

BENCHMARKING SOLVENTS FOR CARBON CAPTURE

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Abstract

Process simulation is used to evaluate the potential of 2-amino-2-methyl-1-propanol (AMP) and sodium glycinate (NaGly) as solvents for CO₂ capture. In terms of regeneration energy (the main energy consumer in capture plants), the performance of a rudimentary MEA-based plant is established first. Pilot plant data on CO₂ absorption into MEA and AMP are shown to be well-reproduced using the ProTreat™ mass and heat transfer rate process simulation tool. The model is then used to project that (1) AMP should enjoy at least a 15% reboiler energy advantage over MEA and (2) NaGly should carry better than a 40% advantage over MEA under the same conditions.

Keywords: sodium glycinate, AMP, energy demands, amine solvents, simulation

1. Introduction

Existing technological approaches to carbon capture (CC) from conventional power plant flue gases are almost all based on solvents. High-strength MEA has received the most attention and is the solvent against which other technologies are usually benchmarked. Other solvents include 2-amino-2-methyl-1-propanol (AMP), piperazine, cold ammonia, a variety of caustic-neutralised amino acids, amine-promoted potassium carbonate, and physical solvents including ionic liquids, a new and interesting class of fluids. Our focus in this paper is with AMP, sodium glycinate, and the MEA benchmark.

CC from atmospheric-pressure flue gas presents a unique set of difficulties usually not experienced in more-conventional gas treating. On the absorption side, problems arise from the gas being at low pressure, and its unavoidable oxygen content. Even a small power plant generates an enormous volume of flue gas at atmospheric pressure which needs sizable power to drive the gas through the contactor. The *driving force* for CO₂ absorption is its partial pressure in an atmospheric-pressure gas. Amine vapourisation losses and oxidative degradation are also problems. The over-riding drawback however is prohibitive regeneration energy requirements.

Fast-reacting carbamate-formers like MEA, although very effective at reacting with and removing CO₂, are energy-intensive to regenerate. However, the technology of using MEA in gas treating is rather better established than other solvents, and it remains high on the list of interesting CC solvents.

The higher loading *potential* of noncarbamate-forming amines (*one* amine molecule for each molecule of CO₂ absorbed) has made the moderately hindered amine AMP more interesting. AMP is a primary amine, but the secondary methyl group shields the amino group to a significant extent, and carbamate formation is made more difficult. Because the reaction product is carbonate rather than carbamate, regeneration energy ought to be lower than for MEA. Steric hindering also means that each CO₂ molecule theoretically uses only *one* AMP molecule, *potentially* doubling the capacity of the solvent.

Academic laboratories began to characterise AMP almost as soon as Exxon's first FLEXSORB® patents were issued more than 20 years ago. In the literature today there are enough phase equilibrium, kinetics, and physical property data of good quality and reliability to allow AMP to be process simulated with fair accuracy. AMP was added to the ProTreat amine simulator's solvent offerings in mid-2009.

Salts of amino acids have been used since 1935 for acid gas removal from refinery, coke oven, and natural gas, among others, mostly in Europe and especially in Germany. These are the so-called Alkazids[®] (potassium salts of *N,N*-dimethylglycine and *N*-methylalanine) developed by BASF. Within the last five years, interest has developed in the sodium and potassium salts of glycine, the simplest amino acid, for CO₂ capture. Sufficient kinetic and equilibrium data have now been published to permit the detailed simulation of a CO₂ capture plant using this solvent. Sodium glycinate (NaGly) has recently been implemented within ProTreat. Unlike AMP, NaGly is a carbamate former because the amino group in neutralised glycine is perfectly capable of reacting with CO₂, just like any other primary amine. It has the advantages of zero volatility (NaGly is a salt), and greater resistance to oxidation (it is already oxidised to an acid) and thermal degradation (NaGly is a small, stable molecule).

1. MEA: Benchmarking Standard

The basis for developing this benchmark and making subsequent comparisons is 30 wt% MEA to remove 3000 tonnes/day (3,300 short tons/day) CO₂ produced by burning coal in a roughly 300 MW power station. By world standards, this is a small power station, but of sufficient scale to be indicative of solvent performance.

We are interested in simply comparing the regeneration energy required by AMP and NaGly relative to MEA, not in developing intricate processing schemes to minimise energy consumption *per se*, nor in minimising water and amine losses from the plant. So as long as comparisons between solvents are made on the same basis, small efficiency gains made by tweaking the flowsheet will have minimal effect. The gas volumes in CO₂ capture are extremely large and providing energy to overcome absorber pressure drop can be significant. Therefore, the PFD included a booster blower but it omitted any peripheral equipment designed to prevent solvent vapourisation losses with the treated flue gas or do any form of heat integration beyond a conventional lean-rich cross-exchanger (Figure 1).

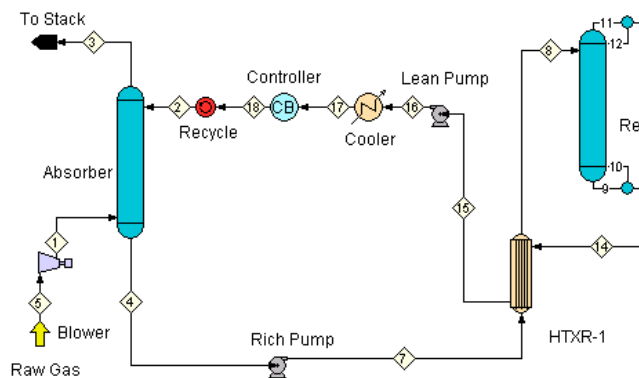


Figure 1. Simplified PFD of a CO₂ Capture Plant

Because only a relatively low recovery of CO₂ is ever required, the most economical way to operate the absorber is with it rich-end pinched. In other words, the loaded solvent should be as close as practicable to being in equilibrium with the entering flue gas—in this case 0.5 mol/mol. So, although the temperature and flow rate may vary, the regenerator is always presented with 30 wt% MEA loaded to 0.5 mol/mol. The discussion mostly focuses on 85% CO₂ recovery and the rich-amine feed temperature to the 20-tray regenerator was set at 96°C (205°F) to avoid a temperature cross in the lean-rich exchanger from a regenerator operated at relatively low pressure (typically 1.5–2.5 bar, 10–20 psig). Mellapak-Plus[™] M252.Y packing was taken as the base case for comparison with AMP. This structured packing has a reasonable specific area of around 250 m⁻¹ (76 ft⁻¹) with special treatment at the top and bottom of each block to reduce pressure drop. It was found that 85% recovery could be safely achieved over a range of solvent rates from 1400 to 2000 m³/s using 115 MW reboiler energy (110 MW barely made 85% recovery at a single solvent flow and 105 MW could not reach 85% recovery at all).

As circulation rate was lowered in the simulations, the rich amine continued to leave the scrubber at essentially a constant loading of 0.5 mol/mol, and the treating capacity lost through reduced circulation was very closely made up by improved regeneration (at constant reboiler duty). At a low enough circulation rate, of course, the stripability limit of the solvent (about 0.1 mol/mol for MEA) is reached

and very little further reduction can be realised; thus, the recovery curve dropped markedly below a circulation rate of about 1,400 m³/hr (6,160 gpm). Conventional gas treating experience would suggest that if the circulation rate can be dropped by 30% while still treating satisfactorily, then the reboiler duty ought to be able to be decreased in the same way, since obviously the solvent has excess capacity that's not being used. However, in the case of CO₂ capture, the absorber is always operated severely rich-end pinched, so this thinking simply doesn't apply.

2. AMP: An Alternative Solvent

AMP (2-amino-2-methyl-1-propanol) has been suggested for years as a viable, less energy-consuming alternative to MEA in CO₂ capture, and a great deal of fundamental information about its phase-equilibrium and reaction-kinetic behaviour with CO₂ has been developed and reported in the literature, mostly sourced from academic institutions. Two very interesting studies at the University of Texas^{1,2} have concluded that AMP is two orders of magnitude slower to degrade oxidatively than MEA and is much more resistant to thermal degradation than MEA. There is also a small amount of pilot plant data that has been collected and reported³, which provided a nice basis for comparison with the ProTreat simulations.

The pilot plant data³ were collected in a 100 mm (4-in) ID column packed with up to 6.55 m (21½ft) of 12.7 mm (½ in) ceramic Berl Saddles. The original data were collected using MEA and AMP (as well as caustic soda). The absorber consisted of six 48-in sections each containing 1.1 m (42 in) of packing and each with a redistributor. Gas and liquid were sampled between sections; however, when sampling the two phases being contacted in an absorber, there is always some question about the integrity of the samples. In the experimental work reported, we found excellent agreement not only with temperature profiles, but also with partial pressure and loading profiles. However, comparisons with pilot plant and full-scale plant data are convincing only if the data themselves have been validated. For the pilot-plant tests discussed here, gas and liquid samples were analysed. This provided two independent means of measuring the rate of CO₂ removal, and it allowed closure of a CO₂ balance to be checked. Experimentally, the CO₂ removal rates from measured loadings were generally greater than measured by GC gas analysis by between 16.8% and 25.9% in contradiction to the claim made by the experimenters that CO₂ balance closures were between -3.14% to +4.35% at worst. Because there was no basis for deciding whether GC or loading analyses (if either) were correct, measured data were averaged between the two results. In the interests of space, graphical comparisons with measured gas composition profiles are not shown. However, the simulations of MEA tended to fall only slightly below the data; the overall comparison was quite good, especially given the rather narrow column diameter even for such small packing (column-to-packing diameter ratio of only 8) and the rather frequent liquid redistribution. These results validate the efficacy of the ProTreat simulator in this particular application.

With AMP the experimentally-measured CO₂ removal by GC differed from the loading measurements by between -37% and +31% despite the fact that mass balances were claimed to close to within better than 10%. Again, space prohibits graphical presentation of the detailed results; however, ProTreat did a creditable job reproducing both the trends and the absolute CO₂ pickup, with simulated and measured CO₂ profiles in the gas differing by no more than 1 – 2% for the reported data across the column.

The same process flow sheet used for MEA simulations was also used for AMP. With the same reboiler duty (115 MW) as used for MEA and a circulation rate of 1800 m³/hr, it was found that whereas MEA achieved 85% removal with 14 m (45 ft) of Mellapak M252.Y, AMP required 21 m (70 ft) of the same packing. AMP absorbs more slowly than MEA because its chemical reaction rate with CO₂ is closer to that of DEA than MEA. However, the phase equilibrium thermodynamics suggests that the heat of absorption into AMP is somewhat lower than into MEA at high temperatures, but a little higher at low temperatures. Therefore, one should expect AMP to regenerate with lower energy consumption. This is borne out by the simulation results shown in Figure 2.

There are several interesting observations to be made. First, there is a minimum circulation rate below which (in this case) 85% recovery cannot be achieved. No matter how hard the solvent is stripped, the limit on lean loading is obviously zero, and once a very low loading is reached, insufficient solvent flow simply lacks the capacity to achieve a specified amount of CO₂ removal. With AMP, typical lean loadings are 0.03 to 0.04 mol/mol (versus 0.25 mol/mol for MEA in the same service with 85% recovery). A more important observation is that there is a minimum required duty that increases with solvent circulation rate. Thus, optimal conditions will occur at the lowest possible circulation rate because then the reboiler duty is also minimal. In this example, with the given equipment configuration

it appears possible to achieve 85% recovery using only slightly more solvent but with at least a 15% energy savings.

AMP is more volatile than MEA so its use would require at least as effective a gas washing scheme as for MEA despite the 2–3°C (3–5°F) cooler outlet gas temperatures. It should also be noted that the solvent circulation rates needed for these two amines are almost the same. This is a consequence of the flue-gas CO₂ partial pressures being too low for AMP to be loaded much above 0.47 to 0.50 mol/mol, almost the same as MEA. Low CO₂ pressures prevent AMP from enjoying the 1 mol/mol loading possible with non-carbamate-forming amines. *In other words, AMP has no more (but no less) capacity for CO₂ than MEA.*

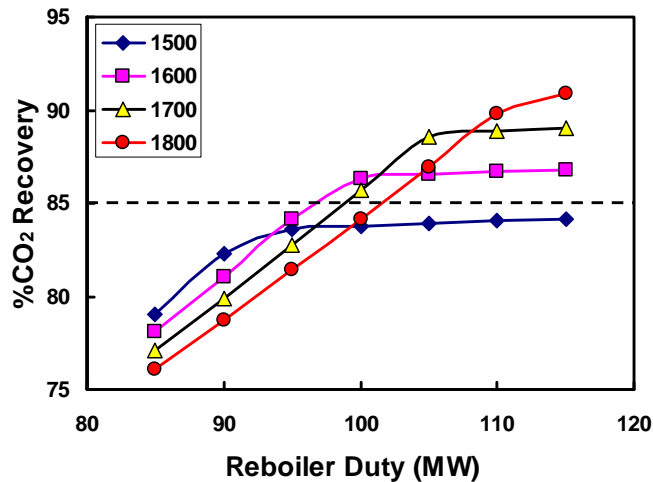


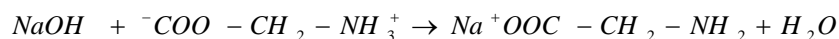
Figure 2. Effect of Reboiler Duty on CO₂ Recovery Using AMP at Four Circulation Rates (m³/s)

3. Sodium Glycinate

Salts of amino acids appear first to have been used commercially for acid gas removal in 1935. The Alkazid® process developed by BASF uses the potassium salts of *N,N*-dimethylglycine and *N*-methylalanine for treating refinery, coke oven, and natural gases. The process appears to be most commonly applied in Europe, especially Germany, although there are instances of its use elsewhere. Glycine is the simplest of the amino acids. In water solution, it exists as a zwitterion:



Because the amino group is protonated, it is complete nonreactive towards CO₂. However, when the acid group is titrated (neutralised) with NaOH or KOH, the amino group deprotonates:



and produces what turns out to be a *highly-reactive* primary amine. In fact, recent data⁴ indicate that NaGly exhibits two to three times the reaction rate of MEA with CO₂, depending on its concentration. Solubility data for CO₂ have also been published^{5,6,7} together with physical property measurements⁷, including pH data. The Deshmukh-Mather thermodynamic model used by ProTreat was regressed to the pH data and to the VLE data and correlations were developed for such physical properties as density, viscosity and surface tension of the treating solutions, and these sub-models were integrated into the simulation software.

Figure 3 shows the simulated effect of reboiler duty on the percentage recovery of CO₂ under the conditions indicated in the legend. The absorber in these cases contained 10 m (35 ft) of FLEXIPAC® 3Y structured packing in a flowsheet, with no attempt to recover vapourisation losses or heat integrate beyond conventional cross-exchange of heat between rich and lean amine streams. All other conditions were as described earlier for the basic MEA plant. At 30 wt% strength NaGly offers a 35% reduction in reboiler duty over MEA. However, when the comparison is made on the basis of equal molar concentrations, as it should be, NaGly uses 42% less reboiler energy than MEA. Instead of consuming 30% of the power plant's output, NaGly consumes only 17%, a phenomenal reduction. How is this explained?

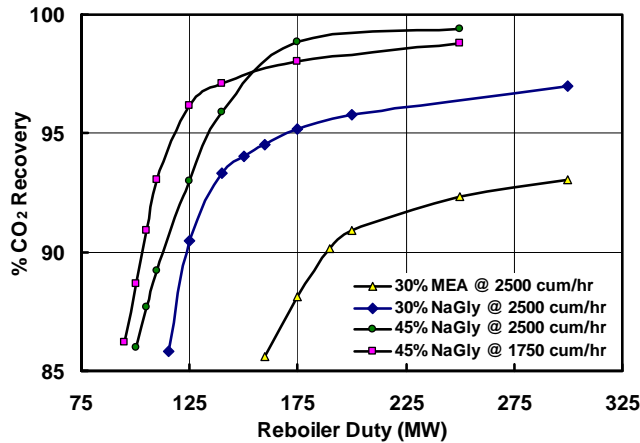


Figure 3. Effect of Reboiler Duty on CO₂ Recovery Using NaGly

As a primary amine, NaGly has a heat of CO₂ absorption very nearly the same as MEA. This results in essentially the same value of the peak temperature (within 2°C) in the absorber although because NaGly reacts faster with CO₂ its temperature profile is sharper than MEA. However, these two amines exhibit different VLE behaviour, as shown in Figure 4. At low loadings, CO₂ has twice the partial pressure above a 45 wt% NaGly solution as above 30 wt% MEA, but at a loading of 0.5 mole/mole the difference is a factor of ten. This makes regeneration of NaGly easier than MEA but the faster kinetics of CO₂ with NaGly results in faster absorption rates than MEA. An alternative view is that it is not necessary to strip NaGly to any lower loading than MEA to achieve the same degree of CO₂ capture, but because the same reboiler duty will strip NaGly much leaner, the reboiler duty can be turned back significantly to achieve the same lean loading as MEA.

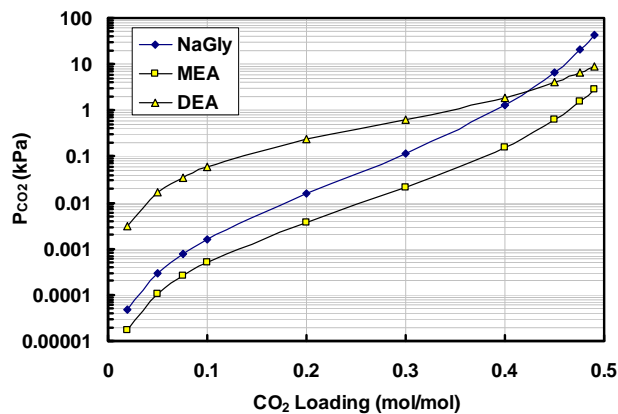


Figure 4. Equilibrium CO₂ Partial Pressures above MEA, DEA and NaGly at 35°C

The exact numerical values quote here should be read with the accuracy of the basic thermodynamic, and to a lesser extent kinetic, data in mind. For example, the kinetic data⁴ presented for potassium glycinate are quite limited and data above 25°C do not exist. However, when combined with two measurements at lower temperatures, a reasonable activation energy for the reaction results. In any event, because the overall performance of a CO₂ capture absorber is limited more by equilibrium considerations than by reaction kinetics, highly precise kinetics is not required.

Unfortunately, with the exception of a few low-pressure measurements, the CO₂ partial pressure data are limited to rather high loadings. But fortunately pH measurements have been reported for unloaded NaGly at several concentrations, which allows a good estimate to be made of the activity coefficient of aqueous NaGly in ProTreat's activity coefficient model. Regressing the high-loading data provides interaction parameters for protonated amine and carbamate with each other and for each with bicarbonate and carbonate. As loading decreases, the CO₂-dependent interactions decrease in importance and the availability of an accurate activity coefficient for NaGly allows extrapolation of the

activity coefficient model to low loadings with reasonable confidence. Therefore, despite the relative scarcity of good data, the performance predictions made above probably have a fair degree of reliability. All the available data when used in a solidly scientific mass transfer rate model point to the high potential of NaGly as a very low-energy solvent for post-combustion CO₂ capture. Certainly the collection of more fundamental VLE and kinetics data over a wider range of temperatures and CO₂ loadings is warranted.

4. Conclusions

On the basis of a simple one-to-one comparison, AMP appears to be a superior solvent to MEA for post-combustion CO₂ capture from a process standpoint. It is much more resistant to oxidative and thermal degradation, and it offers at least a 15% regeneration energy savings over MEA. However, AMP is quite unlikely to be the last word in post-combustion CO₂ capture solvents. In the area of amine-based solvents, what is required is an amine with fast kinetics for reaction with CO₂, and the right thermodynamic affinity for CO₂ so the solvent can be highly loaded, but easily regenerated. It is not necessary that there be a small reaction heat. Indeed, most primary amines have very similar heats of absorption, as do most secondary amines, and most tertiary amines. The shape of the phase equilibrium curves is more important as it dictates the *net* regeneration energy required.

Carbon dioxide reacts 2 to 3 times faster with sodium glycinate than with MEA. It also has substantially higher equilibrium CO₂ backpressures than MEA. This makes it more easily regenerable and at the same time, its faster kinetics allows it to saturate to about 0.5 moles CO₂ per mole of amine in the absorber. In other words, the easy regenerability from high backpressures does not translate into poor absorption. Sodium glycinate appears to require on the order of 60% of the reboiler energy of MEA. Thus, its use seems capable of reducing energy consumption from 30% of the power plant output to maybe only 17%. Fundamental high-quality VLE and pH data taken over a wide range of loadings and temperatures are necessary to sharpen the reliability of these kinds of mass transfer rate-based simulations. Nevertheless, current predictions show sodium glycinate is a very promising post-combustion carbon-capture solvent.

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