweet spot", in other words a solvent flow at which treating is best and above and below which treating is worse. The question is why it exists.
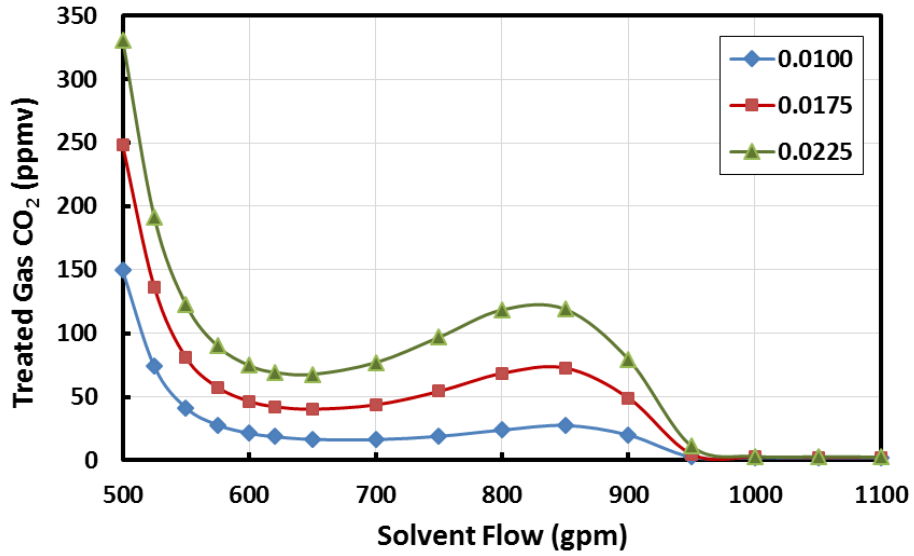
Figure 2   *How absorber performance depends on solvent rate at various lean CO₂ loadings*
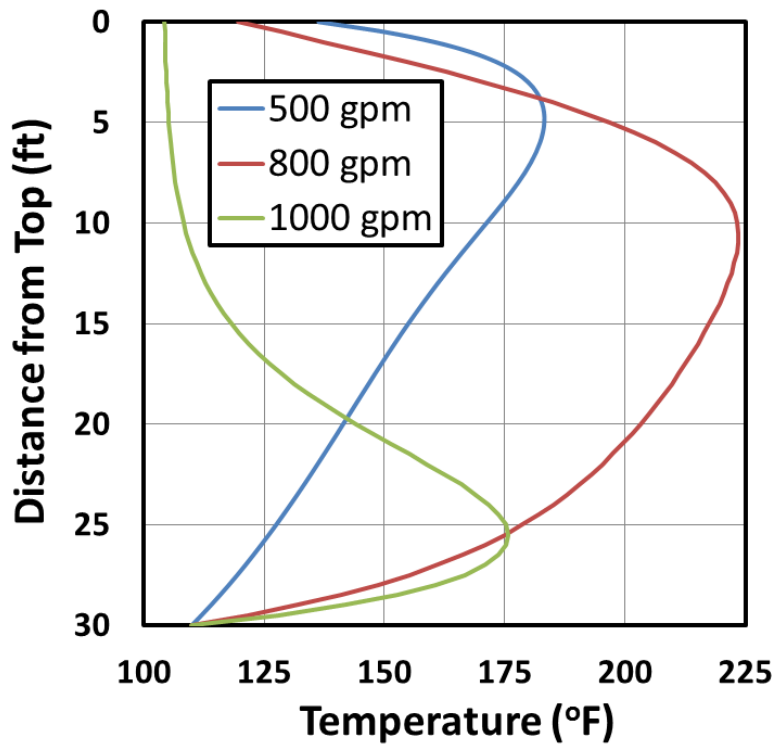

Figure 3   *Absorber gas temperature profiles when lean CO₂ loading is 0.0225 mol/mol*

As the solvent flow varies from 500 gpm to 1,000 gpm for any of the loadings in Figure 2, absorber operation moves from being starved of solvent (i.e. a rich-end pinch) through bulged pinched operation and ultimately ends up in a lean end pinched state (excess solvent available). Under a bulge pinch the temperature in the central part of the column is so high that only the extreme ends are effective in removing CO_2—the center part of the column really does nothing. The absorber behaves as though it has perhaps only 15 or 20 feet of packing, not the 30 feet it actually contains. Thus treating gets progressively worse as the bulge pinched region is entered (at roughly 650 gpm). Once the solvent flow becomes sufficiently high to drive the temperature bulge far enough down the absorber for a lean-end pinch to start forming (roughly 850 gpm), treating starts to improve quite rapidly. Whether or not the 50 ppmv specification on CO_2 is achieved in the intermediate flow rate region depends on lean solvent CO_2 loading.

This kind of behaviour may have process control implications. For example, at the intermediate lean loading of 0.0175, the treated gas was 40–45 ppmv CO_2 over the flow range from 600 to 750 USgpm. To the right of the minimum the way to respond to the gas going off-specification may be not to increase solvent rate. Instead, the right response might be to decrease it, or perhaps to increase reboiler steam or hot oil flow. Without a detailed operating diagram such as the one in Figure 2, operations could probably not do much more than guess at the correct response and hope for the best.

Packing vs. Trays

The behavior of trayed columns is a little different than in packed columns. In a packed absorber, as the solvent flow is increased, the wetted, interfacial area increases as well, and for this reason the mass transfer rate increases quite substantially with solvent flow. This generates high bulge temperatures and can drive the column into a severe bulge pinch. In a trayed column, gas-liquid interfacial area for mass transfer is only a relatively *weak function of liquid rate* and the performance curve typically looks like the one in Figure 4 with the lean solvent loaded to 0.0156 mol/mol. (Note the logarithmic scale.) There is no maximum because the dependence of interfacial area on liquid rate is too weak to drive higher absorption rates and torment the central, flat region into becoming a peak. Nevertheless, there are still lean-end, bulge, and rich-end pinch conditions at the low, medium and high solvent rates similar to, but not as severe as the ones exemplified by the temperature profiles in Figure 3.
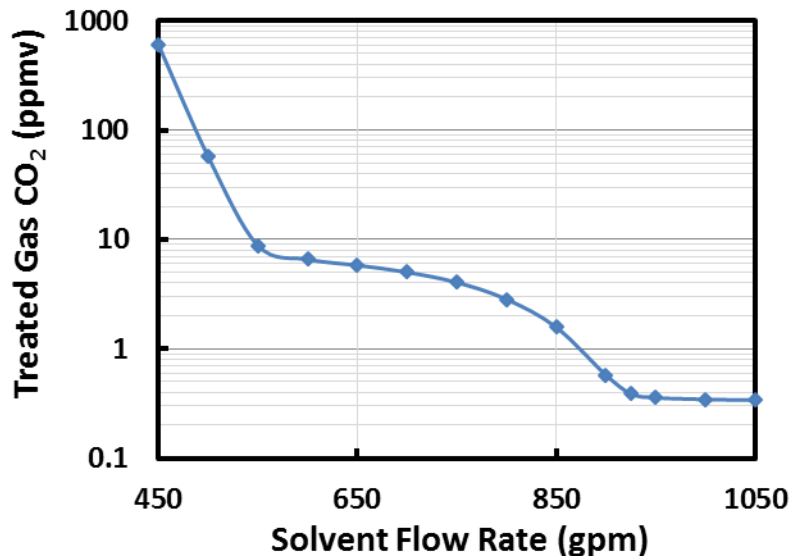
Figure 4   How Solvent Rate Affects Trayed Absorber Performance

Under the conditions of the simulation shown in Figure 4 (30 valve trays and a lean loading of 0.0156 mol/mol), there is no sweet spot, so the preceding discussion does not directly apply. However, there is a radical change in the absorber's response to solvent rate at around 550 gpm. Below this value, treating undergoes a radical decline with decreasing solvent flow, but it is unresponsive for quite a wide range of flows above it. One might call 550 gpm a point of instability. In the present case, 30 trays can treat quite nicely at solvent rates just as low as packing can do. But again, just like packing, there will be a lean solvent CO_2 loading beyond which fully lean-end pinched operation (high solvent flows) will be necessary. It might be noted that lack of a sweet spot and a fairly level operating curve means solvent rate is not a good control variable.

Summary

The difference between packing and trays as well as the effect of packing type and size can be very important in the design of LNG facilities. If your simulator is not *genuinely* based on mass transfer rates, all of this will be missed; all trays and packings will be treated as ideal stages, and using tray efficiencies — even computed ones — will not prevent the design from being subject to considerable uncertainty. In the worst case, the plant may only perform properly well below nameplate rates.

Mass transfer pinch analysis is the key ingredient in achieving a full understanding of how CO_2 absorbers in LNG (and other) plants might respond to process upsets and control strategies. Whether the pinch is at the rich end, the lean end, or the centre of the absorber, a pinch is a region where the actual and equilibrium CO_2 concentrations approach extremely closely to each other, and the concentration difference driving force for absorption disappears. Pinch analysis is unique to genuine mass and heat transfer rate-based simulation, and it is essential in the correct interpretation of sensitivity studies.

Plant simulation and analysis are holistic when the entire treating plant is examined all at once, or at least the isolated equipment item is examined and analyzed using a simulation tool that is based on considering all the factors that affect performance, without idealizations or unwarranted approximations and shortcuts. The ProTreat® simulator is the only available, proven, commercial tool that allows this to be done for gas treating in a computationally robust and completely reliable manner. There is no reason to risk failure using inadequate tools when the right tool is readily available.