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# CO<sub>2</sub> capture by aqueous amines and aqueous ammonia – A Comparison

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## Abstract

This paper presents the results of ASPEN simulations of a carbon-dioxide (CO<sub>2</sub>) removal and recovery plant that captures CO<sub>2</sub> from a 500 MWe (net) conventional coal-fired power plant flue gas stream. At a constant CO<sub>2</sub> recovery rate of 86.5% by weight, the performance of aqueous ammonia solution as an alternative to various aqueous amino solvents (MEA, AMP and MDEA) is compared in terms of the process scenarios, solvent loadings and overall energy consumption. The overall mass transfer co-efficient and CO<sub>2</sub> loading data generated for aqueous ammonia solutions using a laboratory scale wetted wall gas-liquid contactor are also presented.

The ASPEN simulation results in conjunction with the laboratory data show, that capturing CO<sub>2</sub> from coal-fired power plant flue gas, using aqueous ammonia solvent, will require ammonia concentration no more than 5% by weight and absorber temperature 10°C or lower, if the vapor phase ammonia losses are to be contained and the precipitation of ammonium bi-carbonate in the absorber is to be avoided. Under such an operating scenario, the aqueous ammonia based CO<sub>2</sub> capture process has overall energy requirement comparable to the conventional 30% by weight aqueous MEA based process. The ASPEN results further show that 30% by weight AMP based process has the lowest overall energy requirement among the solvents considered in this paper.

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*Keywords:* post-combustion capture; power station; coal; absorption processes

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## 1. Introduction

The monoethanolamine (MEA) process, or variations thereof, is currently the most widely used industrial process for capturing CO<sub>2</sub> from pf-fired power plant flue gas streams. In these plants relatively small quantities of CO<sub>2</sub> are captured to meet the industry demands for dry ice, enhanced oil recovery and food processing applications. However, when this process is applied for the greenhouse gas mitigation purposes to such plants, it has been considered too expensive due to large efficiency and cost penalties involved. Studies by the US DOE [1], IEA [2]

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and CSIRO [3] have generally shown that at such scales the net thermal efficiency of the power plant will drop by about 10 absolute percentage points and the cost of CO<sub>2</sub> capture will be around US \$30-50 per tonne of CO<sub>2</sub> recovered. One solution to overcome these problems is to find a low cost solvent that has higher CO<sub>2</sub> loading capacity and lower energy requirement for regeneration in comparison with the MEA solvent. Tertiary and hindered amines such as, methyl-diethanolamine (MDEA) and amino-methyl-propanol (AMP), that have theoretical CO<sub>2</sub> loading capacity twice that of MEA and the thermal energy requirement for regeneration lower than MEA have been proposed as alternative solvents [4,5]. Recently, Ciferno et al [6] have shown in their desk-top study of suitability of aqueous ammonia as an alternative solvent, that 7% by weight aqueous ammonia solvent has capacity to halve the energy efficiency and cost penalties that are associated with CO<sub>2</sub> capture from coal-fired power plant flue gas when 30% by weight MEA solvent is used. They have also indicated that aqueous ammonia solvent could potentially be used to remove SO<sub>x</sub>, NO<sub>x</sub> and mercury from flue gas during CO<sub>2</sub> capture. Thus, the aqueous ammonia solvent is a multi-pollutant capture medium

This paper assesses the CO<sub>2</sub> capture process performance that is likely to result with aqueous solutions of AMP, MDEA and ammonia as solvents and compares each solvent performance with the conventional 30% by weight MEA solvent. The engineering process simulator software ASPEN™ is used to simulate the CO<sub>2</sub> capture plant and estimate the process performance indicators. To ascertain validity of the simulated process conditions for CO<sub>2</sub> capture by aqueous ammonia solvent, the CO<sub>2</sub> loading and overall mass transfer data were also generated using a laboratory scale wetted wall gas-liquid contactor. The ASPEN predicted gas-liquid equilibrium data for the system NH<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O was also compared with the public domain experimental data [7,8].

## 2. CO<sub>2</sub> capture process flow-sheet

For this study, the coal-fired power plant (500 MWe) is considered to be a typical subcritical type plant in Australia where no flue gas desulphurisation (FGD) systems are installed. A typical Australian bituminous coal with low sulphur content (<1%) is assumed to be the fuel for this plant. The flue gas temperature, pressure and its CO<sub>2</sub> volume content are 120°C, 105 kPa and 12.9% respectively. Figure 1 depicts the general process flow-sheet adopted in the ASPEN process simulation for a CO<sub>2</sub> capture plant that treats the above flue gas. After in-direct heat exchange with the CO<sub>2</sub> lean exhaust gas leaving the absorber, the flue gas (Feed Gas) is pumped into the absorber by a blower. A direct contact type feed gas cooler upstream of the absorber controls the gas temperature at the absorber inlet. After passing through the absorber the flue gas undergoes a water wash section to remove any solvent droplets

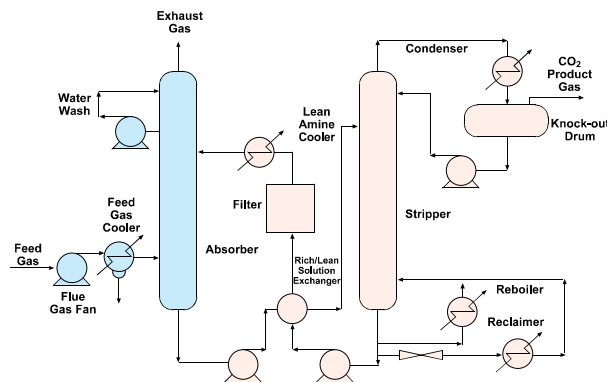


Figure 1: Process flow diagram for CO<sub>2</sub> recovery from flue gas with chemical absorbents

## 3. The CO<sub>2</sub> capture process conditions

With increasing absorption temperature, the physical solubility of CO<sub>2</sub> in the aqueous amino solvent decreases, but the reaction rate of dissolved CO<sub>2</sub> with the amine solvent increases. Hence to strike a balance between physical solubility and reaction kinetics, the flue gas temperature at the absorber inlet is usually kept at around 45°C in the

carried over and then leaves the absorber. The “CO<sub>2</sub> rich” absorbent solution is pumped to the top of a stripper, via a heat exchanger. The regeneration of the solvent is carried out in the stripper. Heat is supplied to the reboiler to maintain the regeneration conditions. The CO<sub>2</sub> product gas leaves the stripper via an overhead condenser. The CO<sub>2</sub>-product is a relatively pure product, with water vapour being the main other component. The “CO<sub>2</sub> lean” absorbent solution, containing far less CO<sub>2</sub> is then pumped back to the absorber via the lean-rich heat exchanger and a cooler to bring it down to the absorber temperature level.

case of 30% by weight MEA solvent based CO<sub>2</sub> capture process [9]. To keep the comparison basis constant, the “CO<sub>2</sub> lean” AMP and MDEA solvent concentrations and the absorber inlet temperature were also kept same as in the case of MEA based process. In addition, in each case the approach temperatures between the hot and cold fluids were kept at 10°C during the heat exchange. Whilst the CO<sub>2</sub> removal level is set to 86.5% for all the solvents, the process conditions for aqueous ammonia solvent are different from those for the above amino solvents. These conditions were determined separately using the ASPEN™ simulator as explained below. It should be noted that in this paper, the refinement of product CO<sub>2</sub> and its compression for the storage are not considered within the scope of the CO<sub>2</sub> capture plant.

In order to obtain the appropriate operating conditions for the aqueous ammonia based CO<sub>2</sub> capture process, the vapour-liquid equilibrium data was first calculated for the system NH<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O at 120°C and 200°C using the ASPEN™ process simulator and then compared with Müller’s experimental data [7,8]. This was necessary to confirm the validity of ASPEN process simulations. Figures 2 and 3 show close agreement between the ASPEN generated vapour-liquid equilibrium data and Müller’s experimental data. The coloured data points on Figures 2 and 3 represent the Aspen generated values for the total system pressure and the partial pressures of CO<sub>2</sub> and ammonia as a function of total CO<sub>2</sub> molality at the fixed value of ammonia molality.

Using the general process flow-sheet concept depicted in Figure 1, detailed ASPEN process simulations were carried out for the aqueous ammonia based CO<sub>2</sub> capture varying the “CO<sub>2</sub> lean” aqueous ammonia feed stream concentration and its temperature. For each case, the flue gas temperature at the inlet to the absorber was kept the same as the feed aqueous ammonia stream temperature. Under these conditions, both the ammonia loss and the reboiler duty were calculated per kg of CO<sub>2</sub> removed as a function of the feed ammonia concentration for 86.5 % CO<sub>2</sub> removal and recovery. In each case, the stripper was assumed to operate at 500 kPa.

Figure 4 shows the results of ASPEN simulations for CO<sub>2</sub> capture using aqueous ammonia solvent at various operating conditions assuming the equilibrium absorption conditions at each stage of the absorber. These results show that both ammonia loss from the system and reboiler duty in the stripper decrease with the decreasing temperature of the absorber. Decreasing the absorber temperature below 5°C has, however, minimum incremental advantages. Increasing the ammonia concentration in the solvent, whilst reducing the reboiler duty at a given absorber temperature, it increases the ammonia loss from the system. The ASPEN simulations additionally showed that with 86.5% CO<sub>2</sub> removal requirement, the ammonia concentration in the aqueous solution at 7.5% and above leads to the ammonium bi-carbonate precipitation in the absorber, if the absorber temperature is 5°C or less.

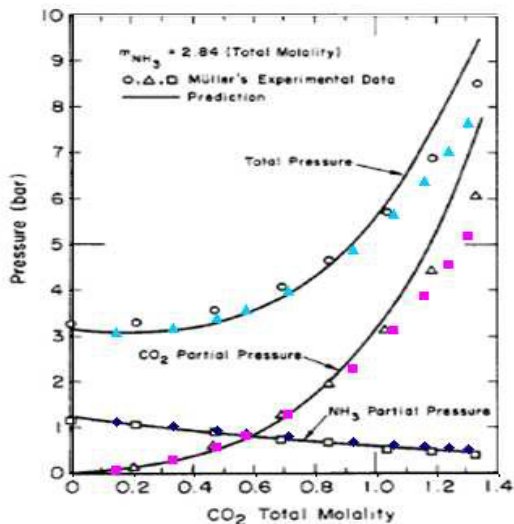


Figure 2: V-L equilibrium data at 120°C for NH<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O system

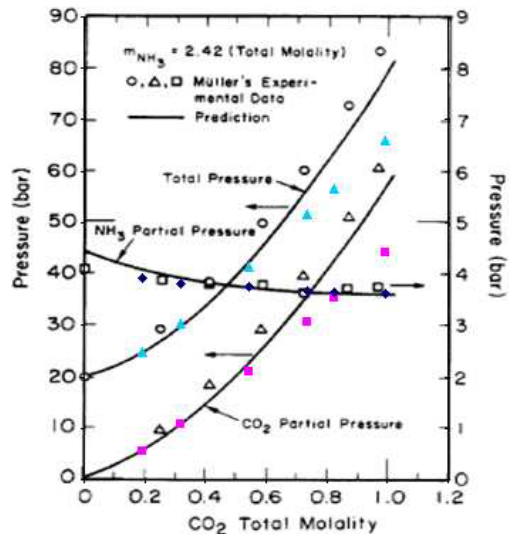


Figure 3: V-L equilibrium data at 200°C for NH<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O system

Therefore, for the minimum ammonia loss and reboiler duty with no precipitation of ammonium bi-carbonate in the absorber, the feed ammonia concentration should be kept below 7% by weight, if the absorber is to operate at 5°C.

Whilst the above operating conditions may be generally recommended for the aqueous ammonia based CO<sub>2</sub> capture process, it should be noted that CO<sub>2</sub> absorption at temperatures below the ambient conditions will require chilling the flue gas as well as the “CO<sub>2</sub> lean solvent” using an appropriate refrigerant. This refrigeration system load may not be helpful in reducing the total energy demand associated with the CO<sub>2</sub> capture process when compared with the MEA based process that is currently available commercially. A decision was therefore made to compare the aqueous ammonia based process by keeping the absorber temperature at 10°C and solvent concentration at 2.5% w/w and 5% w/w.

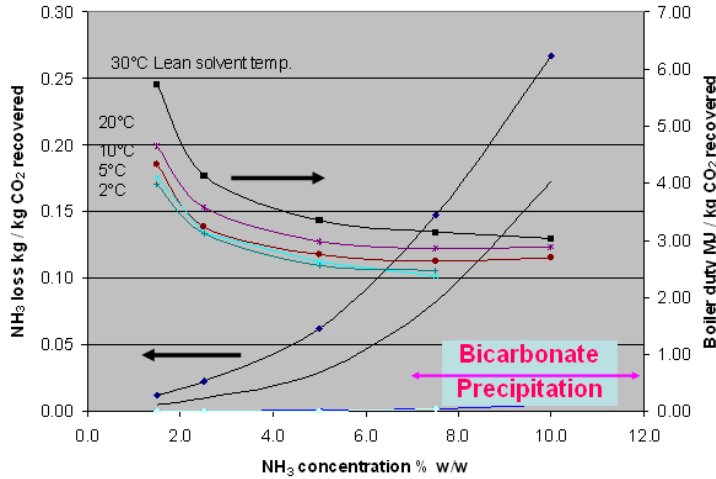


Figure 4: ASPEN simulation results for CO<sub>2</sub> capture at a number of operating conditions with aqueous ammonia solvent

**4. Laboratory and ASPEN simulation results**

Figure 5 shows the overall mass transfer co-efficient for CO<sub>2</sub> absorption as a function of CO<sub>2</sub> loadings for a number of aqueous ammonia and 30% w/w MEA solvents. These data were generated in a laboratory scale wetted wall column absorber which was operated at atmospheric pressure with CO<sub>2</sub> partial pressure varying from 0 to 20 kPa. The details of the absorber and its operating procedures are given elsewhere [10]. It shows that in an absorber operating at 40°C with 30% w/w MEA as solvent, to achieve similar overall mass transfer rates under identical CO<sub>2</sub> loadings, the aqueous ammonia solvent concentration and temperature will have to be at least 10% and 20°C respectively.

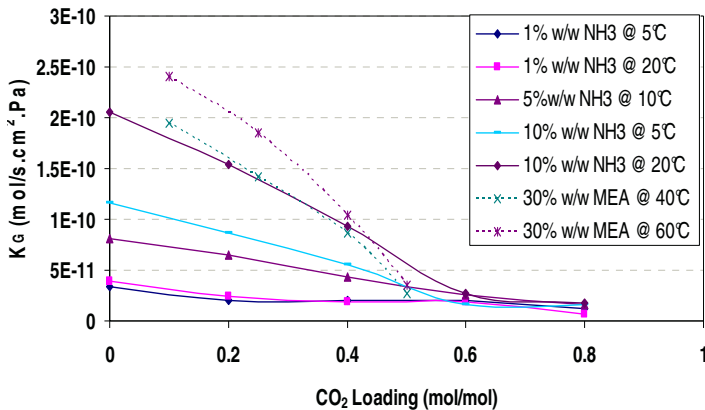


Figure 5: Overall mass transfer co-efficient for CO<sub>2</sub> absorption with aqueous ammonia and 30% w/w MEA solvents as a function of CO<sub>2</sub> loadings

During overall mass transfer measurements at both 5°C and 20°C for 10% w/w aqueous ammonia, the precipitation of solid ammonium bicarbonate was detected at CO<sub>2</sub> loadings of 0.4 mol/mol and higher. This laboratory observation is in-line with the ASPEN predictions shown in Figure 4. Table 1 below shows the ASPEN simulation results for the solvent circulation rate, reboiler heat duty and overall energy demand (includes motive

power) per ton of CO<sub>2</sub> captured in a CO<sub>2</sub> capture plant that uses various solvents for 86.5% CO<sub>2</sub> removal from flue gas. For the amino solvents, the flue gas and the lean solvent inlet temperatures to the absorber were assumed as 45°C and 40°C respectively. In the case of aqueous ammonia solvents, the flue gas and lean solvent inlet temperatures to the absorber were assumed to be 10°C and the refrigeration plant power demand was calculated assuming the co-efficient of performance (COP) equal to 3.

Table 1: Results of ASPEN simulations of a CO<sub>2</sub> capture plant – comparison with amines

Aq. Solvent	Flow Rate (m <sup>3</sup> /ton of CO <sub>2</sub> )	Reboiler Temperature °C	Reboiler Heat Duty (GJ/ton of CO <sub>2</sub> )	Electricity Consumption (GJ/ton of CO <sub>2</sub> )
30% w/w MEA	18.36	119.8	4.17	0.14
30% w/w AMP	15.82	115.9	3.18	0.13
30% w/w MDEA	40.06	112.9	3.82	0.08
2.5% w/w NH <sub>3</sub>	22.32	145.0	4.24	1.87
5% w/w NH <sub>3</sub>	15.88	130.0	2.94	1.42

The simulation results further showed that the total ammonia loss in the vapour phase for 5% w/w aqueous ammonia solvent based CO<sub>2</sub> capture plant is 0.17 kg per ton of CO<sub>2</sub> captured. Whilst the hindered amine AMP has best theoretical performance, the results clearly show that 5% w/w aqueous ammonia solvent has the lowest reboiler heat duty. It is lower than that required for 30% w/w MEA solvent because CO<sub>2</sub> capture via cycling between ammonium carbonate and bi-carbonate has the heat of regeneration 0.61 GJ/ton of CO<sub>2</sub> captured versus 1.92 for MEA. Overall, 5% w/w aqueous ammonia solvent based CO<sub>2</sub> capture has the total energy demand similar to that with 30% MEA based process.

## 5. Conclusion

The ASPEN simulation results in conjunction with the laboratory data show, that capturing CO<sub>2</sub> from coal-fired power plant flue gas, using aqueous ammonia solvent, will require ammonia concentration no more than 5% by weight and absorber temperature 10°C or less, if the vapor phase ammonia losses are to be contained and the precipitation of ammonium bi-carbonate in the absorber is to be avoided. Under such an operating scenario, the aqueous ammonia based CO<sub>2</sub> capture process has overall energy requirement comparable to the conventional 30% by weight aqueous MEA based process, provided the stripper is operated at 500 kPa and the solvent chiller plant has co-efficient of performance equal to 3. The ASPEN results further show that 30% by weight AMP based process has the lowest overall energy requirement among the solvents considered in this paper.

## 6. Future work on the aqueous ammonia process

The preliminary results presented here provide an insight into some of the issues related to the use of aqueous ammonia for post-combustion capture of CO<sub>2</sub>. Further work will focus on the establishment of a pilot plant operating on a flue gas slipstream, which aims to validate the technical performance predicted by the flow sheet simulations using Aspen Plus. This pilot plant will be located at Lake Munmorah in a power plant operated by Delta Electricity, assisting in the assessment of the use of aqueous ammonia under Australian power plant conditions. Important data to be derived from this pilot plant are the heat requirement for solvent regeneration and the ammonia losses. An experimental programme has been defined to enable the performance validation under a variety of conditions. This is currently underway. In addition to this work a study will be executed aimed at the integration of a full-scale aqueous ammonia process into a typical Australian power plant, including the delivery of CO<sub>2</sub> as a supercritical fluid. This study will provide the input data into an overall economic assessment of the aqueous ammonia process in comparison with conventional amine processes.

## 7. Acknowledgements

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## 8. References

1. Ramezan M., et.al., 2007: CO<sub>2</sub> capture from existing coal-fired power plant, US DOE/NETL Report No – 401/110907
2. Riemer P., 1993: The capture of CO<sub>2</sub> from fossil fuel fired power stations, IEA GHG R&D Programme Report No – IEAGHG/SR2
3. Dave, N., et al., 1999: Evaluation of the options for recovery and disposal/utilisation of CO<sub>2</sub> from Australian black-coal-fired power stations, ACARP Final Report, Project No – C7051
4. Gabrielsen, J., et.al., 2006: Modeling of CO<sub>2</sub> Absorber Using an AMP Solution, *AIChE Journal*, Vol. **52**, No. 10, pp. 3443-3451
5. McCann, N, et.al., 2008: Simulation of Enthalpy and Capacity of CO<sub>2</sub> Absorption by Aqueous Amine Systems, *Ind. Eng. Chem. Res.* **47**, 2002-2009
6. Ciferno, J., et al., 2005: An economic scoping study for CO<sub>2</sub> capture using aqueous ammonia. Final Report - DOE/NETL
7. Kawazuishi, K. and Prausnitz, J., 1987: Correlation of Vapor-Liquid Equilibria for the System Ammonia-Carbon Dioxide-Water, *Ind. Eng. Chem Res.*, Vol. **26**, No. 7, pp. 1482-85
8. Muller, G., 1983: Ph.D. Dissertation, University of Kaiserslautern.
9. Fluor's Econamine FG Plus<sup>SM</sup> Technology – An enhanced amine-based CO<sub>2</sub> capture process, presented at 2<sup>nd</sup> national conference on carbon sequestration, Alexandria, VA, May 5-8
10. Rowland, B., et al., 2008: Laboratory investigations of CO<sub>2</sub> capture using aqueous amine and ammonia solvents, CSIRO Draft Report.