# OPTIMAL CHOICE OF IMMOBILIZED, SUPPORTED AMINES FOR $CO_2$ REMOVAL

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## Introduction

Aqueous solutions of amines have long been used by industry as absorbents for acid gas ($CO_2$, $H_2S$) removal, and in fact provide a large percentage of the natural gas sweetening operations[1]. While these chemical solutions have found a dominant position in the natural gas and refinery gas treatment, they have several shortcomings that can be greatly mitigated by immobilizing them into a solid polymeric support, an approach that has been used by NASA to provide regenerative $CO_2$ removal on long-term space shuttle orbiter missions[1].

Recent research in our group has produced a new solid amine $CO_2$ sorbent that has displayed approximately a twofold increase in cyclic $CO_2$ removal capacity over the material presently operated on board the space shuttle. This boost in capacity has been achieved through the application of a stable secondary amine onto a solid non-ionic polymeric support. This new sorbent may have applicability in the global search for methods to reduce greenhouse gas emissions. When combining these solid amine sorbents with a sequestration mechanism, long term, lower energy $CO_2$ sequestration systems may be achieved.

The first and foremost shortcoming presented by aqueous liquid amine systems comes from their corrosive effects on the metal piping systems used to contain them. The combination of acid gases and high pH sorbents can greatly accelerate the corrosive action on many mild steel components (valves, piping and pipe fittings). Numerous additives are frequently added to the aqueous liquid amine systems to minimize foaming, prevent corrosion, and promote the acid gas/ amine reaction. Our solid amine system greatly diminishes the corrosion concern and eliminates the need for many additives like foam depressants.

When applied as a fixed sorbent bed the solid amine system has the potential to simplify the present scrubbing system. Incorporating a solid amine system has the potential for eliminating several of the phase separation steps, as well as requiring a smaller absorbing and desorbing column. The smaller columns come from the higher amine/gas contact efficiency and increased amine density possible with the solid support pellets versus the packed trays typically used in the liquid systems. Finally, eliminating the aqueous carrier liquid offers the potential of lower regeneration energy. The liquid amine systems consistently keep amine concentrations below 30%, chiefly for corrosion concerns, however this reduced concentration raises both the fluid circulation rate and the regeneration energy costs.

## Experimental

### Amine Types.

Figure 1 shows the three amine types for the ethanolamine molecules investigated, monoethanolamine (MEA, primary), diethanolamine (DEA, secondary), and triethanolamine (TEA, tertiary).

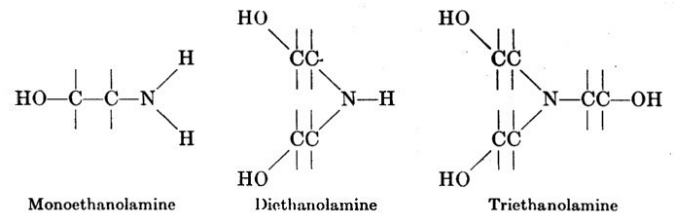


**Figure 1**. Amine Types MEA, DEA, TEA.

These amine types were immobilized into the pores of HP2MG, a poly(methylmethacrylate) support manufactured by Mitsubishi Chemical. This non-ionic polymeric support provided a high surface area (475 $m^2$/gm), large pore volume (1.2 ml/gm) to retain the amine and produced a pseudo-solid acid gas removal bead.

TEPAN a reaction product of TEPA (tetraethylenepentamine) and acrylonitrile, Figure 2, was also investigated for its $CO_2$ removal capacity while loaded onto the same PMMA support. Unlike the MEA, DEA and TEA, this amine, TEPAN, is not an alkanolamine.

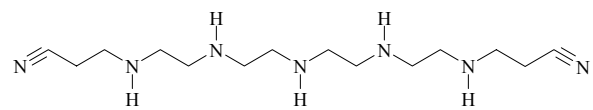

**Figure 2**. Schematic of TEPAN Molecule

### Sorbent Manufacture.

Solvent evaporation with a rotary evaporator was used to immobilize the amine within the pores of the support. In this process we mixed the amine to be impregnated with an equal volume of methanol. The alcohol allowed the amine mixture to diffuse into the bead pore volume much more rapidly. The alcohol also allowed the support to become easily wetted by the amine/alcohol solution, as well as reduced the viscosity of the mixture. We heated the solution and porous beads to 100 °C while under a slight vacuum (~4-8 psia). This step allowed us to evaporate the alcohol from the support while leaving the amine within the pores. After the bulk of the alcohol had been removed as vapor we removed the beads from the flask and tested their capacity for $CO_2$ removal.

### Capacity Measurements

We used a 110 cc aluminum reactor to retain the solid amine beads while testing their capacity for $CO_2$ removal. This reactor used a fine mesh screen at the inlet and outlet face to hold the beads within the reactor volume. An open cell aluminum foam (10% density) was also brazed into the reactor cavity. This foam coupled with the aluminum of the reactor housing provided an essentially isothermal test for both the absorb and desorb cycles. The testing used a fixed inlet concentration of 1 kPa of $CO_2$ with the balance being $N_2$ and water vapor at a total pressure of 1 atmosphere. An IR $CO_2$ analyzer monitored the outlet $CO_2$ concentration during the fixed absorption time period (25 minutes). After the absorb period an equal time (25 minutes) of vacuum desorption allowed the sorbent beads to partially regenerate. The data reported represents the steady state working capacity of the various sorbents. The amines can remove $CO_2$ more effectively with moisture, so the inlet gas stream was maintained at a 7 °C Dew point for all the tests.

## Results and Discussion

Figure 3 shows the comparison between the three amine types. A nearly 50% increase in the amine cyclic utilization was achieved for the secondary amine (DEA) compared with the primary amine (MEA). The slight variation in amine loading was (0.22M vs. 0.26M) removed by normalizing the capacity data based on the total amount of amine present. The low capacity shown by the tertiary amine is not surprising at these low $CO_2$ concentrations. The weak bond formed between the tertiary amine and the $CO_2$ molecule does not provide a ready means for removing the acid $CO_2$ molecule from our gas stream.

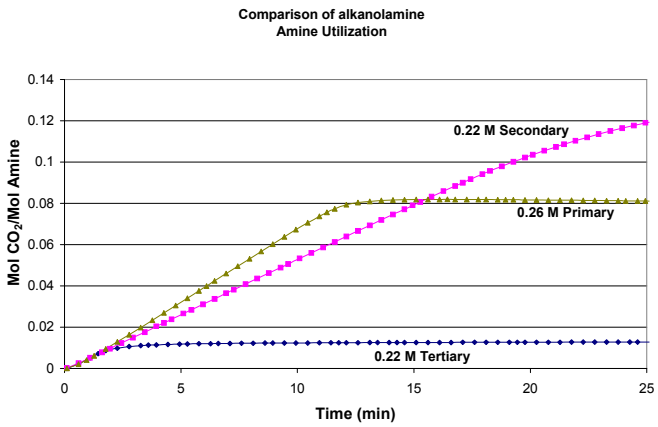


**Figure 3**. Normalized $CO_2$ Removal capacity for Primary (MEA), Secondary (DEA) and Tertiary (TEA) amine.

Figure 4 below shows the effect of amine loading within the support on its utilization in removing the $CO_2$ gas. The 4X (0.114 M – 0.515 M) range in amine loading within the support did not appreciably change the utilization of the amine on the support. This indicates that any surface interaction between the support and the amine did not diminish the activity of the amine for $CO_2$ removal. If interaction between the amine and the support had occurred, we would expect a difference in the amine utilization curves especially at the lower loadings. The shallower slope and lower utilization limit shown by the higher amine loadings in Figure 4 simply are an artifact of the fixed cycle time used. If the cycle had been extended for the higher loading case a similar utilization limit, as shown by the lower loadings, would have been reached.

Table 1 below shows a comparison of the physical/chemical properties of the 4 amines reported in this preprint. All four of the amines show a similar range of pH values. The large range in viscosity values do not provide any indication in the $CO_2$ removal capacity. TEPAN had the highest viscosity and the largest $CO_2$ removal capacity, TEA had the 2nd highest viscosity and showed no capacity for $CO_2$ removal.

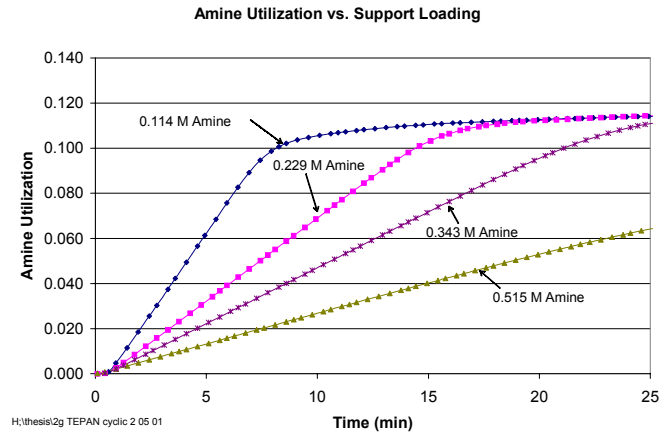


**Figure 4**. Normalized $CO_2$ Removal Capacity for variable loading of TEPAN amine within HP2MG support.

| Amine | pH | Viscosity cp | BP °C | MW |
|---|---|---|---|---|
| MEA | 11.66 | 18.9 | 171 | 61 |
| DEA | 11.32 | 352 | 269 | 105 |
| TEA | 10.55 | 614 | 340 | 149 |
| TEPAN | 10.98 | 750 | | 311 |

**Table 1.** Physical/Chemical Property Data of amine types

## Conclusions

The results of the alkanolamine $CO_2$ removal testing clearly show the higher working capacity displayed by secondary amines. The primary amines also show some effective affinity, but are clearly eclipsed by the secondary amines. The tertiary amines display a very weak capacity for $CO_2$ at the low levels (1 kPa) tested here.

All of the TEPAN amine results shown in Figure 4 display a similar asymptotic limit in $CO_2$ capacity, normalized for the amount of amine present on support. These curves show that the amine and support do not interact, at least in a manner that renders the functional site on the amine molecule unavailable for $CO_2$ removal. The lower amine loadings did not display any reduction in amine utilization as would be expected if surface/amine interaction affected the amine functional group.


## Acknowledgment

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## References


1. Ouellette, F., Winkler, E., Smith, G.," The Extended Duration Orbiter Regenerable $CO_2$ Removal System", SAE 901292, presented at 20th ICES, July 1990
2. Kohl, A., Nielsen, "**Gas Purification**", 5th Ed. Gulf Publishing, Houston TX,1997