Post-combustion CO_2 Capture with Amino-Acid Salts[1]

Ralph H. Weiland
Optimized Gas Treating, Inc.
P.O. Box 125
Clarita, OK 74535, USA
ralph.weiland@ogtrt.com

Nathan A. Hatcher
Optimized Gas Treating, Inc.
311 Bayou Bend
Buda, TX 78610
nate.hatcher@ogtrt.com

ABSTRACT

Conventional amine-based solvents used for post-combustion CO_2 capture suffer from several common drawbacks. The most serious is the prohibitive energy used by solvent regeneration. Others include the additional process complexity needed to address solvent volatility, as well as dealing with oxidative and thermal degradation.

Within the last five years, interest has developed in using the sodium or potassium salt of glycine (NaGly), the simplest primary amino acid, for CO_2 capture. Another proposal (Wagner et al.[5]) is to use the potassium salt of a tertiary amino acid such as dimethylglycine (KDiMGly), promoted with a conventional alkanolamine such as monoethanolamine (MEA).

This paper benchmarks the performance of a 3,000 tonne/day CO_2 capture plant using NaGLy, MEA-promoted KDiMGly and piperazine-promoted KDiMGly against the standard, 30 wt% MEA. Piperazine-promoted MDEA is also considered. The results are striking—the regeneration energy required with piperazine-promoted KDiMGly appears to be about 20% lower that for MEA in an identical plant. Furthermore, solvent rates are lower by about 20%. Combined with a neutralized amino acid's complete lack of volatility, this finding puts caustic-neutralized amino acids into a class of solvents of potential commercial interest. The paper provides a detailed explanation of how and why a process based on NaGly or piperazine-promoted KDiMGly is likely to perform well.

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1. INTRODUCTION

Post-combustion carbon capture is an applications area within gas treating with its own unique set of difficulties. Very few capture plants of any size have been built, so much of the discussion on carbon capture should correctly use the future tense. Huge gas volumes at essentially atmospheric pressure provide very little driving force for CO_2 absorption to take place so contactors will be of very large diameter, and filled with structured packing to minimize pressure drop associated with large gas volumes. Focus to date has been predominantly on thermally regenerable solvents, usually amine-based, although other technologies such as ionic liquids and enzyme solutions (carbonate anhydrases) are receiving serious attention.

The benchmark solvent is 30 wt% corrosion-inhibited MEA, originally developed by The Dow Chemical Company and currently offered by Fluor under the name Econamine FG Plus[SM]. One of the drawbacks of conventional amines is their high volatility. The contactors in carbon capture are designed to be highly rich-end pinched. In other words, the plants are designed to operate at minimum reboiler duties and minimum circulation rates to keep energy consumption at the lowest possible level. The present obsession with lowering energy needs is quite understandable given that the energy required for an MEA-base carbon capture plant represents roughly one third of the plant's power generation capability. Energy consumption escalates dramatically as the CO_2 recovery requirement is increased. Thus, post-combustion carbon capture plants are intended only to remove the first 85% or so the CO_2 in the flue gas. Minimum circulation, minimum regeneration energy, and bulk CO_2 removal rich-end pinch the column and conspire to produce a large temperature bulge near the top of any well-designed contactor. The treated gas then will tend to be quite hot, making amine volatility losses very high. Thus, an amine with minimal vapour pressure is desired. Amino acids neutralized with an alkaline metal hydroxide are perfect candidates because they are indeed salts, and have zero vapour pressure.

Solvent regeneration consumes the overwhelming majority of the energy needed for CO_2 capture using thermally-regenerable solvents. A well-designed and optimised capture system for a 300 MW power plant will consume about 100 MW of the power plant output, most of it for solvent regeneration. Thus, anything that can be done to lower regeneration energy has a huge potential benefit to capture plant efficiency.

Another challenge peculiar to all post-combustion CO_2 capture plants is the unavoidable presence of oxygen caused by the use of excess combustion air in furnaces. Most amines react readily with oxygen and form a host of degradation products, some of which can lead to foaming and corrosion. Amino acids are naturally occurring materials that evolved to function very effectively in an oxygen-rich atmosphere and are quite resistant to oxidation. However, amino acids are almost pH neutral and their amino group is already protonated so they do not react with CO_2. In the first part of this paper we discuss the amino acids and how they can be made reactive. In the second part comparisons are made between MEA, NaGly, MEA-promoted KDiMGly and piperazine-promoted KDiMGly. It is also pointed out why promoted MDEA is not a candidate for post-combustion carbon capture.

2. BASE CASE — 3,500 MTPD CO_2 CAPTURE PLANT

To compare solvents readily on an equitable basis, a completely non-optimised plant for removing 85% of the CO_2 from a 300 MW station was selected as the basis. This amounts to the removal of about 3,000 tonnes/day (mtpd) of CO_2 from the combustion gas (at 85% removal efficiency). The raw gas was assumed to contain 13 mol% CO_2, 86.8 mol% N_2 and 0.2 mol% O2 at 70 mbar and 43°C (110°F). The absorber was simulated with 20 m of Mellapak M250.X structured packing and was sized for 50% of flood. Absorber pressure drop was generally about 20 mbar. The column bottom pressure was assumed to be 70 mbar. The regenerator was simulated with twenty 4-pass trays with feed to tray 3 from the top, and it was sized for 70% jet and downcomer flood.

Solvent compositions of amines were taken at the most commonly-used or conventional values, namely 30 wt% MEA, 45 wt% NaGly, 40 wt% KDiMGly, 45 wt% MDEA, and in the case of promoted amines, a 30:15 wt% mixture of KDiMGly:MEA and promotion with 5 wt% piperazine in the cases of KDiMGly and MDEA. Lean solvent temperature was set at 43°C, the same as the raw gas, and a temperature approach of 5.5°C (10°F) was arbitrarily chosen for the cross exchanger.

Apart from the normal lean-rich cross exchanger, no attempt was made to heat integrate or in any way optimise plant configuration for any amine or blend. No doubt better results could be obtained for any given solvent by paying attention to heat integration, optimizing temperature approaches in heat exchangers, more carefully selecting lean amine temperature, etc. so as to minimize OPEX and CAPEX. However, our objective was a simple comparison on a reasonably equitable basis between neutralized amino acids and MEA. Figure 1 shows the base flowsheet.
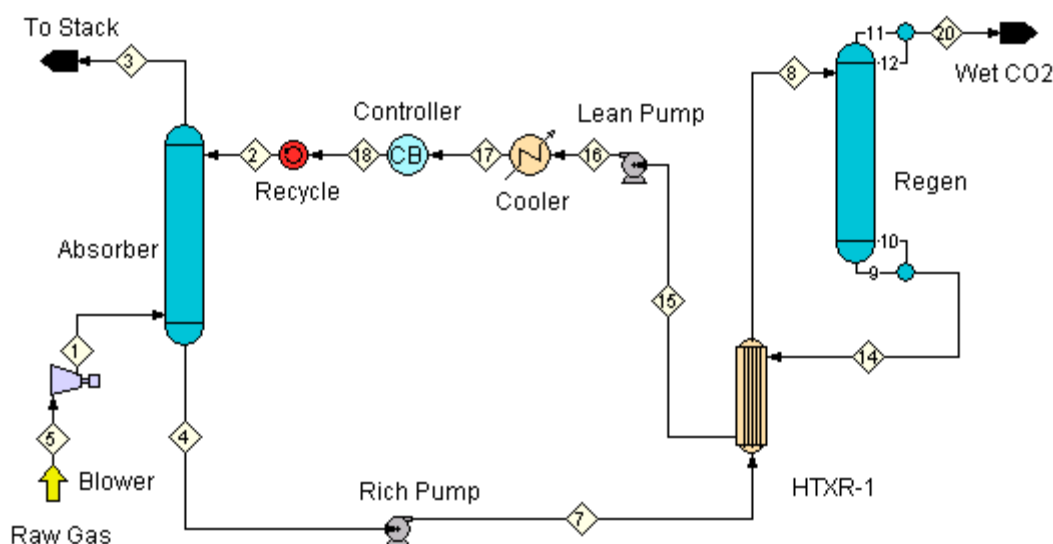

Figure 1   PFD of Rudimentary Carbon Capture Plant

## 3. AMINO ACIDS AS CARBON CAPTURE SOLVENTS

Salts of amino acids appear first to have been used commercially for acid gas removal around 1935. The Alkazid® process developed by IG Farbenindustrie, and later

formally by BASF AG after its reëstablishment in 1952, uses the potassium salts of *N,N*-dimethylaminoacetic acid (also known as the potassium salt of dimethylglycinate) and *N*-methylalanine for treating refinery, coke-oven, and natural gases. It is noteworthy that refinery and especially coke-oven gases are two of the most severely aggressive treating services from contamination and solvent degradation standpoints. The process appears to have been most commonly applied in Europe, especially Germany, although there are instances of its use elsewhere.

Glycine, the simplest of the amino acids, will be used as a model for a generic amino acid. In water solution, it exists as a zwitter[2] ion

$$^-COO - CH_2 - NH_3^+$$
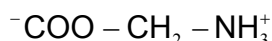
Because the amino group is protonated, it is completely nonreactive towards CO_2. In fact, when heat stable salts are present in a treating solution, their acidic nature results in protonation of the amino group. When H_2S is absorbed by an amine, again the amino group acts as a proton sink and it becomes protonated (and consumed) on a mole-for-mole basis. One of the ways in which heat-stable-salt-contaminated solvents can be (temporarily) recovered is by addition of caustic soda, being very careful not to add too much and create permanent lean loading. So, when the acid group is titrated (neutralized) with NaOH or KOH, the amino group deprotonates and the amine is returned to its reactive state. If the amine is an amino acid, its deprotonation converts the zwitterion into a fully active amine:

$$NaOH + {}^-COO - CH_2 - NH_3^+ \rightarrow Na^+ {}^-COO - CH_2 - NH_2 + H_2O$$
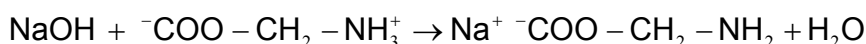
In the case of glycine, it produces what turns out to be a *highly-reactive primary* amine. With dimethyl glycine, the commercial product of neutralization (Alkazid DIK) is the potassium salt:

$$K^+ {}^-COO - CH_2 - N - (CH_3)_2$$

Here, the amino group in potassium dimethyl glycinate (KDiMGly) is *tertiary*, and is therefore incapable of reacting directly with CO_2, but it is perfectly capable of acting as a sink for the proton formed by CO_2 hydrolysis in water. The key then is the deprotonation of the inactive, protonated amino group in the amino acid zwitterion through its precise titration with caustic soda or caustic potash. The zwitterion can then release the fully-active amino group.


4. COMPARING SOLVENTS

4.1. Benchmark MEA

With the configuration of the plant, tower details, and combustion gas flow and composition completely fixed, once the solvent and its strength are selected there are

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[2] The German word Zwitter means hybrid (hermaphrodite in biology)

really only two parameters that can be varied with appreciable effect on performance, namely, solvent circulation rate and reboiler duty. The benchmark is 30 wt% MEA. Figure 2 shows CO_2 recovery as a function of solvent circulation rate with reboiler duty (MW) as parameter.
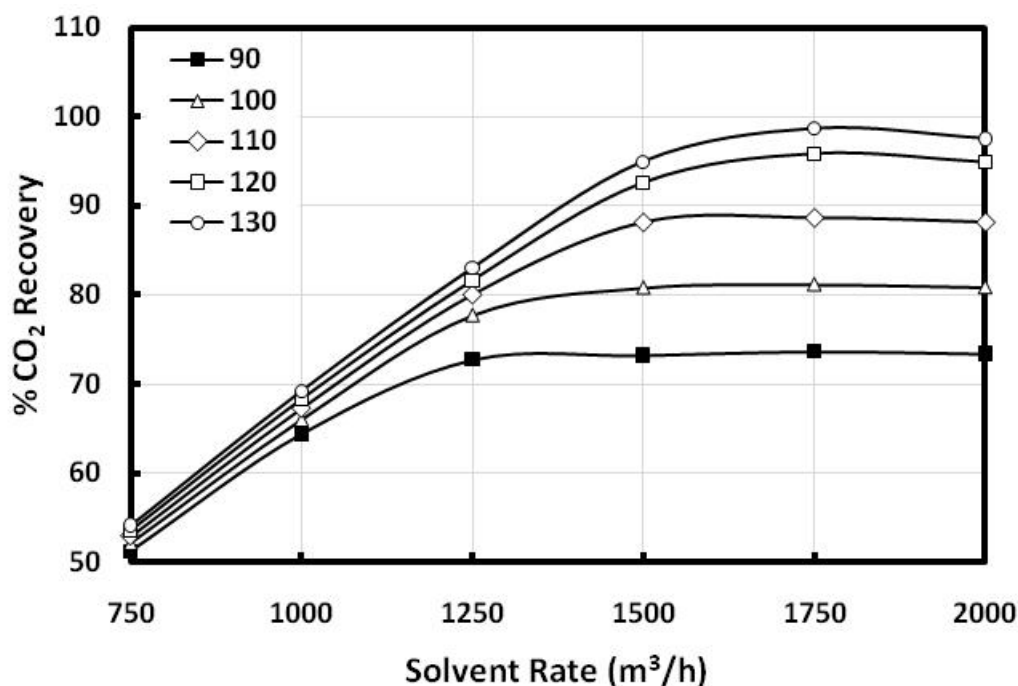
Figure 2   Effect of solvent rate at various reboiler duties on CO_2 capture efficiency using MEA

If the solvent rate is too low, no amount of reboiler duty will provide the solvent with enough capacity to absorb 85% of the CO_2 (the usual removal goal is 85%). But at around 1 500 m^3/hr, a reboiler duty of about 105 MW appears to be needed to achieve the removal goal. This is close to the generally-accepted, but staggering one-third of plant power output. It is also interesting to note that higher removal efficiencies come at the cost of rapidly increasing energy demands. Further, as the circulation rate is increased beyond what is really required, no benefit accrues because the given reboiler duty is just sufficient to remove the given amount of CO_2. If the circulation rate is increased to an extreme, of course, efficiency slowly drops off because the energy needed to take the rich feed from the temperature leaving the cross exchanger to the temperature on the feed tray slowly rises. In the vicinity of the minimum circulation rate needed to achieve the desired efficiency, higher rates provide no benefit, and lower rates slowly depress the efficiency.

4.2. Sodium Glycinate

The data of Kumar et al.[2] indicate that NaGly exhibits two to three *times* the reaction rate of MEA with CO_2, depending on its concentration. Solubility data for CO_2 have been published recently by Song et al.[4] and Harris et al.[1]; Lee et al.[3] report physical property measurements, including pH data. The Deshmukh-Mather thermodynamic model used by ProTreat was regressed to the pH and VLE data while correlations were

developed for such physical properties as density, viscosity and surface tension of the treating solutions. Figure 3 shows the dependence of recovery efficiency on circulation rate and reboiler duty and looks very similar to the MEA results of Figure 2. The required reboiler duty is almost identical to MEA, although 85% recovery can be achieved with only 1 250 m^3/hr of solvent rather than the 1 500 m^3/hr needed by MEA. The reason will become apparent later.
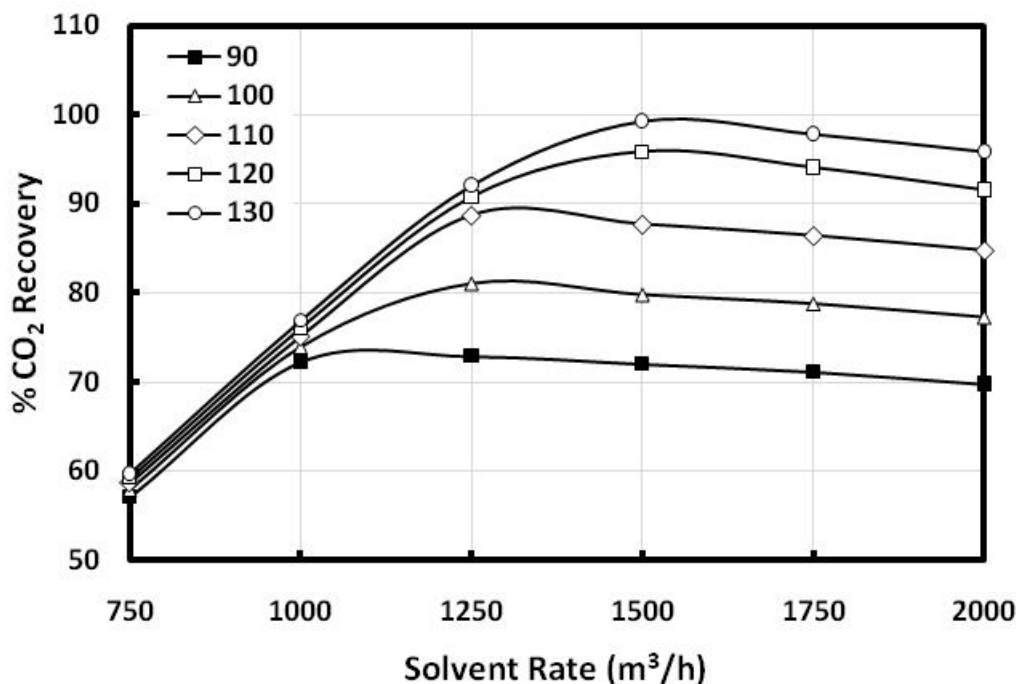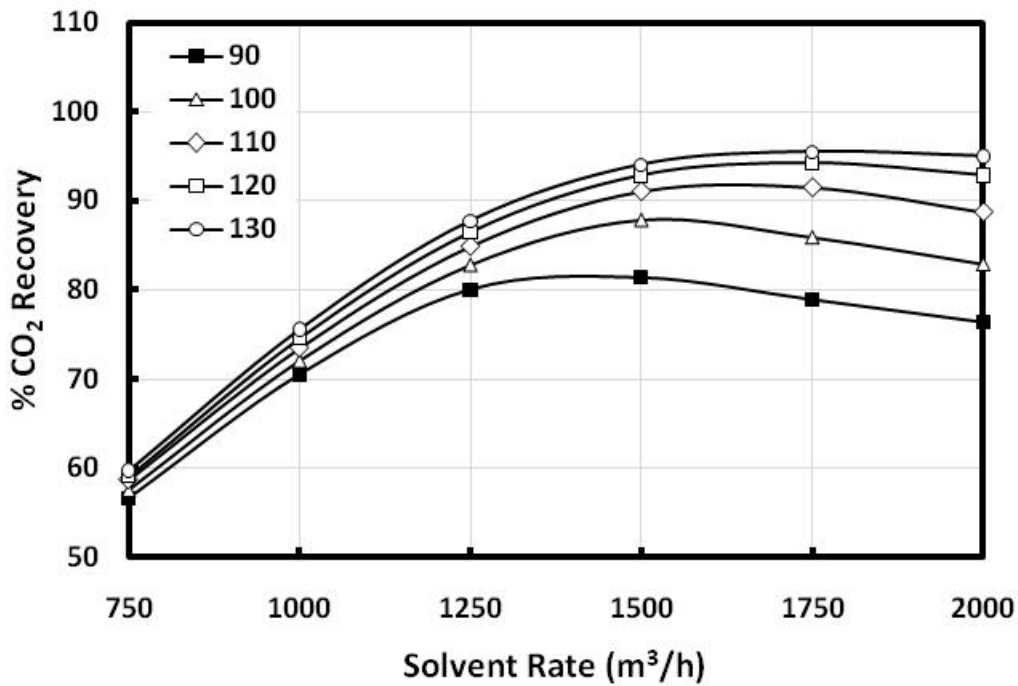

Figure 3   CO$_2$ capture efficiency using 45 wt% NaGly

4.3. Potassium Dimethyl Glycinate

4.3.1. MEA Promoter
KDiMGly has a tertiary amino group that is incapable of reacting with CO_2 to form carbamate. Lack of significant chemical reaction rate, therefore, suggests that CO_2 will experience significant difficulty getting into solution, although KDiMGly may still have very high capacity. Absorption must be promoted using a fast-reacting amine such as MEA or piperazine. Figure 4 shows simulated recoveries using 30 wt% KDiMGly promoted with 15 wt% MEA. Simulation of a variety of concentrations indicated that this particular combination most easily reached 85% CO_2 recovery with the least expenditure of energy. Nevertheless, the energy consumption using this mixture was simulated to be roughly 95 MW, only about 10% less than 30 wt% MEA. It appears from this figure that the replacement of a substantial fraction of high capacity ingredient (KDiMGly) with an equally-large fraction of fairly slowly reacting MEA, (which also has a half-mole-per-mole capacity limit for low CO_2 partial pressure gas), is not a very effective way to use the potentially higher capacity of KDiMGly.

Figure 4   CO₂ capture efficiency using 30 wt% KDiMGly with 15 wt% MEA

4.3.2. *Piperazine Promoter*

The effect of using promoting 40 wt% KDiMGly 5 wt% piperazine is shown in Figure 5. It can be seen that 82 or 83 MW reboiler duty will easily allow 85% CO_2 recovery.
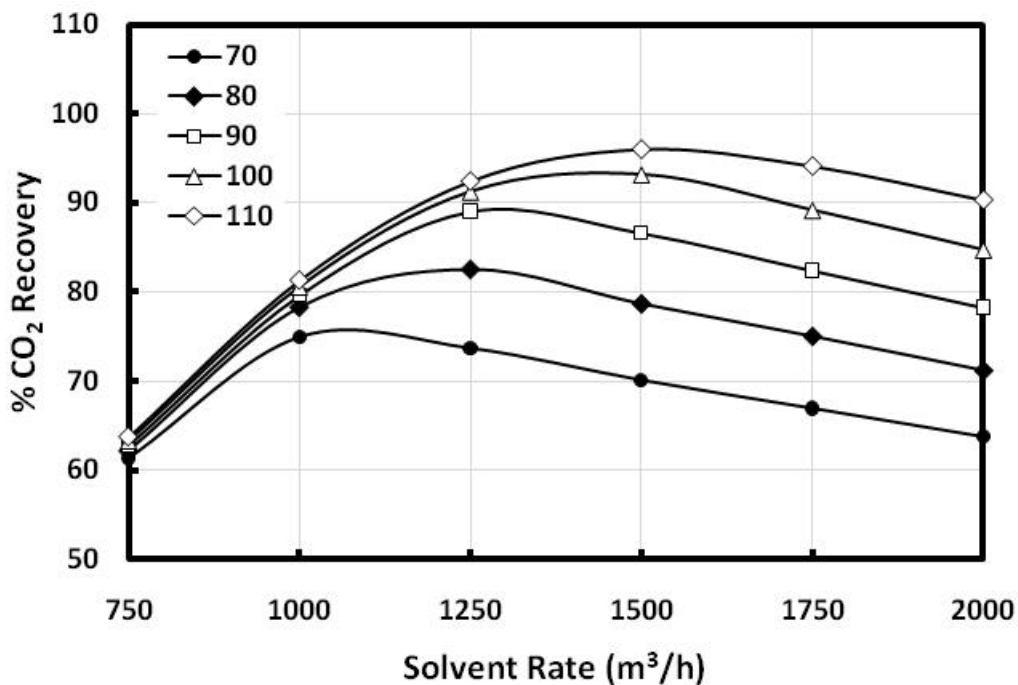
Figure 5   CO₂ capture efficiency using 40 wt% KDiMGly with 5 wt% piperazine

This is roughly a 20% reduction over MEA with a lower solvent rate (1 250 m^3/hr versus 1 500 m^3/hr for MEA). When used as a promoter, 5 wt% piperazine is a typical concentration.

The purpose of the promoter (MEA or piperazine) is to enhance the rate of CO_2 absorption, not to alter the solvent's inherent capacity. Although the promoter will also alter the vapor liquid equilibrium (solvent capacity for CO_2), the effect is relatively minor. Indeed, the tertiary amino acid already has a potentially much higher CO_2 capacity than MEA or NaGly, but the absorption rate is quite limited by the very slow kinetics of CO_2 hydrolysis. In other words, until the already-absorbed CO_2 can be hydrolysed, there is simply no room for any further absorption. Thus, making the CO_2 disappear rapidly via formation of an intermediate carbamate(which subsequently dissociates into carbonate and reforms the reactive amine) accelerates the absorption process without increasing the solvent capacity. Piperazine reacts with CO_2 nearly 10 times faster that MEA, so (i) much less of it is needed (it replaces less KDiMGly) and (ii) it enhances absorption rates many fold over MEA.

4.4. MDEA

If KDiMGly is so effective for CO_2 capture, the question naturally arises as to whether MDEA promoted with piperazine might do just as well. Simulations were run for 45 wt% MDEA promoted with 5 wt% piperazine under similar conditions of circulation rate and reboiler duty already used for MEA and promoted KDiMGly. Figure 6 shows simulation results over a range of higher reboiler duties.
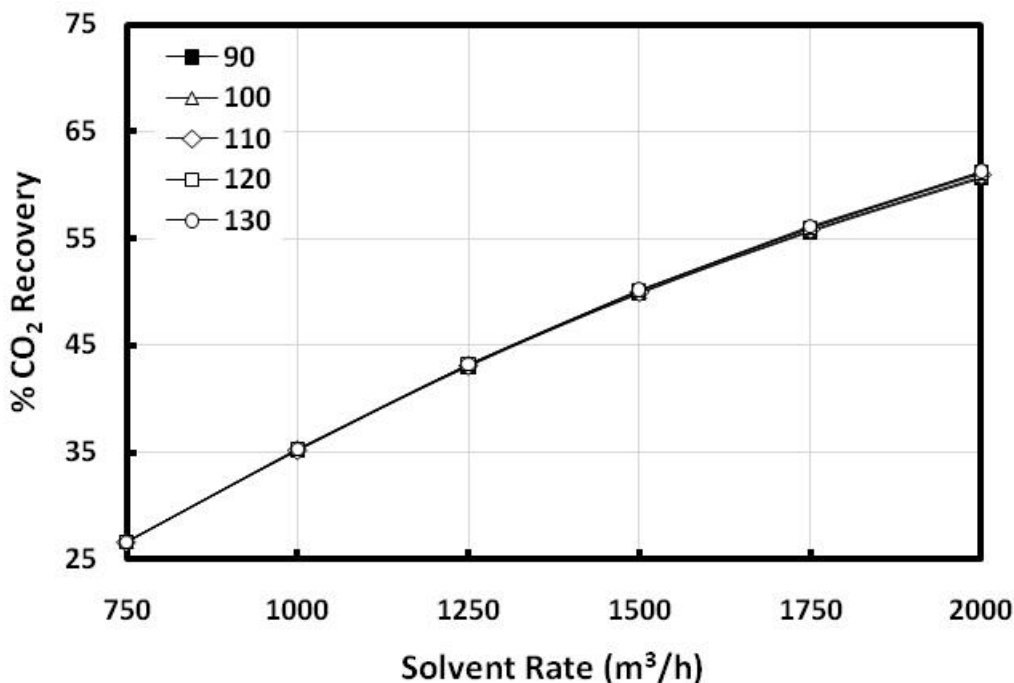

Figure 5   **CO₂ capture efficiency using 45 wt% MDEA with 5 wt% piperazine**

At solvent rates typical of those used to this point, piperazine promoted MDEA appears incapable of reaching even 65% recovery, let alone the 85% desired. Indeed, at best this solvent has performance similar to grossly under circulated piperazine-promoted KDiMGly. The explanation must lay in the nature of MDEA versus KDiMGly vis à vis capacity and CO_2 equilibrium partial pressures.

5. DISCUSSION OF SIMULATION RESULTS

There are several interesting questions raised by the simulation results, including:
- Why does NaGly require almost identical reboiler duty to MEA but can achieve the same recovery with 20% less solvent flow?
- What makes KDiMGly such an effective solvent when promoted with piperazine?
- Why is MDEA so ineffective in this application, even when promoted with piperazine?
- What are the relative roles played by vapour-liquid equilibrium, kinetics and heats of reaction and absorption? Put more bluntly, what are the characteristics of a good capture solvent?

Before starting to answer these questions, it is worth rëexamining the unique aspects of carbon capture versus the more conventional treating of natural, refinery, and synthesis gases. In traditional gas treating, the target is almost always a gas that is relatively high purity with respect to at least one component. For example, natural gas transmission pipelines are restricted to conveying gas with only parts per million concentrations of H_2S. Ammonia synthesis gas is limited to about 1,000 ppmv CO_2. Such applications require a well-stripped solvent, and a well-stripped solvent requires considerable reboiler energy input. In carbon capture, on the other hand, the goal is bulk removal of CO_2 with about 15% of the original CO_2 left in the gas, and a truly lean solvent is not needed. Indeed, the required leanness of the solvent barely allows it to be referred to as "lean", at least by traditional gas treating standards. In many situations only one or two stages of flash regeneration is needed. This means that reboiler duties can be turned right down and simultaneously the solvent run at absolutely minimum rates, just sufficient to meet an 80 or 85% removal goal. The key difference from conventional treating is that solvent lean loadings can be quite large because treating is limited by absorber rich-end conditions, not by a lean-end pinch created by seeking a high purity gas product.

The main concern in the contactor is ensuring absorption rates are high enough for treating to be done in a column of reasonable height. Height is controlled largely by reaction kinetics. The concern in the regenerator is producing a solvent just lean enough to have the requisite potential for holding the specified quantity of CO_2. Obviously there is a balance to be struck between the solvent's flow rate and its loading potential such that reboiler energy is minimized.

So-called specialty amines or promoted solvents are all traditionally MDEA-based. The purpose of most (but not all) solvent additives is to provide higher reaction rates between the solvent components and CO_2, which will enhance absorption rates into MDEA. It is easy to see from Table 1 why piperazine is such an effective promoter. It

reacts with CO_2 nearly ten times faster than even MEA. Data in Table 1 are based on second-order kinetics at 25°C.

Table 1   Reaction Rate Constants of Gas Treating Amines and Amino Acid Salts With CO_2

Amine	Reaction Rate Constant (L·mol^{-1}s^{-1})
MEA[P]	6,000
DGA[P]	4,500
DEA[S]	1,300
DIPA[S]	100
Piperazine[S]	59,000
MMEA[S]	7,100
MDEA[T]	4
AMP[P]	600
NaGly[P]	8,000
KDiMGly[T]	~0

P = Primary, S = Secondary, T = Tertiary

The value of the kinetic rate constant is unrelated to the primary or secondary nature of the amine (although it does appear from the literature to be related to the amine's pKa value). MDEA and KDiMGly are tertiary amines, they do not form carbamates, and they react with CO_2 hardly at all. The value 4 L·mol^{-1}s^{-1} for MDEA is indicative of the extent to which MDEA is purported to catalyse CO_2 hydrolysis. Because they are tertiary they do not strictly have the half-mole-per-mole stoichiometric loading limit of the carbamate formers. But their lack of reactivity demands the use of promoters. Obviously, if one is to promote CO_2 absorption, piperazine is the chemical to use. Its drawback is a higher relative volatility than most other amines; however, a small water-wash section at the top of the absorber will recover most, if not all, vapourisation loss.

Table 2 shows representative values for the heats of absorption of CO_2 into a variety of amines and amino acid salts.   Values are integral from 0 to 0.30 loading.   The tertiary

Table 2   Heats of Absorption of CO_2 into Various Amines and Amino Acid Salts at 25°C

Amine	Heat of Absorption (kJ·gmol^{-1})
MEA[P]	84
DGA[P]	83
DEA[S]	76
DIPA[S]	73
Piperazine[S]	76
MMEA[S]	54
MDEA[T]	58
AMP[P]	85
NaGly[P]	85
KDiMGly[T]	55

P = Primary, S = Secondary, T = Tertiary

amines have quite a bit smaller heats of absorption than the primary and secondary amines because there is no carbamation reaction. With the exception of MMEA, the heat of absorption appears to correlate with the primary, secondary or tertiary nature of the amine (indicated by a superscript appended to the amine's name in the tables).

MDEA and KDiMGly are both tertiary, neither reacts to any extent with CO_2, and both show low heat of absorption. One might expect some equivalence between them vis à vis their piperazine-promoted performance in CO_2 capture. Yet KDiMGly is very effective; whereas, MDEA is completely ineffective. A comparison of vapor-liquid equilibrium behavior between the various amines is revealing (Figure 6). The partial pressure of CO_2 over MDEA is on the order of 100 times higher than over KDiMGly at the same solution loading. For a 13% CO_2 combustion exhaust gas, 45% MDEA is completely saturated with CO_2 at a mole loading of only 0.3 (mol CO_2 per mole of MDEA). With 85% CO_2 recovery, the treated gas is about 2% CO_2 and the equilibrium loading in MDEA is 0.1 mol/mol. In a rich-end-pinched absorber, obviously MDEA is going to have to be stripped to a much lower lean loading than KDiMGly to accommodate the same loading increase. Deeper stripping requires more energy. To make matters worse, the loading capacity of MDEA even if 100% stripped is only 0.3 mol/mol, whereas, KDiMGly can easily absorb twice as much CO_2; therefore, the circulation rate required for MDEA will be much higher than for KDiMGly and this will put a tremendous additional load on the regenerator. This can be clarified with an illustrative case.

For piperazine promoted 40 wt% KDiMGly at 1 250 m3/h and 90 MW reboiler energy, 89% of the CO_2 is recovered with the solvent loading going from 0.118 (lean) to 0.647 (rich), i.e., a loading increase of 0.529 mol/mol. For piperazine promoted 45% MDEA under otherwise identical conditions, the lean loading goes from 0.0034 (lean) to 0.231 (rich) with a total loading increase of only 0.228 mol/mol. Yes, MDEA can be stripped to much lower levels but this advantage is far outweighed by its much lower loading capacity at the rich end of the absorber where the equilibrium backpressure of CO_2 over
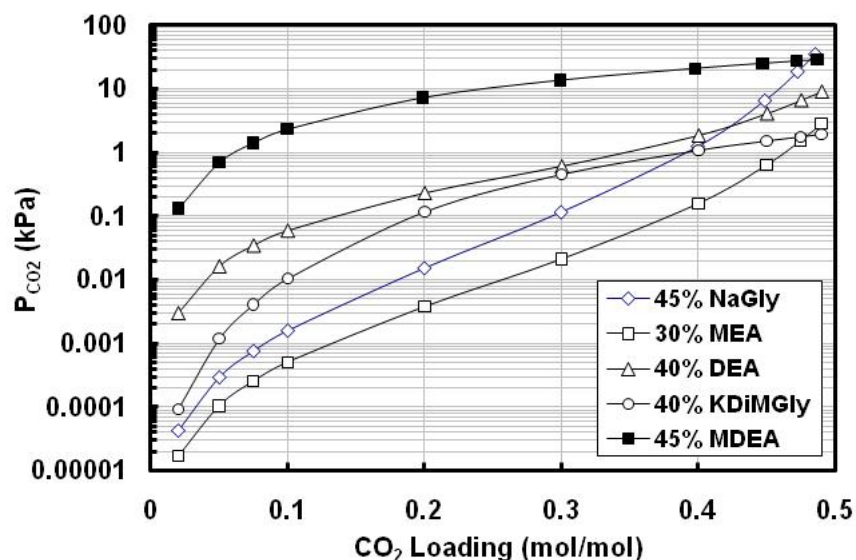

Figure 6   **Equilibrium partial pressures of CO_2 above various amine solutions at 35°C**

the solvent is decisive. In fact, piperazine-activated MDEA certainly performs far worse than any other amine in this application.

It is also noted that MEA does not appear to be a particularly good promoter because too much has to be added to be effective, and this will probably require the displacement of a significant fraction of the lower-energy component, KDiMGly. The greatest benefit is had by maximizing the concentration of KDiMGly and using the minimum promoter possible. The caveat, however, is that KDiMGly becomes quite viscous at high concentrations and this will be detrimental to the absorption rate of CO_2 because of the effect of high liquid viscosity on the liquid-side coefficient for mass transfer.

6. OTHER CONSIDERATIONS

Piperazine-promoted KDiMGly offers significant energy savings over MEA and MEA-promoted KDiMGly. But there are other advantages to amino-acid salts in general. The salts of amino acids are completely nonvolatile simply because they are salts. Of course, losses can occur by means other than vapourisation, such as entrainment from columns, and leaks and spills. Amino acids also tend to be quite resistant to oxygen—their natural habitat is an oxygen-containing environment. On the down side, they are known to be corrosive and to require stainless metallurgy.

7. SUMMARY

Amino acid salts have been considered as post combustion CO_2 capture solvents and piperazine-promoted KDiMGly has been shown to have promise and significant advantages over MEA and certain other amines and blends. All of this has been done without direct experimentation, but rather on the basis of a solid, scientific, fundamental mass transfer rate model for columns, plus measurement of a few physico-chemical properties of the solvent chemicals involved.

The basic mass and heat transfer rate model itself has been tested extensively against actual plant performance data for many years, and it has been shown to be capable of true performance *prediction*, frequently with uncanny accuracy. The fact that no adjustable parameters were used (such as efficiencies or residence times within tower internals) builds assurance that it really is predicting (rather than fitting) performance data. The fundamental soundness of the mass-transfer-rate approach is what allows the confident prediction of the performance of full-scale plants just from laboratory measurements of such things as vapour-liquid equilibrium, solvent pH, reaction kinetics, and solvent physical properties.

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