

CO₂ Removal with DEA-Promoted Hot K₂CO₃¹

Ralph H. Weiland, G. Simon A. Weiland, Mathew Bailey

Optimized Gas Treating, Inc.
212 Cimarron Park Loop
Buda, TX 78610

Carbonate processes in ammonia production are characterized by both absorbers and regenerators running very hot (typically ranging from 100 – 130°C) so that heat integration in the form of large lean-rich cross exchangers is unnecessary. Regeneration is driven by a pressure swing from a high absorber pressure to a low regenerator pressure, but is aided by steam stripping, as opposed to the temperature swing and predominantly steam stripping typical of amine systems. Still, removing CO₂ remains energy intensive, and a variety of conservation schemes is used.

High temperatures in CO₂ service make for a very corrosive environment. To avoid the use of corrosion inhibitors, vessels are usually stainless clad and process piping is also stainless. Characteristically, the absorber and regenerator tend to be very tall (50 – 60 m overall) holding five or six beds of random packing, each between 5 and 8-m deep. Indeed, as will be seen, these towers tend to be grossly over height.

Process Chemistry

Aqueous potassium carbonate and bicarbonate exist exclusively as K^+ , HCO_3^- and CO_3^{2-} ions. When CO₂ dissolves into water it forms carbonate and bicarbonate ions, and very little is present as molecular CO₂. Hot potassium carbonate solutions are an ionic soup and the notion that these ions are associated with each other in the form, for example, of K_2CO_3 is quite fictitious. Carbon dioxide hydrolyses in solution with the hydroxide ion available from dissociated water:



The hydrogen ion that remains after hydrolysis immediately and instantaneously reacts with carbonate to form bicarbonate:

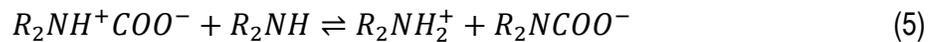


Potassium is merely a spectator ion. It takes no part in any reactions and, beyond affecting the ionic strength of the solution and its non-ideality, potassium itself has no effect on the solubility of CO₂ in Hot Pot solutions. The vapour-liquid equilibrium associated with the solubility of CO₂ in Hot Pot is modelled in the ProTreat® simulator on the basis of a concentrated solution of electrolytes.

The rate of the CO₂ hydrolysis reaction (Reaction 2) is fairly slow because the OH^- ion concentration is low, and CO₂ is a sparingly soluble gas. This leads to quite tall absorption and

¹ Nitrogen + Syngas, September–October, 2018

regeneration towers without a promoter. DEA is a secondary amine and reacts readily with CO₂, so its addition to carbonate solutions tends to speed up the absorption process considerably. DEA reacts with CO₂ according to the simplified scheme:



Reaction (4) occurs at finite rate while Reaction (5) involves only a proton transfer and so is instantaneous. Apart from the three molecular species CO₂, DEA, and of course water, the solvent again is an electrolyte soup and when combined with Hot Pot, the correct way to determine CO₂ solubility is with an electrolyte model. This is the way ProTreat simulation does phase equilibrium calculations.

The amine of choice for promoting Hot Pot is DEA. As a secondary amine, DEA binds less strongly to CO₂ so carbamate decomposition in the regeneration step requires less energy. MEA reacts faster with CO₂, which for the same molar concentration would enhance the absorption rate; however, the cost is a higher regeneration energy requirement compared to DEA, and MEA's absorption rate advantage can be easily achieved using DEA with a small amount of additional packing. As will be seen, a small amount of DEA also somewhat lowers the CO₂ equilibrium backpressure over the treating solution.

Fractional Conversion

Fractional Conversion, F_c , is the extent to which a carbonate solvent is saturated with CO₂:

$$F_c = \frac{\frac{1}{2}[KHCO_3]}{[K_2CO_3]_o}$$

If the solvent is promoted with DEA, then Fractional Conversion is:

$$F_c = \frac{\frac{1}{2}[KHCO_3] + [DEACOOH]}{[K_2CO_3]_o + [DEA]_o}$$

The subscript 'o' signifies the concentration of the component in the completely CO₂-free state, i.e., the fresh solvent before it has been exposed to carbon dioxide. The *DEACOOH* molecule is equivalent to *R₂NCOO⁻* in Equation (5). These definitions are the exact equivalents of the term 'loading' as used in amine treating in the natural gas and refining industries.

Effect of DEA on Equilibrium Solubility of CO₂ in Hot Pot

The ProTreat® simulator was used to develop solubility curves for CO₂ in Hot Pot with and without DEA. The cases considered were 30 wt% K₂CO₃ and 30 wt% K₂CO₃ + 2.5 wt% DEA because the latter corresponds to the solvent formulation in the case study to be considered later. Figure 1 shows the extent to which 2.5% DEA reduces the CO₂ backpressure at absorber lean-end conditions. Fractional Conversions between 0.1 and 0.25 have CO₂ levels in the gas between 100 and 3,000 ppmv. Using 2.5 wt% DEA reduces equilibrium CO₂ pressures between 10 and 40% (i.e., the ppmv ratio is 0.6–0.9). As it turns out, this is a significant but not a large effect compared with the effect of the DEA reaction on absorption, and especially regeneration, rates

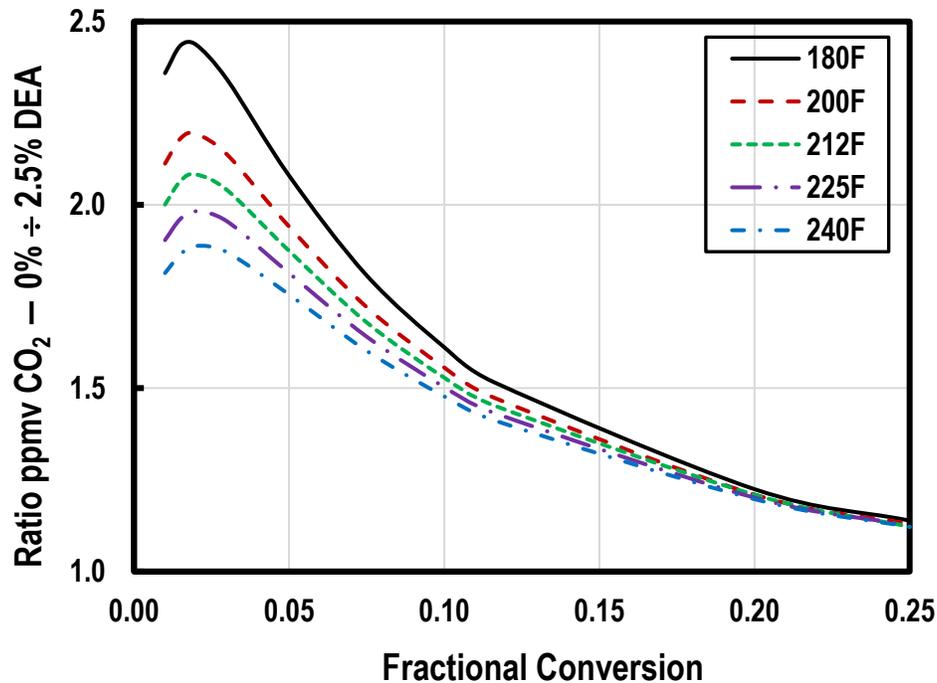


Figure 1 Effect of DEA on CO₂ in Gas at Equilibrium, Shown as the Ratio of ppmv CO₂ without DEA to ppmv CO₂ with 2.5 wt% DEA

Case Study – 1,000 MTPD Ammonia Plant

The case study is based on a 1,000 MTPD ammonia plant. The CO₂ section uses the two-stage DEA-promoted Hot Pot system shown in Figure 2. The simplified drawing omits several energy conservation measures but retains the features essential to the discussion. Table 1 shows the parameters pertinent to the raw ammonia syngas (Stream 3).

Table 1 Condition of Raw Syngas Entering Absorber (Dry Basis, Stream 3)

Parameter	Value
Temperature, °C	124
Pressure, barg	31
Flow, 1000's Nm ³ /h	160
Composition, mole %	
Carbon Dioxide	17.4
Methane	0.90
Hydrogen	60.6
Carbon Monoxide	0.17
Nitrogen	20.7
Argon	0.23

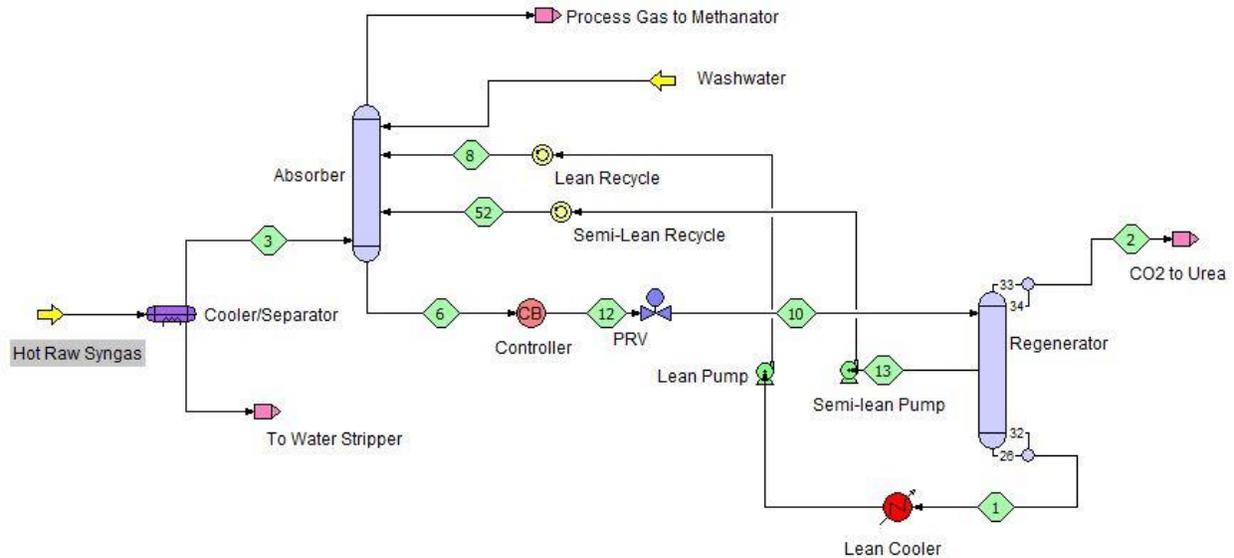


Figure 2 Simplified Schematic of Benfield Two-stage CO₂ Removal System

Both towers contained more than one type and size random packing in multiple beds. The absorber had two water wash trays at the top, and a total of 32 metres of packing distributed roughly equally between the lean (2,600-mm diameter) and semi-lean (4,250-mm diameter) tower sections. The regenerator was 5,000mm diameter above the semi-lean draw point holding 25.6 metres of packing and 3,050 mm diameter in the lean section with 18 metres of packing.

This plant actually operates with 30 wt% potassium carbonate and 2.5 wt% DEA and the performance parameters predicted by the ProTreat® simulator were very close to measured data without the need for any adjustment or manipulation of *any* parameters to achieve agreement between simulation and measurement. In other words, *the simulation is fully predictive without adjustable parameters*. The same unit was simulated without DEA, all other parameters being identical between the two cases. The effect of DEA on overall performance of both absorber and regenerator is summarized in Table 2. Obviously, using 2.5 wt% DEA provides a very satisfactory synthesis gas.

Non-promoted Hot Pot leaves enough additional CO₂ in the treated gas to result in roughly a 7.4 MTPD loss in ammonia production. At the notional value of USD 300 per metric ton, this lost production is worth about USD 2,220 daily in unrealized revenue. However, hydrogen makeup and energy are additional costs and, when these are factored in, the cost of the additional CO₂ slip is really about USD 7,800 per day for this size plant. The question is what is happening in the columns to produce these not insubstantial differences.

Table 2 System Performance using Promoted vs. Non-promoted Hot Pot

	DEA-Promoted	Non-promoted
CO ₂ in Treated Gas, ppmv	350	1,530
Lean Solvent Fractional Conversion	0.116	0.203
Semi-Lean Fractional Conversion	0.541	0.563
Rich Solvent Fractional Conversion	0.691	0.739

Absorber

Figure 3 shows and compares how CO₂ concentration is changing across the absorbers in the two cases. Apart from the obviously lower CO₂ slip with DEA promotion, there are several other notable observations.

Firstly, regardless of promotion, the full benefit of using a semi-lean stream is realized in the bottom five metres of packing—the next 12 metres do absolutely nothing towards removing CO₂. Also the benefit of promotion is fairly small in the semi-lean section (lower half of the plot) because the Fractional Conversion is already high there, thus, most of the DEA has already been converted to carbamate.

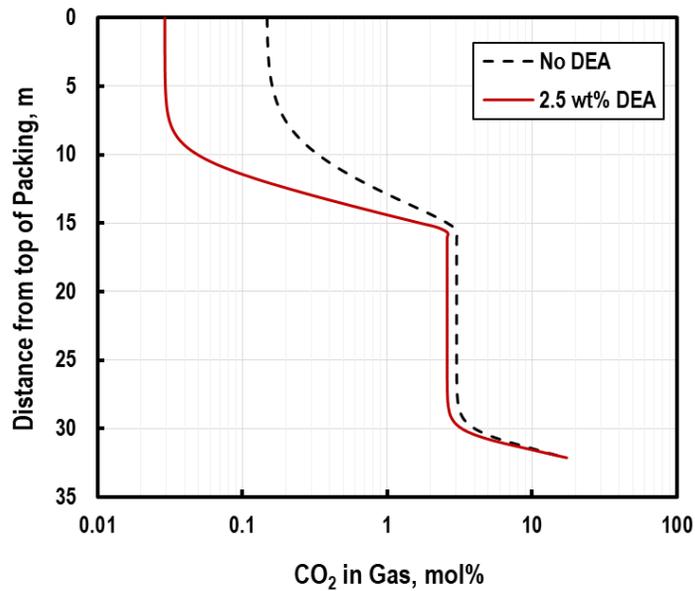
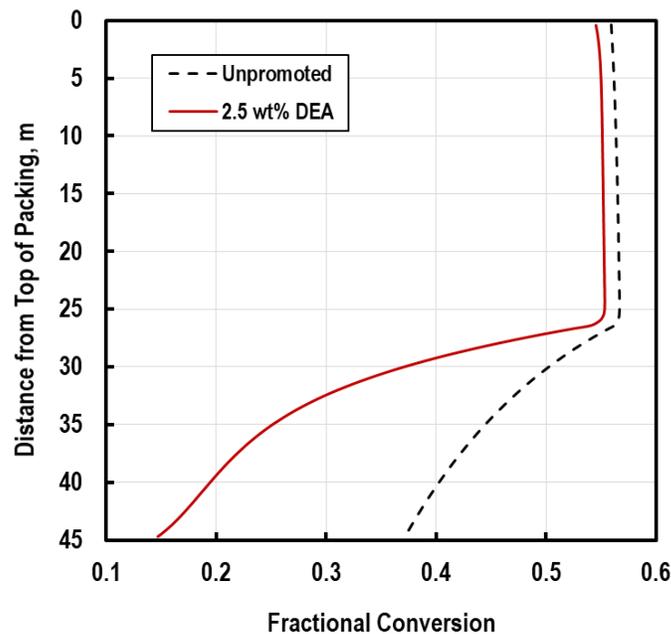


Figure 3 How CO₂ Concentration Changes through the Absorber (note log scale)

The differences in the lean section of the absorber (upper half of the plot) are more striking. Without DEA promotion, CO₂ continues to be slowly removed across almost the entire lean (polishing) section. However, the addition of 2.5 wt% DEA drops the CO₂ concentration to 350 ppmv so quickly that the top five metres of packing are not even needed. Of perhaps greater value is knowing that *the lean section is completely lean end pinched*. This means simply that *the final treating is determine by the lean solvent's Fractional Conversion*. If there is enough packing in the absorber and if the split between lean and semi-lean sections is properly chosen, this will almost invariably be the case. This absorber (like many Benfield absorbers) is over-packed and over-height by about a *factor of two*; however, these profiles suggest that where one's attention should really be focused is on the regenerator because it is there that the lean and semi-lean solvents are produced.

Regenerator

Figure 4 shows how CO₂ strips out and reduces the Fractional Conversion to its final value in the lean solution as the solvent flows through the regenerator. In both cases a large fraction of the dissolved CO₂ in the loaded solvent flashes off in the PRV (21.4% when promoted, 24.7% when not). As the solvent flows down the top 25 metres of packing, no stripping at all takes place—the upper section might as well not be there! Indeed, the upper 25 metres of packing, all the auxiliary internals such as distributors, and the 30 or so metres of tower shell are an unnecessary capital investment. The primary reason for this is that the stripping steam is metered to provide proper stripping of the 10% of the total solvent flow that actually reaches the lean (lower half) section. The other 90% could be immediately withdrawn as an essentially flashed semi-lean solvent without entering the regenerator at all. Although it is contacted by a flow of stripping steam, the steam flow is inadequate and quite incapable of having a significant effect.



**Figure 4 Promotion with DEA Greatly Improves Regeneration.
Note that there is Additional Stripping in the Regenerator**

Below the semi-lean draw point the vapour-to-liquid flow ratio is high enough for the stripping vapour to actually strip CO₂ from the solvent. However, it is easy to see from Figure 4 that CO₂ strips from DEA-promoted Hot Pot a lot more easily than from its non-promoted equivalent. With the non-promoted solvent, there are no reactions to enhance mass transfer—stripping is purely a physical process. With DEA promotion, however, the decomposition of DEA carbamate enhances the mass transfer rate of stripping by factors of from four in the semi-lean section up to 70 at the bottom of the lean section, and the lower the Fractional Conversion, the greater the enhancement to the stripping rate. Thus, the Fractional Conversion of the fully stripped DEA-promoted solvent is roughly one-half the non-promoted value (0.116 versus 0.203).

Summary

There are a number of little-known (perhaps unknown) characteristics of Hot Pot and DEA-promoted Hot Pot that have a profound effect on the potential economics and efficacy of CO₂ removal using standard Hot Pot and Benfield processes. This article has discussed only one specific example of the CO₂ removal section of an ammonia plant; however, the operating conditions in this case are fairly typical, and the observations and conclusions have general validity. In particular the ProTreat® mass transfer rate-based simulator was used to show the effect of spiking a 30 wt% Hot Pot solvent with 2.5 wt% DEA on (1) CO₂ solubility, (2) absorber performance, and (3) regenerator performance:

- The equilibrium CO₂ partial pressure over the promoted solvent may be as low as one-half the value in the non-promoted case. However, the effect is already weakening when Fractional Conversions approach values typical of treating with Hot Pot and Benfield technologies ($F_c \approx 0.1$), and it weakens further as Fractional Conversions get even higher. Nevertheless equilibrium pressures at the absorber lean end can be 25% lower when DEA is used as a promoter.
- The main effect of DEA is on the mass transfer (absorption and stripping) rates in both the absorber and regenerator as actualized by reaction kinetics enhanced by DEA.
- In an absorber, only the bottom few metres of packing in the semi-lean (bulk removal) lower section are useful for CO₂ removal. About the upper two-thirds provides no treating whatsoever.
- In the lean (gas polishing) upper section of the absorber, using DEA can reduce the amount of packed height needed for treating or it can extend the lean-end pinch region to insulate the column from process upsets. Even without DEA, the entire polishing section performs useful work.
- Benfield absorbers frequently contain at least twice the amount of packing that is actually needed.
- In a lean-end pinched absorber, the quality of the treated gas is determined almost solely by the Fractional Conversion of the lean solvent, i.e., by regenerator performance, provided other operating conditions are what they should be.
- In the case examined here, the regenerator section used to produce semi-lean solvent could as well be replaced by a flash drum, saving about half the tower height.
- The presence of DEA allows the Fractional Conversion of the fully-lean to be reduced by a factor of two. This permits much cleaner syngas to be produced without incurring more than the cost of the additive.

With the exception of the effect of DEA on equilibrium CO₂ partial pressure, all the other findings are a direct result of using the ProTreat simulator's true mass and heat transfer rate-basis in the analysis. Without doing these calculations on a rate basis, none of these observations could have been made. There is no substitute for a simulator that does all calculations rate-based, without approximations or simplifications.

Perhaps the most important finding is that if the CO₂ unit is properly designed, what really determines treated gas quality is the performance of the regenerator, which can be greatly improved by using DEA as a promoter.