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**ASSESSMENT OF THE AQUA AMMONIA PROCESS AS AN OPTION FOR
CO₂ CAPTURE FROM COAL-FIRED POWER PLANTS**

RESEARCH REPORT 68

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Context Statement

An objective of the Centre's project on greenhouse gas reduction options is to maintain a watching brief on prospective technology developments.

This study was undertaken to assess the prospects for aqua ammonia solvents under development and testing by overseas commercial and research interests. Using mass and energy flows various process options are simulated to determine and compare the performance of the chosen solvents. While the conclusions of this study differ from others in the published literature, the validation of such simulated results will become evident in the application, testing and demonstration of these and several other chemical solvent options relevant to post combustion capture technologies.

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Executive Summary

This report investigates the benefits of the aqua ammonia process currently being investigated by the US DOE's NETL laboratory as an alternative to the MEA solvent-based process for capture and recovery of CO₂ from the flue gases of a conventional pf-fired power plant.

ASPEN Plus software has been used to perform the material and energy balances over the absorption/desorption cycle in this study. The aqua ammonia solvent has been considered both as an aqueous solution of ammonia gas and as an aqueous solution of ammonium carbonate salt. The comparison with the standard commercial process using a 30% by weight MEA has been carried out on the basis of CO₂ absorption capacities of the solvents, solvent losses, liquid circulation rates between the absorption and regeneration towers, and the regenerator heat duty required for 90% CO₂ capture and recovery from flue gas.

The ASPEN Plus process simulation, as well as the thermodynamics of the chemical reactions occurring during absorption and regeneration, clearly show that (i) reaction equilibrium favours formation of ammonium bicarbonate in the spent solution, and (ii) it is difficult to stop complete decomposition of ammonium bicarbonate to ammonia gas and carbon dioxide at the temperatures used in the regenerator. This latter finding conflicts to some extent with the desk-top studies of the US/DOE where they were assessing the economics of the aqua ammonia process. In their study they assumed that partial decomposition to ammonium carbonate is the only reaction that occurs during solvent regeneration. Our simulation results also show that a substantial quantity of water is vaporised in the regenerator to strip out absorbed CO₂ from the spent solution and this is not accounted for by the US DOE study. As a result, our predicted overall solvent losses and regeneration heat duties for the aqua ammonia process are substantially higher those assumed in the US DOE study, and furthermore compare poorly with the MEA-based process.

The results of this investigation are summarised in the Table below. They show that the aqua ammonia process in any form is not a viable alternative to the conventional MEA process as:

- NH₃ losses in the absorption/desorption cycle exceed what would be acceptable from both environmental and operating cost viewpoints
- The energy demand for the solvent regeneration is significantly greater than for the MEA-based process

- The poor CO₂ absorption capacity of ammonium carbonate solvents would lead to much larger and consequently more costly contacting systems being required than for the MEA process.

The aqua ammonia process also creates two additional problems, separation of NH₃ from the flue gas stream leaving the absorber and separation of NH₃ from the CO₂ stream exiting the regenerator. At present, there are no known economic processes to separate NH₃ either from nitrogen or carbon dioxide in a way that would allow the use of aqua ammonia solvent as a substitute for the conventional MEA process.

Comparison of the Aqua Ammonia and MEA Processes

| Case | 1 | 2 | 3 | 4 | 5 | |
|--|-------------------------------|-------------------------------|------------------------------|--|---|----------------------|
| Absorbing solution | 15% wt NH _{3(aq)} | 15% wt NH _{3(aq)} | 7% wt NH _{3(aq)} | 7% wt (NH ₄) ₂ CO _{3(aq)} | 19.6% wt (NH ₄) ₂ CO _{3(aq)} | 30% wt MEA |
| Regenerator type | Multistage Column | Single stage | Single stage | Single stage | Single stage | Multistage Column |
| Solvent circulation rate (litres/kg CO₂ recovered) | 8.1 | 8.0 | 12.3 | 77.2 | 38.1 | 17 |
| CO₂ absorption* (kg CO₂/kg NH₃, (NH₄)₂CO₃ or MEA in solution entering absorber) | 0.91 | 0.92 | 1.22 | 0.18 | 0.12 | 0.36 |
| Solvent losses (kg NH₃ or MEA/kg CO₂ recovered) | 1 | 0.71 | 0.41 | 0.09 | 0.26 | 0.002 |
| Regenerator heat duty (MJ/ kg CO₂ recovered) | 45.0 | 17.7 | 28.8 | 10.2 | 6.8 | 4.2 |

* This is kg CO₂ absorbed per kg of NH₃, (NH₄)₂CO₃ or MEA in the solution that is fed to the absorber.

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1. Introduction

The monoethanolamine (MEA) process, or variations thereof, is currently the most widely used industrial process for capturing CO₂ from pf-fired power plant flue gas streams. In these plants relatively small quantities of CO₂ are captured to meet the industry demands for dry ice, enhanced oil recovery and food processing applications. However, this process has generally been considered too expensive to be used for applications directed at greenhouse gas mitigation due to excessively large quantities of CO₂ that must be captured and the relatively high costs of this process. Studies by Riemer (1993) and Dave et al (1999) have 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 CO₂ capture will be around US \$30 per tonne of CO₂ recovered. In addition, the product CO₂ will have little commercial value, as the quantities of CO₂ produced would saturate any market, and in any case long-term sequestration is the driver for the application. Such high energy and cost penalties are due to the limited equilibrium CO₂ loading capacity for the MEA solvent (0.5 mole CO₂ per mole of MEA), the irreversible degradation of MEA in the presence of SO_x and NO_x, the need for extraction of large quantities of low to medium pressure steam (around 4 MJ per kg of CO₂ absorbed) from the steam cycle for regeneration of the spent MEA solvent and the corrosion potential of the solvent on equipment.

2. The Aqua Ammonia Process

One solution to overcome the above problems is to find a low cost solvent that can minimize energy requirements, the equipment size and corrosion problems. Yeh and Bai (1999) have suggested an aqueous solution of NH₃ (aqua ammonia) as an alternative solvent for removing CO₂ from flue gas. Injection of ammonia gas or aqueous ammonia to remove NO_x is a common process in power plants (e.g. selective catalytic reduction or thermal de-NO_x). The NH₃ gas or its aqueous solution is also an excellent reagent for removing SO₂ and HCl from waste gas streams. Reaction of aqueous NH₃ with CO₂ produces ammonium bicarbonate that can be subsequently decomposed at temperatures above 60°C to release ammonia gas and CO₂. Thus, an aqueous solution of NH₃ could potentially be used to capture simultaneously all three major acid gases (SO_x, NO_x and CO₂) from a pf-fired power plant flue gas stream. Though sulphate and nitrate salts of ammonia may be produced during CO₂ absorption and they are stable in comparison with the bicarbonate, these salts have applications as fertilizer. In fact, ammonium bicarbonate is also a fertiliser. Roughly 43% of the nitrogenous fertilizer used in China is ammonium bicarbonate, which according to Zhou et al (2001) is exclusively produced by washing syngas from atmospheric pressure coal gasifiers with aqueous ammonia solution.

The aqua ammonia process would seem to be an attractive option for the capture of CO₂ from power station flue gases given that

- It can remove all the acidic gases simultaneously,
- The decomposition temperature of ammonium bicarbonate at ambient pressure is low for recovery of CO₂ and regeneration of ammonia, and
- Carbon steel could be used as the material of construction.

In early 2004, Powerspan Inc and the US DOE/NETL entered into a research agreement to explore the commercial viability of aqua ammonia as an alternative to MEA solvent. A recent desktop study by Ciferno et al (2005) of US DOE/NETL suggests that aqua ammonia has several economic advantages over the MEA process for capturing 90% of the CO₂ from the flue gases of a 400 MWe (net) pf-fired power plant. In their report they summarise the advantages of aqua ammonia as being:

- The net power plant efficiency (HHV basis) increases from 29% with MEA to 34% for aqua ammonia - the base power plant efficiency without CO₂ capture is 40% (HHV).
- The cost of CO₂ avoided decreases from US \$47 per tonne with MEA to \$27 per tonne with aqua ammonia.
- The cost of electricity decreases from US 7.6 cents per kWh with MEA to 6.4 cents per kWh with aqua ammonia, the base cost of power supply without CO₂ capture being US 4.6 cents per kWh.

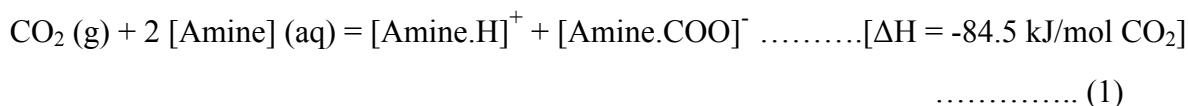
Ciferno et al (2005) further claim that when an aqua ammonia solvent based scrubbing system is used as a multi-pollutant control system (CO₂, SO_x, NO_x and Hg removal), the cost of CO₂ avoided is only US \$14 per tonne and the cost of electricity reduces to US 5.5 cents per kWh as separate de-SO_x and de-NO_x systems are no longer required. Their analysis assumes that CO₂ is produced in a sequestration ready form at 10 MPa(g).

In coming to the above conclusions Ciferno et al (2005) have based their work on previous studies by Bai and Yeh (1997), Yeh and Bai (1999) and more recent laboratory studies on absorption of CO₂ by aqueous ammonia (Resnik, Yeh and Pennline, 2004).

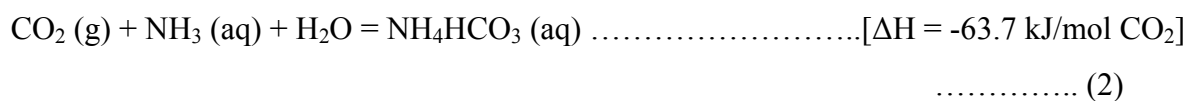
This study by CSIRO Energy Technology for the CCSD is directed at independently verifying the advantages as claimed above for the aqua ammonia process over the MEA-based process.

3. Thermodynamics and Kinetics of CO₂ Absorption

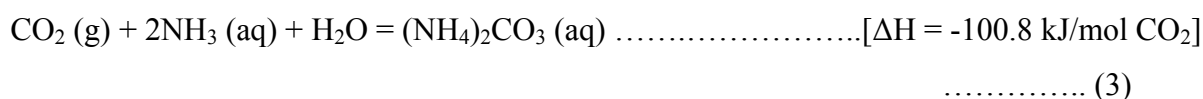
Absorption of CO₂ by aqueous solutions of MEA follows the reaction:



For absorption by ammonia the reactions are:



and



Thus, the absorption process is exothermic with both solvents and temperature rise occurs in the absorption apparatus as noted by Yeh and Bai (1999). However, whereas in normal industrial practice lean 30% by weight MEA solvent enters the absorption tower at 40 °C, Yeh and Bai (1999) recommend that absorption of CO₂ by the aqua ammonia solution be conducted at temperatures below 40°C to avoid excessive ammonia vaporisation losses.

It should be noted from the above reactions that both ammonium carbonate and bicarbonate products could be obtained upon absorption of CO₂ by aqua ammonia and the CO₂ loading of the spent solution on a molar basis could be twice that achievable with the MEA solvent if all the ammonia is converted to the bicarbonate form. Bai and Yeh (1997) confirm in their laboratory investigations that the spent aqua ammonia solution essentially contains ammonium bicarbonate and the solution pH remains between 7.9 and 8. Considerations of the free energies (and equilibrium constants) for the various competing reactions (Appendix A) would also support the observation that ammonium bicarbonate is the major component of the spent ammonia solution.

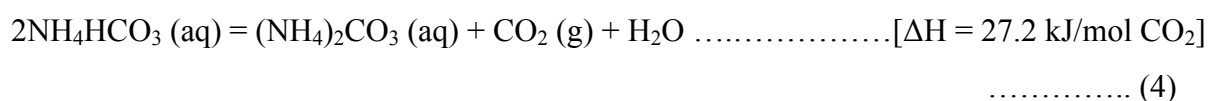
At a constant temperature of 25°C and atmospheric pressure, Yeh and Bai (1999) have measured the CO₂ absorption capacity of the aqua ammonia solvent as a function of ammonia concentration using simulated flue gas (CO₂ concentration 16% by volume). Table 1 lists these results. It should

be noted that over the same concentration range, the maximum CO₂ absorption capacity of the aqueous amine solvent is only 0.4 kg per kg of MEA.

Table 1 – CO₂ absorption capacity of the aqua ammonia solvent at 25°C

| Ammonia Concentration (% by weight) | Absorption Capacity (kg CO₂ / kg NH₃) |
|--|--|
| 7 | 1.2 |
| 14 | 1.1 |
| 21 | 0.95 |
| 28 | 0.9 |
| 35 | 0.85 |

Yeh and Bai (1999) also noted in their CO₂ absorption studies that the CO₂ removal efficiency reached its maximum (99%) when a CO₂ loading capacity of 1.2 kg per kg of NH₃ was achieved with 7% by weight aqua ammonia. Ciferno et al (2005) have, therefore, used 7% by weight ammonia concentration in their analysis. They have assumed that the CO₂ absorber runs at 27°C, and that regeneration of the spent solution can be achieved by simply heating the solution to 82°C at atmospheric pressure. They therefore assume that the process of regeneration does not require steam to be raised in a reboiler so that the regenerator heat duty does not involve latent heat of vaporisation of water. Ciferno et al (2005) further assume that ammonium bicarbonate undergoes partial decomposition to produce ammonium carbonate according to the reaction given below rather than complete decomposition to NH₃ and CO₂ gases:



Thus their concept of the aqua ammonia process is one where the solution composition cycles between ammonium carbonate and ammonium bicarbonate so that there is minimal free ammonia present in the system. Since the heat of reaction for the above equilibrium is nearly 3 times lower than that for the reaction of MEA with CO₂, Ciferno et al (2005) envisage that the steam demand and hence the overall energy penalty for using aqua ammonia as a solvent for CO₂ capture must be proportionately lower. They have also noted that the purchase price for the industrial grade ammonia solution (30% by weight) is approximately one-sixth of that of 30% by weight MEA

absorbent in the world market. These are the bases for their claimed advantages of the aqua ammonia process.

It should be noted however that the decomposition of ammonium bicarbonate in aqueous solution is unlikely to stop at the carbonate, and that subsequent decomposition of the carbonate is more likely to produce NH₃ and more CO₂ as gaseous products, particularly at temperatures exceeding 60°C. Table 2 shows the ratio of equilibrium constants for partial decomposition (Equation 4) and complete decomposition (the reverse of Equation 2 with NH₃ in the gaseous phase) at various temperatures, indicating that it would be difficult to stop the reaction going past the carbonate form at temperatures above 60°C.

Table-2 - Ratio of equilibrium constants for partial and complete decomposition of ammonium bicarbonate

| Temperature (°C) | Equilibrium Constant Ratio (Partial to Complete) |
|-----------------------------|---|
| 20 | 7.98 |
| 30 | 3.02 |
| 40 | 1.21 |
| 50 | 0.52 |
| 60 | 0.23 |
| 70 | 0.10 |
| 80 | 0.05 |
| 90 | 0.02 |
| 100 | 0.01 |

4. Methodology

An examination of the literature, particularly the experimental observations of Bai et al (1997, 1999), backed up by ASPEN Plus simulations of CO₂ capture and recovery plant using aqua ammonia as a solvent were used to assess the claims made by Ciferno et al (2005) in their report. Particular emphasis has been given to the difference in the plant operating conditions between the MEA and aqua ammonia solvents, the separation of ammonia from CO₂ on regeneration and the comparative losses of both solvents likely to occur in the industrial environment.

For the ASPEN Plus simulation of the aqua ammonia process we considered five cases:

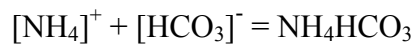
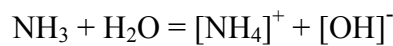
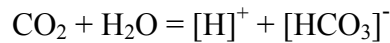
- Case 1 - Absorption by 15% aqueous ammonia solution entering the absorber. In this case, the solvent regeneration is assumed to occur in a multistage column with stripping and absorption sections, similar to what might be used with MEA.
- Case 2 - Absorption by 15% aqueous ammonia solution entering the absorber. In this case, regeneration is assumed to occur in a single stage flash regenerator similar to that considered by Ciferno et al (2005). This case gives some insight to the sensitivity of the process to the configuration of the solvent regeneration step.
- Case 3 - Absorption by 7% aqueous ammonia solution entering the absorber. In this case, regeneration is assumed to occur in a single stage flash regenerator similar to that considered by Ciferno et al (2005). This case gives some insight to the sensitivity of the process to the solvent concentration.
- Case 4 - Absorption by 7% ammonium carbonate solution entering the absorber (equivalent to an ammonia concentration of 2.5%). Solvent regeneration from the bicarbonate form back to the carbonate occurs in a single stage flash regenerator. It is assumed that makeup ammonia is added to the ammonium carbonate solution as it returns to the absorber.
- Case 5 - Absorption by 19.6% aqueous ammonia solution entering the absorber (equivalent to an ammonia concentration of 7%). This case is, perhaps, closest to the condition assumed by Ciferno et al (2005). The solvent regeneration from bicarbonate form to carbonate form and makeup ammonia addition are the same as in Case 4. This case gives some insight to the sensitivity of the process to the solvent concentration when aqueous ammonium carbonate is the solvent.

The lean aqua ammonia/carbonate solutions were considered to enter the absorber at 30°C in each case, while the flue gas temperature at the inlet of the absorber was assumed to be 40°C. The flue gas composition for the simulation (Table 3) was same as that used by Ciferno et al (2005). The process flowsheet (Figure 1) for the gas pre-wash, CO₂ absorption and solvent regeneration operations was essentially the same as used in a previous study conducted by Dave et al (1999), where CO₂ capture and separation from a pf-fired power plant flue gas by the MEA solvent process was investigated in great detail. For estimation of the material and energy balance with aqua ammonia solvent, the electrolyte NRTL property package within the ASPEN Plus software was used.

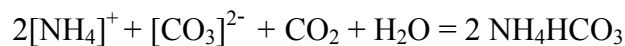
Table 3 - Flue gas composition and other process data

| Flue Gas Components (mass fraction) | |
|--|---------------------------|
| Moisture | 0.045 |
| CO ₂ | 0.191 |
| N ₂ | 0.718 |
| O ₂ | 0.045 |
| CO | 848 ppm |
| Total Gas Flow Rate (kg/hr) | 1.84232 x 10 ⁶ |
| Gas Temperature (°C) | 110 |
| Gas Pressure (kPa) | 110 |

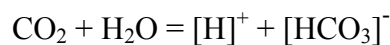
The following ionic reactions were assumed to take place in the CO₂ scrubber:



For those cases where the aqueous solution of ammonium carbonate [(NH₄)₂CO₃] was the feed solvent for absorption of CO₂, solution concentration was determined in terms of equivalent amounts of [NH₄]⁺ and [CO₃]²⁻ ions and the CO₂ absorption reaction in the scrubber was assumed to take place as follows:



The CO₂ regeneration was assumed to occur via the following reactions:



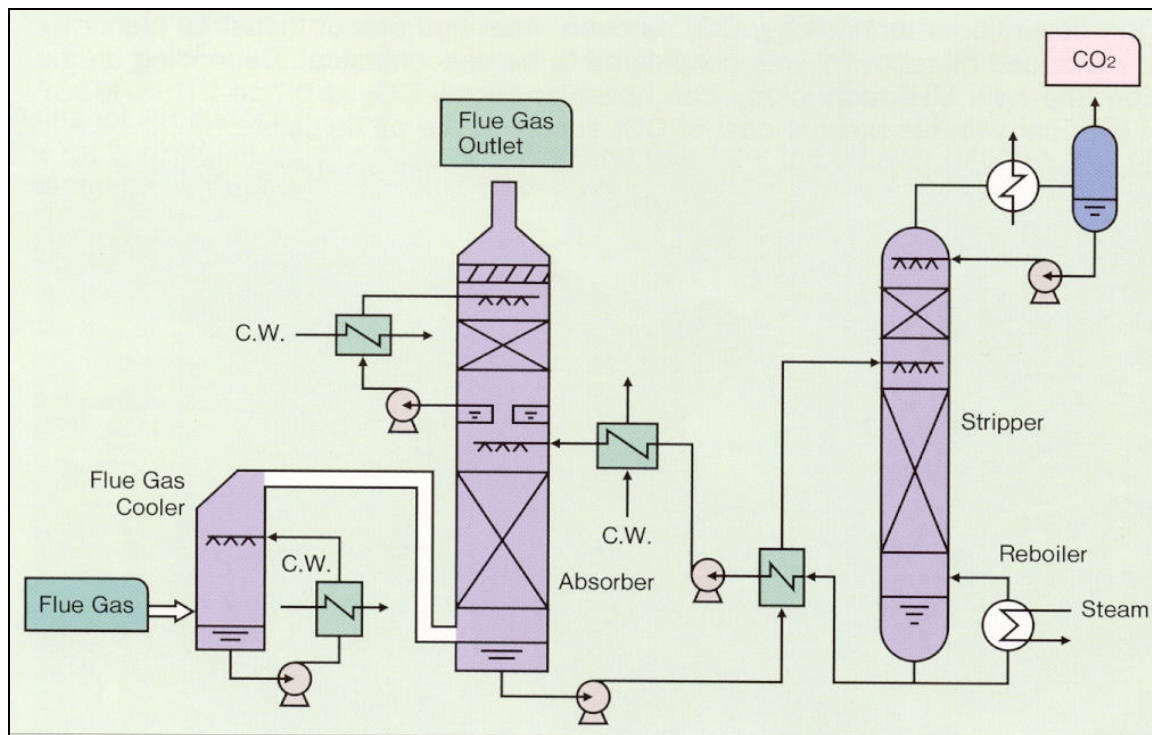
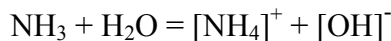


Figure 1 – CO₂ absorption and desorption process scheme

The ASPEN Plus simulation with the MEA solution was not performed since sufficient public domain information is currently available to estimate the likely performance of such a system for purposes of the present study. However, it is noted here that current industrial practice for capturing CO₂ from a pf-fired power plant flue gas is to use 30% by weight MEA solution and have the lean MEA solution enter the absorber at 40°C, while pre-washed flue gas enters the absorber at 45°C.

5. Results

5.1 Case 1 - 15% by Weight Aqua Ammonia (MEA Type Process Configuration)

The ASPEN Plus simulation results show that with 15% by weight aqua ammonia as absorbent, a two theoretical stage absorber and an eight theoretical stage solvent regenerator are required to capture and recover 90% of the CO₂ present in the flue gas stream, if the process scheme is same as that used for the MEA solvent. Of the eight stages in the regenerator, ammonium bicarbonate decomposition occurs in the two theoretical stages at the bottom of the regenerator, one of which is

the reboiler. The remaining stages simply act as product CO₂ washing stages to minimize NH₃ loss through the overhead partial condenser.

For 90% CO₂ capture, the lean aqua ammonia flow rate required in the scrubber is 2.3×10^6 kg/hr. Due to the exothermicity of ammonium bicarbonate formation, the solution temperature rises from 30°C (at the inlet) to 44°C (at the outlet). Similarly, the flue gas temperature rises from 40°C at the inlet to 44°C at the outlet. In order to minimize the overhead NH₃ losses, the CO₂ lean flue gas needs to be cooled to 30°C by scrubbing with water and the ammonia laden water recycled to the absorber. Even under these conditions, approximately 48.6% of ammonia originally present in the aqua ammonia solvent is lost with the CO₂ lean flue gas, i.e. 0.53 kg of NH₃ is lost per kg of CO₂ captured. As a result, the ammonia concentration in the CO₂ lean flue gas becomes 15.9% by volume. These results are similar to the observations made recently by Yeh et al (2005). These authors have observed in their laboratory scale absorber operated in a cyclic absorption/regeneration mode that 43% of ammonia originally present in a 14% by weight aqua ammonia solvent is lost during a 3-cycle test when the absorber is operated at 27°C. Such a large loss of NH₃ in the CO₂ lean gas would have in itself serious environmental as well as operating cost implications if it were allowed to occur.

Since the CO₂ recovery tower has to operate with an overhead CO₂ product stream pressure of at least 10 kPa(g) and the pressure drop across the tower is usually at least 20 kPa, the pressure at the bottom of the tower would need to be at least 130 kPa absolute. To attain 90% recovery of CO₂ (i.e. recover all of the absorbed CO₂ from the spent solution), the regenerator bottom temperature would need to be kept at 106°C and the spent solution heated from 40°C (as obtained at the absorber outlet) to 77°C before it enters the regenerator according to the ASPEN Plus simulation. The required reboiler duty from our simulation is around 45 MJ per kg of CO₂ recovered.

The ASPEN Plus simulation results show that the regenerator overhead condenser temperature is 58°C and the product CO₂ stream needs to be cooled further to 30°C to reduce overhead NH₃ losses. This, of course, assumes that no chemical reactions occur in the overhead stream between NH₃, CO₂ and moisture despite such reactions being highly likely, as shown in Appendix A. Even under these conditions, 0.52 kg of NH₃ is carried over with every kg of CO₂ leaving the top of the regenerator, i.e. 56% by volume.

In this case the absorbing solution is considered to be a solution of aqueous ammonia which is entering the top of the absorption tower. Overall, 0.91 kg of CO₂ is absorbed per kg of NH₃ in the

solvent feed stream and nearly 1 kg of ammonia is lost for every kg of CO₂ captured and recovered from the flue gas when 15% by weight aqua ammonia solvent is used. In order to balance such large losses, the ASPEN Plus simulation shows that 1.29×10^6 kg/hr of 26.1% by weight aqueous ammonia solution is required as makeup and the liquid circulation rate between the absorber and desorber is 8.1 litres per kg of CO₂ recovered. The required reboiler duty from our simulation is extremely high, at around 45 MJ per kg of CO₂ recovered. It is therefore clear that there is nothing to be gained from using a multistage regeneration tower to control NH₃ losses and that one would be better off using a single stage flash regenerator of the type used by Ciferno et al (2005).

5.2 Case 2 - 15% by Weight Aqua Ammonia (Flash Regenerator)

In this case, the ASPEN Plus simulation shows that the spent solution will have to be heated to 104°C prior to flash separation of CO₂, i.e. the configuration used in the study by Ciferno et al (2005) To reduce the overall heat load, the spent solution could be preheated to 62°C by heat exchange with the stream leaving the bottom of the flash regenerator. The overall regenerator duty then reduces to 17.7 MJ per kg of CO₂ recovered. The overhead gas stream leaving the regenerator, after cooling to 30°C, shows 0.14 kg of NH₃ carried over with every kg of CO₂ recovered, i.e. 26% NH₃ by volume.

Again in this case the absorbing solution is considered to be a solution of aqueous ammonia which is entering the top of the absorption tower. According to the simulation, 0.92 kg of CO₂ is absorbed per kg of NH₃ in the feed solvent and the overall NH₃ loss during absorption and recovery of CO₂ is 0.71 kg per kg of CO₂. In order to balance such large losses, the ASPEN Plus simulation shows that 9.2×10^5 kg/hr of 26.1% by weight aqueous ammonia solution is required as makeup and the liquid circulation rate between the CO₂ scrubber and regenerator is 8 litres per kg of CO₂ recovered.

5.3 Case 3 - 7% by Weight Aqua Ammonia

ASPEN Plus simulations show that the two theoretical stage absorber used in the previous cases is also adequate for 90% CO₂ capture by 7% by weight aqua ammonia solvent. In this case, 3.7×10^6 kg/hr of lean solvent at 30°C is required to be fed to the absorber. The solution temperature rises to 44°C due to exothermicity of the reaction. The temperature of the flue gas stream rises from 40°C to 46°C as it passes up the absorption tower. The carryover of NH₃ in the CO₂ lean gas after cooling to 30°C is calculated to be 8.9% by volume, i.e. 33.8% of ammonia originally present in the fresh

solvent is lost or 0.28 kg of NH₃ lost per kg of CO₂ captured. Yeh et al (2005) have observed in their laboratory scale absorber that around 30% of ammonia originally present in 7% aqua ammonia is lost as carry over in the CO₂ lean gas at 27°C in a 3-cycle test.

To regenerate the spent aqua ammonia solvent, it needs to be heated to 106°C prior to flash separation of CO₂ in a single stage flash regenerator as suggested by Ciferno et al (2005). To reduce the overall heat load, the spent solution could be preheated to 72°C by heat exchange with the stream leaving the bottom of the flash regenerator. The overall regenerator duty then becomes 28.8 MJ per kg of CO₂ recovered. The overhead gas stream leaving the regenerator, when cooled to 30°C shows 0.13 kg of NH₃ carried over with every kg of CO₂ recovered, i.e. 24% by volume. According to the simulation, 1.22 kg of CO₂ is absorbed per kg of NH₃ in the feed solvent and the overall NH₃ loss during absorption and recovery of CO₂ is 0.41 kg per kg of CO₂. In order to balance such large losses, the ASPEN Plus simulation shows that 6.3 x 10⁵ kg/hr of 26.1% by weight aqueous ammonia solution is required as makeup and the liquid circulation rate between the CO₂ scrubber and regenerator is 12.3 litres per kg of CO₂ recovered.

5.4 Case 4 - 7% by Weight Aqueous Ammonium Carbonate

ASPEN Plus simulations show that the two theoretical stage absorber used in the previous two cases is also adequate for 90% CO₂ capture by 7% by weight aqueous ammonium carbonate solvent (corresponding to 2.5% by weight NH₃). However, in this case 2.5 x 10⁷ kg/hr of CO₂ lean solvent at 30°C needs to be fed to the absorber. The solution temperature rises to 34°C as it passes through the absorber due to the exothermicity of the reaction. In this case the temperature of the flue gas stream drops from 40°C to 31°C as it passes up the absorption tower. The carryover of NH₃ in the CO₂ lean flue gas at 30°C is only 0.9% by volume in this case, i.e. ammonia loss is 0.03 kg per kg of CO₂ captured.

To regenerate the spent solvent and recover CO₂, the solution needs to be heated to only 88°C prior to flashing in a single stage regenerator. Again to reduce the overall heat load, the spent solution could be preheated to 67°C by heat exchange with the stream leaving the bottom of the flash regenerator. The overall regenerator duty then becomes 10.2 MJ per kg of CO₂ recovered. After cooling to 30°C the overhead gas stream leaving the regenerator carries 0.06 kg of NH₃ with every kg of CO₂ recovered, i.e. 12% by volume. According to the simulation, the overall NH₃ loss during absorption and recovery of CO₂ is therefore 0.09 kg per kg of CO₂, and 0.18 kg of CO₂ is absorbed per kg of ammonium carbonate in the feed solvent. In order to balance the ammonium carbonate

concentration in the lean solvent returning to the absorber, 26125 kg per hour of ammonia gas needs to be added to the solution and the liquid circulation rate between the CO₂ scrubber and regenerator rises to 77.2 litres per kg of CO₂ recovered.

5.5 Case 5 - 19.6% by Weight Aqueous Ammonium Carbonate

With 19.6% by weight aqueous ammonium carbonate solvent (corresponding to 7% by weight NH₃) 1.3 x 10⁷ kg/hr of CO₂ lean solvent at 30°C needs to be fed to the two-stage absorber for 90% capture of CO₂. The solution temperature rises to 38°C due to the exothermicity of the reaction. The temperature of the flue gas stream drops from 40°C to 33°C in this case as it passes up the absorption tower. The carryover of NH₃ in the CO₂ lean gas at 30°C is 3.8% by volume, i.e. ammonia loss is 0.11 kg per kg of CO₂ captured.

To regenerate the spent solvent and recover CO₂, the solution needs to be heated to 82°C prior to flashing in a single stage regenerator. To reduce the overall heat load, the spent solution could be preheated to 60°C by heat exchange with the stream leaving the bottom of the flash regenerator. The overall regenerator duty then becomes 6.8 MJ per kg of CO₂ recovered. After cooling to 30°C the overhead gas stream leaving the regenerator, carries 0.15 kg of NH₃ with every kg of CO₂ recovered, i.e. 26% by volume. According to the simulation, the overall NH₃ loss during absorption and recovery of CO₂ is 0.26 kg per kg of CO₂ and 0.12 kg of CO₂ is absorbed per kg of ammonium carbonate in the feed solvent. In order to balance the ammonium carbonate concentration in the lean solvent returning to the absorber, 82035 kg per hour of ammonia gas needs to be added to the solution. The liquid circulation rate between the CO₂ scrubber and regenerator is 38.1 litres per kg of CO₂ recovered.

5.6 30% by Weight MEA Solvent

The ASPEN Plus simulation of CO₂ capture and recovery using 30% by weight MEA solvent (a standard commercial application) was not undertaken in this study since there is enough information already in the public domain to provide a satisfactory comparison. Past studies by Dave et al (1999) and the public domain literature indicate that the reboiler heat duty for 90% CO₂ capture from a pf-fired power plant flue gas is around 4.2 MJ per kg of CO₂ recovered. The overall MEA loss (85% strength) is only 2 kg per tonne of CO₂ recovered and both the CO₂ lean and rich gas streams have a MEA carryover of less than 1ppmV. The solvent circulation rate in this case is around 17 litres per kg of CO₂ removed.

6. Discussion

A comparison of the important performance parameters for the various processes is shown in Table 4. A preliminary assessment of the aqua ammonia process shows that it is hampered by excessively large ammonia losses even in the case where an aqueous solution of ammonium carbonate is used as the solvent.

6.1 Absorption by Aqueous NH_3

The overall ammonia losses decrease from 1 kg to 0.41 kg per kg of CO_2 recovered as the aqua ammonia solvent strength is reduced from 15% to 7% by weight NH_3 . The carryover of NH_3 in the CO_2 lean flue gas decreases from 15.9% to 8.9% by volume as the aqua ammonia solvent strength is reduced from 15% to 7% by weight, while the carryover of NH_3 in the CO_2 rich gas stream also decreases from 56% (for the MEA type regenerator configuration) to 24% by volume as the aqua ammonia solvent strength decreases. Such large concentrations of NH_3 in the CO_2 lean and rich gas streams would have serious environmental as well as operating cost implications if it were allowed to occur. The large concentration of free ammonia in the CO_2 rich gas stream is also likely to have adverse impact on the CO_2 sequestration economics.

The ASPEN Plus simulation results show that 0.9 kg and 1.2 kg of CO_2 are absorbed per kg of NH_3 in the 15% and 7% by weight feed aqua ammonia solvent respectively. These results are identical to observations made in laboratory studies by Bai and Yeh (1997) and Yeh and Bai (1999). Both ammonium carbonate and bicarbonate are formed in the spent solution and both can be completely dissociated to ammonia, carbon dioxide and water in the regenerator at temperatures above 90°C . The molar ratio of ammonium bicarbonate to carbonate in the spent solution rises from 4.16 to 5.15 at a temperature of 44°C as the aqua ammonia strength is reduced from 15% to 7% by weight NH_3 . Thus, ammonium bicarbonate is the predominant species formed upon absorption of CO_2 by aqueous ammonia solution. If aqueous ammonia is to be used as the solvent, then a regeneration temperature of approximately 104°C to 106°C is required, much higher than the 82°C suggested by Yeh et al (2004) and Ciferno et al (2005). However, a careful examination of the study by Ciferno et al (2005) shows that they are actually using ammonium carbonate as the solvent, and that 82°C is the regeneration temperature for the spent ammonium bicarbonate solution containing an equivalent of 7% by weight NH_3 .

Table 4 – Comparison of aqua ammonia and MEA processes

| Case | 1 | 2 | 3 | 4 | 5 | |
|--|-------------------------------|-------------------------------|------------------------------|--|---|----------------------|
| Absorbing solution | 15% wt NH _{3(aq)} | 15% wt NH _{3(aq)} | 7% wt NH _{3(aq)} | 7% wt (NH ₄) ₂ CO _{3(aq)} | 19.6% wt (NH ₄) ₂ CO _{3(aq)} | 30% wt MEA |
| Regenerator type | Multistage Column | Single stage | Single stage | Single stage | Single stage | Multistage Column |
| Solvent circulation rate (litres/kg CO₂ recovered) | 8.1 | 8.0 | 12.3 | 77.2 | 38.1 | 17 |
| CO₂ absorption* (kg CO₂/kg NH₃, (NH₄)₂CO₃ or MEA) | 0.91 | 0.92 | 1.22 | 0.18 | 0.12 | 0.36 |
| Solvent losses (kg NH₃ or MEA/kg CO₂ recovered) | 1 | 0.71 | 0.41 | 0.09 | 0.26 | 0.002 |
| Regenerator heat duty (MJ/ kg CO₂ recovered) | 45.0 | 17.7 | 28.8 | 10.2 | 6.8 | 4.2 |

* This is kg CO₂ absorbed per kg of NH₃, (NH₄)₂CO₃ or MEA in the solution that is fed to the absorber.

For CO₂ absorption in 15% by weight aqua ammonia solvent, the MEA process type multistage regenerator system has a reboiler duty of 45 MJ per kg of CO₂ recovered compared to 17.7 MJ per kg of CO₂ recovered for the single stage flash regenerator system suggested by Ciferno et al (2005). This is due to the extra heat used in vaporising the water that is eventually returned to stripping section of the column, as reflux from the overhead condenser, where it is used to strip NH₃ from the CO₂ rich gas stream. Compared to the single stage flash generator, approximately 23,200 kg/h extra water reports to the overhead condenser with the multistage regenerator. With 7% by weight aqueous ammonia using the single stage regenerator the reboiler heat duty rises to 28.8 MJ per kg of CO₂ absorbed, reflecting an increase in the sensible heat requirements at the larger circulation rates required.

Thus when aqueous ammonia is used as the absorbent, the heat duty is well in excess of the 4.2 MJ per kg of CO₂ absorbed required with 30% by weight aqueous MEA solvent. This is probably due to the higher heats of reaction for the complete dissociation of ammonium carbonate and bicarbonate compared with that for the amino carbamate, [Amine.COO]⁻, (compare Reactions 2 and 3 with Reaction 1).

6.2 Absorption by Aqueous Ammonium Carbonate

Cases 4 and 5 provide the best comparison with the study of Ciferno et al (2005) where they appear to have used an aqueous solution of ammonium carbonate as the solvent (see Section 3). It is not clear, however, what concentration of ammonium carbonate they had in their system as they only make reference to using 7% aqueous ammonia as the makeup solution. It should be noted that 7% by weight ammonium carbonate solution has an ammonia content equivalent to 2.5% by weight. Similarly, a 19.6% by weight ammonium carbonate solution will have an ammonia content equivalent to 7% by weight. Cases 4 and 5 were designed to cover both of these concentrations due to the uncertainty as to what concentration Ciferno et al. (2005) actually used.

According to the simulation results, the overall NH₃ loss increases from 0.09 kg to 0.26 kg per kg of CO₂ recovered as the ammonium carbonate solution strength increases from 7% to 19.6%. The carryover of NH₃ in the CO₂ lean flue gas stream also increases from 0.9% to 3.8% by volume as the aqueous ammonium carbonate solvent strength is increased from 7% to 19.6% by weight, while the carryover of NH₃ in the CO₂ rich gas stream leaving the regenerator increases from 12% to 26% by volume. Such large losses of NH₃ in the CO₂ lean and rich gas streams again would be unacceptable from environmental and operating cost viewpoints. The large concentration of free

ammonia in the CO₂ rich gas stream is also likely to have adverse impact on the CO₂ sequestration economics.

The ASPEN Plus simulation results show that 0.12 kg and 0.18 kg of CO₂ are absorbed per kg of (NH₄)₂CO₃ with the 19.6% and 7% by weight ammonium carbonate solutions respectively. Due to such poor absorption capacity for CO₂ (in comparison with an equivalent aqueous ammonia solvent), the ammonium carbonate solvent circulation rate within the absorption/desorption cycle needs to be as high as 77 litres per kg of CO₂ absorbed. It should be noted that this circulation rate is roughly five times more than that encountered with 30% by weight MEA solvent. This would result in much larger contacting equipment being required with the ammonium carbonate systems for the same CO₂ separation duty. Hence, the fixed capital, equipment maintenance and utilities related costs of the aqueous ammonium carbonate system would be much higher than for the MEA system.

According to the simulation, both ammonium carbonate and bicarbonate are present in the spent absorbent solution and both are completely dissociated to ammonia, carbon dioxide and water in the regenerator. It should be noted that ammonium carbonate is available commercially only as a mixture of ammonium bicarbonate and ammonium carbamate, and that it exists in the aqueous solution through the ionic equilibrium between bicarbonate and carbonate ions (see Section 4). The ASPEN simulation shows that the molar ratio of ammonium bicarbonate to carbonate increases from 2.5 in the feed solution to 5.6 in the spent solution for nominally 7% by weight aqueous ammonium carbonate. For 19.6% by weight aqueous ammonium carbonate, this ratio increases from 1.5 to 2.8 as the CO₂ absorption proceeds. Thus, ammonium bicarbonate is the predominant species formed upon absorption of CO₂ by aqueous ammonium carbonate solution. The solvent regeneration temperature of approximately 82°C to 88°C predicted by our simulation is similar to that suggested by Yeh et al (2004) and Ciferno et al (2005).

The ASPEN Plus simulation shows that the regenerator heat duty for the best-case scenario of 19.6% by weight aqueous ammonium carbonate solvent (equivalent to 7% by weight aqueous NH₃) is 6.8 MJ per kg of CO₂ recovered. This is roughly 70% higher than that observed with the 30% by weight aqueous MEA solvent. Ciferno et al (2005) have estimated the regenerator heat duty to be 3.2 MJ per kg of CO₂ recovered. Their calculations assume that only partial decomposition of ammonium bicarbonate occurs in the regenerator (reactions 2 and 3 are ignored and only reaction 4 accounted) and no vapourisation of water takes place in the regenerator. The ASPEN Plus simulation shows that in the best-case scenario of 19.6% by weight aqueous ammonium carbonate

solvent, approximately 134,000 kg of water needs to vapourise from the spent solution in the regenerator bottom at 82°C to strip out absorbed CO₂.

7. Conclusions

The above results clearly imply that the use of either an aqueous ammonia solution or an aqueous ammonium carbonate solution for CO₂ capture and separation is unlikely to reduce the energy demand or equipment size compared to the conventional MEA system. In fact, it creates two additional problems, namely, separation of NH₃ from the flue gas stream leaving the absorber and separation of NH₃ from the CO₂ stream exiting the regenerator. At present, there are no known economic processes to separate NH₃ either from nitrogen or carbon dioxide in a way that would allow the use of aqua ammonia solvent as a substitute for the conventional MEA process. The large makeup requirements with the aqueous ammonia/carbonate systems would greatly outweigh any cost advantages that these chemicals might have over MEA.

In their analysis Ciferno et al (2005) avoided such issues by assuming that,

- There is no carryover of ammonia with the CO₂ lean and rich gas streams leaving the absorber and regenerator respectively,
- There are no ammonia losses with the liquid effluent streams leaving the CO₂ capture and recovery circuit,
- A partial decomposition of ammonium bicarbonate to ammonium carbonate takes place in the regenerator.
- No vapourisation of water from the spent solvent occurs in the regenerator, and
- The adverse impact of the high solvent circulation rates (compared to the MEA process) between the CO₂ absorption and recovery units on the size of the contacting equipment is negligible.

This present study shows that the aqua ammonia process in any form is clearly unsuitable as an alternative to the conventional MEA system for CO₂ capture and recovery from power station flue gas streams as:

- NH₃ losses in the absorption/desorption cycle exceed what would be acceptable from both environmental and operating cost viewpoints
- The energy demand for the solvent regeneration is significantly greater than for the MEA-based process

- The poor CO₂ absorption capacity of ammonium carbonate solvents would lead to much larger and consequently more costly contacting systems being required than for the MEA process.

8. References

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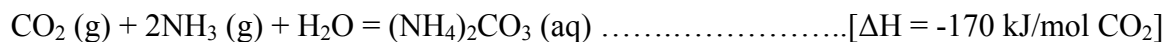
Appendix A - Reactions of CO₂ with aqua ammonia solution

The reactions relevant to the absorption of CO₂ by aqueous ammonia are as follows:

Reaction 1



Reaction 2



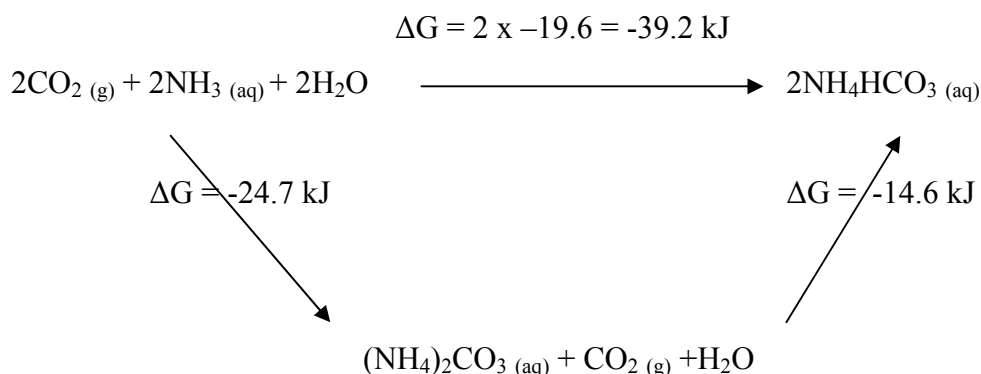
Reaction 3



The heats of reaction, free energies of formation and equilibrium constants for these reactions are shown in the table below:

| Temp. °C | ΔH (kJ) | | | ΔG (kJ) | | | Equilibrium Constant (K) | | |
|-------------|---------|--------|--------|---------|--------|--------|--------------------------|--------|--------|
| | Reac 1 | Reac 2 | Reac 3 | Reac 1 | Reac 2 | Reac 3 | Reac 1 | Reac 2 | Reac 3 |
| 20 | -98.7 | -170 | -27.2 | -19.6 | -24.7 | -14.6 | 3117 | 24870 | 391 |
| 30 | -100 | -172 | -28.0 | -16.9 | -19.7 | -14.2 | 813 | 2456 | 269 |
| 40 | -102 | -174 | -29.3 | -14.1 | -14.6 | -13.8 | 227 | 275 | 187 |
| 50 | -103 | -176 | -30.5 | -11.3 | -9.6 | -13.0 | 67.2 | 34.4 | 131 |
| 60 | -105 | -177 | -31.4 | -8.5 | -4.2 | -12.6 | 21.1 | 4.78 | 93 |
| 70 | -106 | -179 | -32.6 | -5.5 | 0.8 | -12.1 | 6.96 | 0.73 | 66 |
| 80 | -108 | -182 | -33.9 | -2.6 | 6.3 | -11.3 | 2.41 | 0.12 | 48 |
| 90 | -109 | -183 | -35.1 | 0.4 | 11.7 | -10.9 | 0.87 | 0.02 | 35 |
| 100 | -111 | -185 | -36.0 | 3.4 | 16.7 | -10.0 | 0.33 | 0.004 | 25 |

The relation between these three reactions is shown below for the case at 20°C:



Thus from a consideration of free energy changes it is clear that ammonium bicarbonate is the preferred product rather than ammonium carbonate.