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## **Aqua ammonia process for simultaneous removal of CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>x</sub>**

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**Abstract:** Experimental research work in applying aqueous ammonia solution for the simultaneous reduction of acidic gaseous emission from fossil fuel-fired utility plants is currently being performed at the National Energy Technology Laboratory. The traditional monoethanolamine process for CO<sub>2</sub> removal suffers the disadvantages of low carbon dioxide loading capacity, equipment corrosion, amine degradation by SO<sub>2</sub> and O<sub>2</sub> in flue gas, and high energy penalty during absorbent regeneration. The aqueous ammonia process can simultaneously remove CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub>, plus HCl and HF that may exist in the flue gas. There could be oxidation of SO<sub>2</sub> and NO prior to contacting the aqueous ammonia absorbent. Test results pertaining to the ammonia/carbon dioxide reaction in a semi-continuous reactor system are presented. The parametric effects of sparger design, reaction temperature, and ammonia concentration on gas loadings and absorption rates are discussed. Regeneration test results, including solution-cycling between the regeneration and absorption steps to determine a realistic loading capacity for the ammonia solutions are also presented.

**Keywords:** absorption, aqueous ammonia, ammonium bicarbonate, ammonium nitrate, ammonium sulfate, carbon dioxide loading, desulfurisation, fertilizer, heat of reaction, monoethanolamine, oxidation, regeneration.

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## 1 Introduction

There is a serious concern that large amounts of carbon dioxide (CO<sub>2</sub>) being emitted into the atmosphere through human activities, mainly through the burning of fossil fuels, could cause global climate changes. The CO<sub>2</sub> concentration level in the atmosphere should, therefore be stabilised or reduced to a level that the world community can agree upon. The cost of capturing CO<sub>2</sub> from power generation point sources using current technology is very high. It is estimated that the energy penalty from using the well known monoethanolamine (MEA) process for CO<sub>2</sub> capture from coal-fired power plants is about 35% [1], but can be lowered to about 15% in a best case scenario [2]. While these MEA-based technologies are commercially viable to produce CO<sub>2</sub> for the food processing and chemical manufacturing industries, they are considered to be too costly for the removal of CO<sub>2</sub> from power plant flue gases for potential sequestration purposes. Recently, a number of energy efficient proprietary solvents have been developed that are based on either sterically hindered amines or formulated amines. These amines could save regeneration costs by up to 40%; the separation cost per ton of CO<sub>2</sub> ranges from 40 to 70 US dollars [3]. However, an economic tradeoff in capital costs would likely occur, since the slower reacting amines will require a larger absorber (longer gas-liquid contact time) to achieve the same CO<sub>2</sub> capture as compared to MEA.

The MEA process suffers the following disadvantages for CO<sub>2</sub> separation from flue gases:

- low carbon dioxide loading capacity (kg CO<sub>2</sub> absorbed per kg absorbent)
- high equipment corrosion rate
- amine degradation by SO<sub>2</sub>, NO<sub>2</sub>, HCl and HF, and oxygen in flue gas which induces a high absorbent makeup rate
- high energy consumption during high temperature absorbent regeneration.

When capturing CO<sub>2</sub> from coal or petroleum-derived combustion flue gas, the MEA process requires that SO<sub>2</sub> be removed first from the flue gas stream, since MEA is degraded by SO<sub>2</sub> and oxygen, forming irreversible degradation products. The annual cost of MEA makeup is high because of degradation, even after most of the SO<sub>2</sub> is removed from the flue gas in an upstream flue gas desulphurisation process. NO<sub>x</sub> must also be eventually removed from the flue gas before it is discharged into the air in order to meet present and future gaseous emission limits. NO<sub>x</sub> removal would occur upstream of the CO<sub>2</sub> absorber. Low NO<sub>x</sub> burners and/or selective catalytic reduction would be required to reduce the NO<sub>x</sub> level.

It is envisioned that the current widely utilised MEA Process could be replaced with a single Aqua Ammonia Process to capture all three major acid gases (SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>) plus HCl and HF, which may exist in the flue gas. Since SO<sub>2</sub> and NO<sub>x</sub> emissions must comply to certain emission limits, a single process to capture all acidic gases is expected to reduce the total cost and complexity of emission control systems. Currently there is no emission limit on CO<sub>2</sub>, although a limit on CO<sub>2</sub> emission may become a reality in the future. Unlike the MEA Process, the Aqua Ammonia Process does not have absorbent degradation problems that are caused by sulphur dioxide and oxygen in flue gas and does not cause equipment corrosion, as in the case of MEA. Other economic reasons in considering the ammonia process exist.

The major byproducts from the Aqua Ammonia Process include ammonium sulphate, ammonium nitrate, and ammonium bicarbonate. Ammonium sulphate and ammonium nitrate are well known fertilisers for certain crops. Ammonium bicarbonate has been utilised by certain developing countries as a crop fertiliser for over 30 years with proven results in farmland practice which enhanced crop root development and leaf growth [4]. Ammonium bicarbonate was rated by Kirk-Othmer [5] as having definite fertilising value but cannot compete with other ammonium compounds, for example, ammonium sulphate or urea. China produces a so-called Modified Ammonium Bicarbonate (MAB), which is a stabilised, less volatile, form of ammonium bicarbonate produced by the addition of a patented additive (Chinese patent: ZL90105012). Ammonium bicarbonate also has other industrial usages. For instance, the baking industry uses the powder to produce gases in baked goods without leaving any solids behind. Another example is for removal of calcium sulphate scales on heat exchanger tubes. More usages can be found in the Encyclopedia of Chemical Technology.

As an alternative to using ammonium bicarbonate byproduct as a fertiliser, the ammonia (NH<sub>3</sub>) content in ammonium bicarbonate could be regenerated for recycling. Ammonium bicarbonate decomposes at the relatively low temperature of 60°C [6]. This compares with a 120°C regeneration temperature for MEA solutions. Ammonia gas and carbon dioxide gas can be separated by using ammonia's high solubility-in-water property. Carbon dioxide in pure form will subsequently be separated.

To facilitate the control of multipollutants, the proposed control process would pretreat the flue gas by oxidising sulphur dioxide (SO<sub>2</sub>) and nitric oxide (NO) to SO<sub>3</sub> and NO<sub>2</sub>, respectively, in an oxidation step before treating the flue gas with aqueous ammonia in a wet scrubber. NO<sub>x</sub> nominally consists of approximately 97% NO and 3% NO<sub>2</sub>, but only NO<sub>2</sub> can dissolve readily in an ammonia solution to form NH<sub>4</sub>NO<sub>3</sub>. SO<sub>2</sub> is oxidised to SO<sub>3</sub> during the oxidation step and will form ammonium sulphate when reacted with ammonium hydroxide. SO<sub>2</sub> was not oxidatively treated in General Electric's Ammonium Sulphate Process, currently Marsulex Ammonium Sulphate Flue Gas Desulphurisation technology [7–9]. Rather, SO<sub>2</sub> reacts with ammonium hydroxide to form ammonium sulphite, followed by forced air to oxidise sulphite to sulphate. Ammonium sulphate is less volatile than ammonium sulphite, making ammonium sulphate a less volatile fertiliser. Furthermore, the aqueous ammonia process can remove any HCl and HF from the flue gas.

The Ammonium Sulphate Process does not reduce NO, which constitutes a vast majority of the NO<sub>x</sub>. There is a commercial process currently in operation, which utilises ammonia for removal of SO<sub>2</sub> and NO<sub>x</sub> in flue gas, in a hybrid wet and dry mode [10]. This AMASOX and NO<sub>x</sub> removal technology is operated by Krupp Koppers GmbH in Germany. It is not a simultaneous removal process, rather, SO<sub>2</sub> is first removed in a wet scrubber using aqueous ammonia as the absorbent, which is similar to the Marsulex technology. The Koppers process goes a step further and after SO<sub>2</sub> removal, the flue gas is reheated to at least 300°C and NO<sub>x</sub> is reduced in a SCR reactor using ammonia gas for NO<sub>x</sub> destruction. The saleable byproduct is ammonium sulphate in slurry form, which can be used directly as a fertiliser or can be reprocessed into crystal form if longer distance transportation is required to sell the byproduct. Neither Marsulex [8] nor Koppers [10] discusses the subject of CO<sub>2</sub> capture by ammonia solution. Only enough ammonia solution is sprayed to react stoichiometrically with SO<sub>2</sub> in the flue gas, and thus any minute change in CO<sub>2</sub> concentration in flue gas is not noticeable. It should be noted that

SO<sub>2</sub> concentration in flue gas is only a small fraction of the CO<sub>2</sub> concentration, and the ammonia solution reacts preferentially with SO<sub>2</sub>. Walsh's report [8] discussed Dakota Gasification Plant's Ammonium Sulphate Process in some detail. Again, the fate of CO<sub>2</sub> in flue gas was never discussed. Marsulex sells ammonium sulphate fertiliser, and for every ton of ammonia, four tons of fertiliser is produced. Marsulex's process increases the value of ammonia from 70 to 400%, depending upon the location of the plant producing it and normal market fluctuations.

Currently, there is only one known commercial process that uses ammonia to simultaneously remove SO<sub>2</sub> and NO<sub>x</sub> from flue gas within one reactor and produce mixed ammonium sulphate and nitrate fertiliser [9]. This Ebara E-Beam process, with one plant in operation in China, uses a high energy flux of electrons to irradiate the flue gas stream in an effort to oxidise SO<sub>2</sub> and NO<sub>x</sub>. Ammonia is injected into the flue gas and reacts with the acid precursors to form ammonium sulphate and ammonium nitrate particulates. The particulates are collected downstream in an electrostatic precipitator or fabric filter and transferred to a storage silo. The higher the applied electron beam power the more efficient the SO<sub>2</sub> and NO<sub>x</sub> removal. In other words, it is a tunable process, but it could be with a steep energy penalty. High energy beam or irradiation techniques, in general, are not the only methods to oxidise SO<sub>2</sub> and NO<sub>x</sub>.

Gas-phase oxidation of nitric oxide to NO<sub>2</sub> can be accomplished by strong oxidisers. One oxidation procedure is carried out by injecting liquid hydrogen peroxide into the flue gas; the H<sub>2</sub>O<sub>2</sub> vaporises and dissociates into active hydroxyl radicals which oxidise the NO to NO<sub>2</sub> [11]. Hydrogen peroxide as an oxidant can also be effective in aqueous solutions [12]. Nitric oxide can also be oxidised at low to moderate temperature using ozone [11,13,14]. Ozone may be replaced by chlorine dioxide to oxidise NO [13].

Very few research reports in the usage of ammonia for CO<sub>2</sub> capture exist, but the most noted ones are from Bai and Yeh [15] and Yeh and Bai [16]. Bai's 1997 publication reported obtaining crystalline solids of NH<sub>4</sub>HCO<sub>3</sub> by sparging CO<sub>2</sub> into ammonium hydroxide solution, and in the 1999 publication, data were published comparing maximum CO<sub>2</sub> loading capacity in MEA solution and in ammonium hydroxide solution on an equal weight-of-absorbent basis. It was concluded that the maximum CO<sub>2</sub> removal efficiency by NH<sub>3</sub> absorbent can reach 99% and the CO<sub>2</sub> loading capacity can approach 1.20 kg CO<sub>2</sub>/kg NH<sub>3</sub>. On the other hand, the maximum CO<sub>2</sub> removal efficiency and loading capacity by MEA absorbent are 94% and 0.40 kg CO<sub>2</sub>/kg MEA, respectively, under the same test conditions. In other words, ammonia's CO<sub>2</sub> loading is three times that of MEA's. Yeh *et al.* [16] plotted liquid absorbent temperature versus time during the CO<sub>2</sub> absorption experiment and observed that the heat of reaction with MEA was greater than with ammonia. They also found that the purchase price for industrial grade NH<sub>3</sub> solution is approximately one-sixth of that of the MEA absorbent on the same weight basis in the world market. NETL's own preliminary research in aqueous ammonia scrubbing of CO<sub>2</sub> in a packed bed absorber produced similar CO<sub>2</sub> removal results [17] as compared to Yeh *et al.* [16].

In view of the shortcomings of the MEA process for CO<sub>2</sub> capture, Wolsky *et al.* [18] suggested that future research efforts should be directed toward developing better solvents for the removal of CO<sub>2</sub>. An ideal absorbent should have a CO<sub>2</sub> loading capacity of at least 1.0 kg of CO<sub>2</sub> per kg of solution and that the regeneration energy requirement must be much lower than the MEA process.

The Aqua Ammonia Process seems to have avoided the shortcomings of the MEA process. In consideration, the following apply:

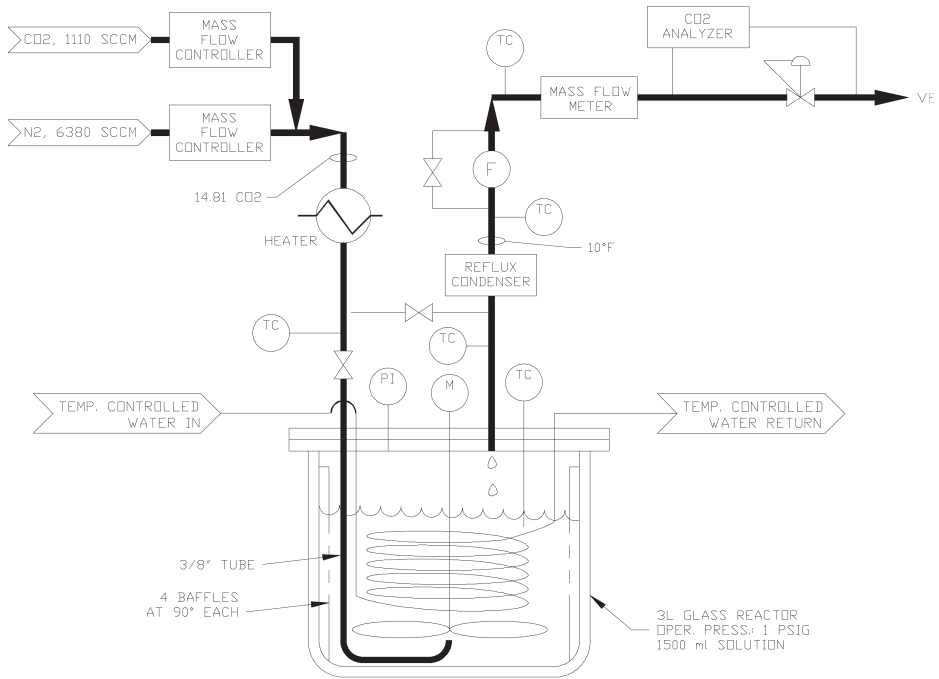
- aqueous ammonia has high loading capacity
- aqueous ammonia does not pose a corrosion problem
- there is no absorbent degradation problem, thus reducing absorbent makeup rate
- the energy requirement for absorbent regeneration is predicted to be much lower than in the MEA process.

Prior to this study, it has been estimated that thermal energy consumption for CO<sub>2</sub> regeneration using the Aqua Ammonia Process could be at least 75% less than if the MEA Process is used for CO<sub>2</sub> absorption and regeneration. Above all, the saleable, income-producing byproducts, ammonium sulphate and ammonium nitrate as fertiliser alone, will promote the burning of cheap and abundant high-sulphur coals. Higher sulphur content coals will generate higher income for the power plants and lower the cost of power generation. At this point, it is uncertain if there is market for ammonium bicarbonate fertiliser. Therefore, it is assumed that ammonium bicarbonate will be decomposed and ammonia will be recycled to the CO<sub>2</sub> capture system where carbon dioxide will be recovered and eventually sequestered.

## **2 Experimental**

The CO<sub>2</sub> absorption rate studies were performed in a semi-continuous flow reactor as shown in Figure 1. The simulated flue gas consists of 15% vol CO<sub>2</sub> and 85% vol N<sub>2</sub>. The gases were supplied by compressed gas cylinders and the flow controlled by mass flow controllers. The CO<sub>2</sub> absorber was a 3-litre glass container filled with 1500-ml aqueous ammonia solution. Pressure was near atmospheric; total gas flowrate was 7500 sccm. The temperature of the absorber was controlled with a cooling/heating coil, through which temperature-controlled water flowed. The baseline condition for the tests was 80°F. The simulated flue gas entered the absorber through one of two cylindrical-shaped sintered metal spargers for most of the parametric studies. The sparger was made of sintered stainless steel (2 micron pore). The dual sintered metal spargers were installed after several failed test runs, that were caused by plugging of the sparger due to ammonium bicarbonate crystal formation.

The vent gas from the absorber was sent through a coil, which was immersed in an ice bath, reducing the gas temperature to 35°F to condense the vapour escaping from the absorber. The condensed vapour and carried-over mist from the absorber was drained periodically. The vent gas volumetric flowrate was measured by a bagmeter. The gas from the bagmeter was then analysed for unreacted CO<sub>2</sub> gas before being vented. An Horiba Model VIA-510 CO<sub>2</sub> Analyser gave continuous readings. The CO<sub>2</sub> concentration-versus-time data were used to calculate CO<sub>2</sub> absorption rates and to totalise the amount of CO<sub>2</sub> absorbed. Data were recorded every ten seconds for the duration of a test. The baseline condition for the tests was 80°F, utilising a 14% ammonia solution.

**Figure 1** Aqua ammonia semi-continuous reactor

After the first series of tests that were used to gather rudimentary kinetic information, several improvements were made to the system. The vent line volumetric flow meter was replaced by a mass flow meter to allow continuous vent flow measurements. The ice bath was replaced with a reflux condenser, reducing the gas temperature to 10°F, assuring that negligible water vapour was present in the vent line. The spargers were replaced with an open tube and a mechanical mixer with a six-blade Rushton-type turbine impeller operating at 1400 rpm was installed. The impeller speed at which gross recirculation of gas into the liquid occurs was calculated to be 748 rpm, using a correlation of Lee and Tsui [19]. Provisions were made to take liquid samples during the test for chemical analysis. In the data reduction scheme, it was assumed that the major constituents from the regeneration tests were N<sub>2</sub>, CO<sub>2</sub>, and NH<sub>3</sub>. The N<sub>2</sub> flow was measured by the inlet mass flow controller. The total flow from the reactor was measured by the outlet flow meter. The CO<sub>2</sub> flow was calculated based on the total flow and the CO<sub>2</sub> concentration. The NH<sub>3</sub> flow was calculated by difference. The modified system was used to determine the effect of cycling the solution between the absorption and regeneration steps.

Regeneration of the solution was performed using a majority of the equipment described above, with the following exceptions. A 2-litre reactor was used to minimise the reactor headspace. The nitrogen gas flow was reduced to approximately 1000 sccm and was utilised only as a sweep gas to reduce the residence time to the CO<sub>2</sub> IR analyser (i.e. the nitrogen did not flow through the reactor, but was connected to the vent line). The solution was heated using the cooling/heating coil. The solution temperature was ramped

from 120°F to as high as 190°F, with liquid samples taken at each step. The CO<sub>2</sub> regenerated and the NH<sub>3</sub> evaporated were totalised with data taken every ten seconds. The regeneration was investigated for solutions containing various mixtures of ammonium bicarbonate and of ammonium carbonate in water or spent ammonia solutions which had undergone an absorption step.

Solutions of 7, 10.5, and 14% ammonia were used in cycling tests to determine the potential effective utilisation rates available for the aqueous ammonia solutions. As before, ammonia solutions were made by mixing A.C.S grade ammonium hydroxide solutions with water to provide the desired concentrations. For the cycling tests, the mixer with open tubing was utilised at 80°F. After the initial absorption test, the resultant solutions were thermally regenerated to 180°F. The absorption/regeneration cycle was repeated for a total of three cycles, anticipating that the amount of CO<sub>2</sub> absorbed in the absorption step and regenerated in the regeneration step would equilibrate by the third cycle.

### **3 Discussion of results**

The CO<sub>2</sub> absorption rate by aqueous ammonia solution was calculated by CO<sub>2</sub> breakthrough concentration versus time. Experiments were run at 60, 80, and 100°F, respectively. Five sparger designs were initially tested for their effects on CO<sub>2</sub> absorption rates with the aqueous ammonia solution. Regeneration tests were performed on standard solutions. Additionally, cycling tests were conducted.

#### *3.1 Effect of sparger types*

The effect of sparger types was initially conducted using 14% ammonia solution at 80°F absorber temperature. During the test, 7500 scfm of simulated flue gas (15% CO<sub>2</sub>, 85% N<sub>2</sub>) bubbled through the sparger and into 1.5 litre of absorbent. Concentration of CO<sub>2</sub> from the vent was continuously monitored for absorption rate calculations. Five sparger types/designs were tested and are discussed below.

##### *3.1.1 Sintered metal, flat panel with 1-micron pores*

The sintered stainless steel sparger of 3–7/8-in diameter was lowered into the reactor at approximately 1 inch above the bottom of the glass reactor (5-in diameter). The CO<sub>2</sub>-laden stream flowed into the solution through the sparger while the breakthrough concentration of CO<sub>2</sub> was measured continuously with the CO<sub>2</sub> analyser. This sparger provided excellent gas distribution in the reactor. The gas bubbles broke up into a cloud-like foaming layer within the top half of the solution in the reactor. It was expected that at the end of CO<sub>2</sub> breakthrough curve, the CO<sub>2</sub> concentration would reach 15%, which is the CO<sub>2</sub> inlet concentration to the reactor. However, at about 7% CO<sub>2</sub> concentration, the sparger pressure drop increased and the gas flow was shut off by a pressure drop protective device. After encountering additional failed tests, it was determined that the blockage must be caused by the formation of crystalline ammonium bicarbonate; wet seed crystals lodged in the sintered metal pores. White powder was observed after the glass reactor was dried. Bai and Yeh [15] observed white powder in their experimental apparatus (implying a dry condition). During testing, if the gas flow was stopped for a short time (ten minutes or so), the extent of the blockage would decrease.

### 3.1.2 Cylindrical shaped sintered metal with 2-micron pores

The flat panel sintered metal was replaced with a cylindrical-shaped sparger ( $3/8$ -in dia and  $2^{3/4}$ -in active length) with 2 micron pores. It also experienced similar blockage problems as the flat sintered metal sparger.

### 3.1.3 Tubing with $1/64$ -in diameter holes or with $1/16$ -in holes

Since the invisible crystal seeds can easily plug up the sintered metal micron-sized pores, a simple holes-in-tubing sparger was installed in the reactor. Nonetheless, pluggage still occurred, but at a much delayed pace, even for the larger diameter holes. Thirty holes were drilled in each  $2^{1/4}$ -in long and  $3/8$ -in diameter piece of tubing. This simpler sparger allowed the breakthrough  $\text{CO}_2$  concentration to reach 14%, only 1% below the reactor inlet  $\text{CO}_2$  concentration. Although this was a huge improvement over the sintered metal sparger, a much slower  $\text{CO}_2$  absorption rate into the absorbent occurred, due to the much larger bubble size causing poor gas-liquid contact. Poor gas-liquid contact resulted in more unreacted  $\text{CO}_2$  escaping through the vent line.

### 3.1.4 Dual-sparger design

To take advantage of the apparent re-dissolving of the crystals with no gas flow, a design connecting two of the cylindrical sintered metal spargers (see above) with a common feed line was used. The gas enters the reactor through one of the cylindrical spargers. When pressure builds up, the one sparger is isolated while the gas flow is switched to the other. It was speculated that the crystals lodged in the pores re-dissolve into the solution if  $\text{CO}_2$  gas is stopped for a short time.

### 3.1.5 Mixer with open tubing

To further reduce the possibility of plugging the reactor, the system was modified to allow for a mechanical mixer to be installed through the reactor head. The mixer powered a six bladed, high shear radial impeller. Four baffles extended the length of the reactor at a 90-degree angle from the wall. The gas was introduced with stainless steel tubing ( $3/8$  in) that was bent so that the gas was introduced in the centre of the reactor flowing vertically. The impeller, operating at 1400 rpm, was located 0.25 in above the tubing outlet. It should be noted that although progress was made toward the goal of  $\text{CO}_2$  breakthrough, formation of the precipitate was still significant enough to plug the open end of the tubing after approximately 5 g-moles of  $\text{CO}_2$  were absorbed in the solution.

Figure 2 shows the effect of the types of spargers. The two lowest curves show the slowest  $\text{CO}_2$  absorption rates. The tubing with the  $1/16$ -in diameter holes exhibits the lowest  $\text{CO}_2$  absorption rate, followed by the tubing with  $1/64$ -in diameter holes. The sintered metal spargers and the open tube utilising the mixer all had essentially equivalent absorption rates as a function of the amount of  $\text{CO}_2$  absorbed. For these tests, the  $\text{CO}_2$  absorption rates of all three sintered spargers and the open tube with the mixer have nearly merged. The implication is that in these systems, the reaction kinetics dominates the reaction; the gas-liquid contact is of secondary importance. This along with gas pressure drop is important with respect to reactor optimisation and economic considerations.

**Figure 2** Effect of sparger types (CO<sub>2</sub> absorbed)

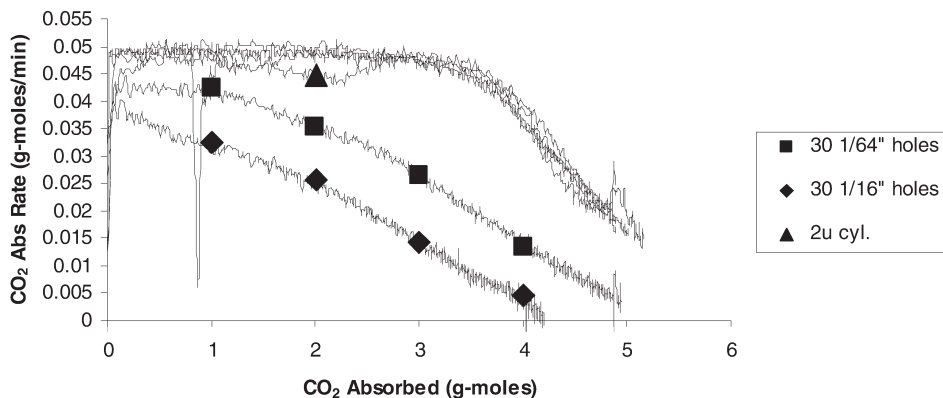
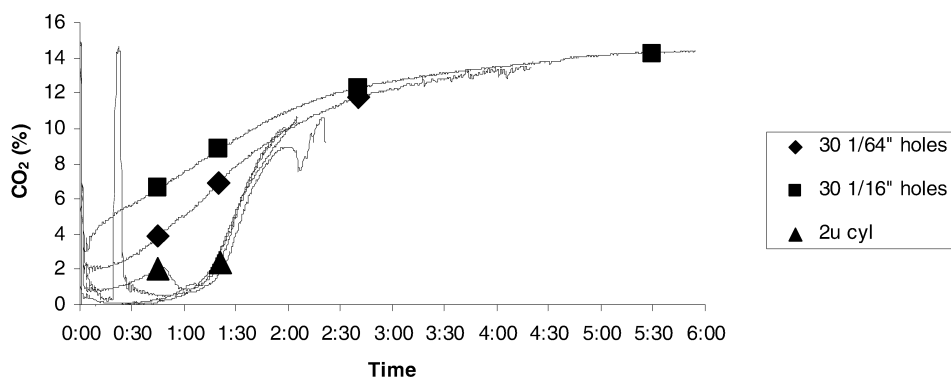


Figure 3 shows the raw data used to produce Figure 2. It is a plot of CO<sub>2</sub> concentration in the vent gas versus time elapsed since the experiment began. The sintered-metal spargers and the open tube utilising the mixer offer the higher rate of CO<sub>2</sub> depletion. The top curve (sparger with larger holes) exhibits the slowest rate of CO<sub>2</sub> removal or the highest concentration of unreacted CO<sub>2</sub> breakthrough. The reaction was able to proceed further for the sparger with holes for two reasons: the larger holes were more difficult to plug, and the slower reaction rates provided time for the ammonia in the solution to evaporate, lowering the potential ammonium salt concentration. The lower salt concentration is also evidenced by the fact that the total amount of CO<sub>2</sub> absorbed (Figure 2) is less for the tubing with holes.

**Figure 3** Effect of sparger types (CO<sub>2</sub> % vs. time)



### 3.2 Effect of $\text{NH}_3$ concentration in solution on absorption rate

The effects of ammonia concentration on  $\text{CO}_2$  absorption rate are illustrated in Figures 4–6. Although the initial absorption rates are similar, as the  $\text{CO}_2$  absorption reaction progresses, the rates are higher for the solutions with higher ammonia concentrations. As expected,  $\text{CO}_2$  took longer to break through the solutions having higher ammonia concentration. For overall absorptivity of  $\text{CO}_2$ , the data patterns indicate that it is more advantageous to use a higher concentration ammonia solution as  $\text{CO}_2$  absorbent. The conclusions are the same at all three reaction temperatures. All the tests were run with the dual cylindrical sparger design as discussed in the previous section. The sudden rise of reaction rates coincided with switching from the plugged cylinder to the clean cylinder. The clean cylinder allowed normal  $\text{CO}_2$  flow to enter the reactor without the hindrance by the seed crystals of  $\text{NH}_4\text{HCO}_3$  product.

Figure 4  $\text{CO}_2$  absorption rate at 60°F

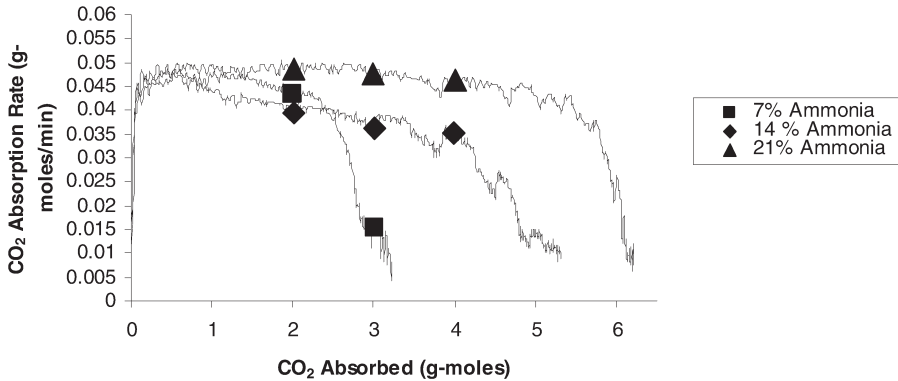
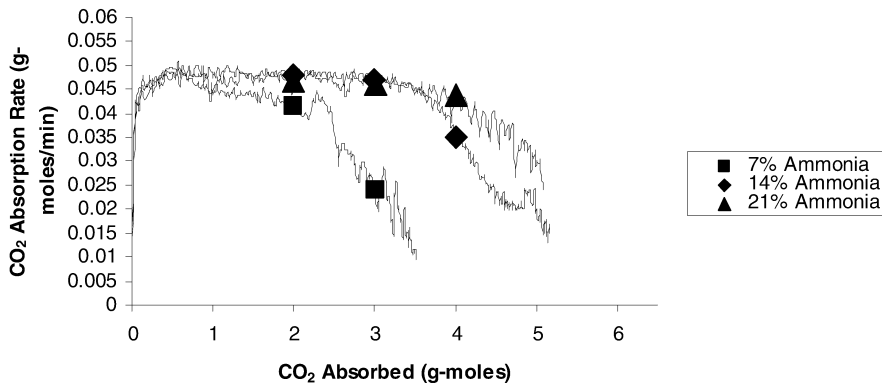
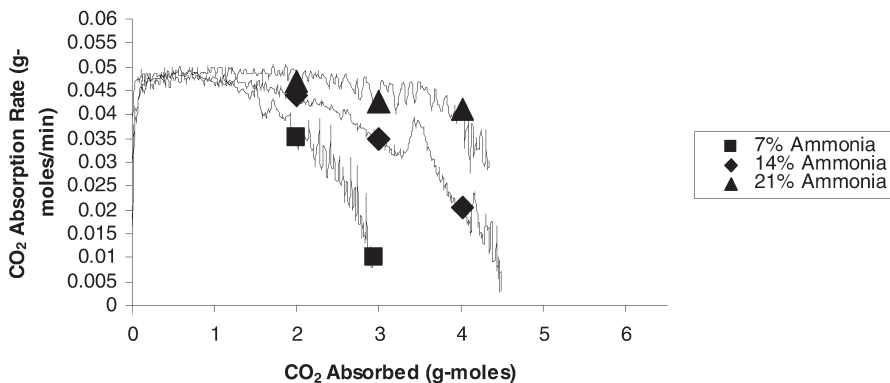


Figure 5  $\text{CO}_2$  absorption rate at 80°F



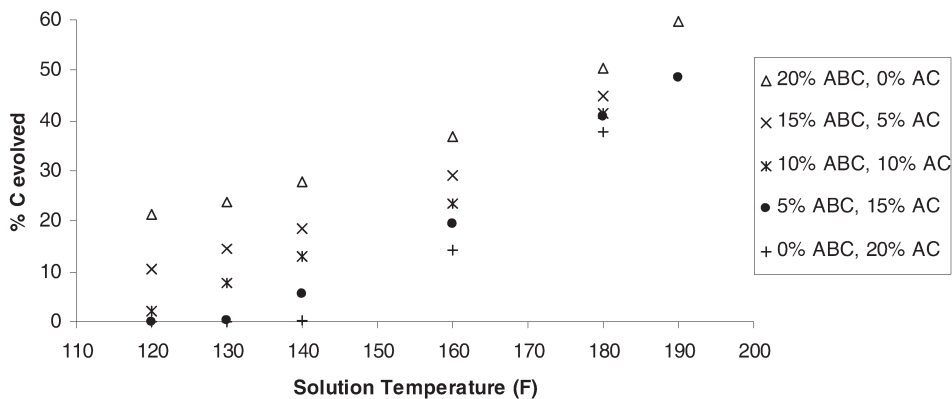
**Figure 6**  $CO_2$  absorption rate at 100°F

### 3.3 Effect of reaction temperature on absorption rate

Three reaction temperatures (60, 80, and 100°F) were tested at ammonia solution concentrations of 7, 14, and 21%. The results are also shown in Figures 4–6. Dual cylindrical spargers were used in all tests. Because the decomposition temperature of  $NH_4HCO_3$  is near 140°F, reactor temperatures above 100°F were not considered. The net amount of  $CO_2$  absorbed decreases with increasing temperature, and it may be favourable to operate the reactor at the low temperatures. Yeh and Bai [16] reported that  $CO_2$  absorption capacity of ammonia solution (28% concentration) decreased by 11% between reaction temperatures 50 and 104°F. As the temperature approached the ammonium carbonate/bicarbonate decomposition temperature, the  $CO_2$  absorption rate decrease was expected. The concentration and temperature effects are important considerations when determining the reaction kinetics.

### 3.4 Regeneration of ammonium bicarbonate and ammonium carbonate

Figure 7 shows the amount of carbon dioxide liberated by thermal regeneration from standard solutions of ammonium bicarbonate (ABC) and ammonium carbonate (AC) as a function of temperature. The dependent variable in Figure 7 represents the total percentage of the original carbon in the solution that was evolved up to that temperature. It is evident that as the proportion of bicarbonate in the solution increases, the carbon dioxide is more easily regenerated. It is demonstrated that as much as 60% of the carbon in the solutions can be regenerated, which in a continuous process would free the ammonia for the absorption cycle.

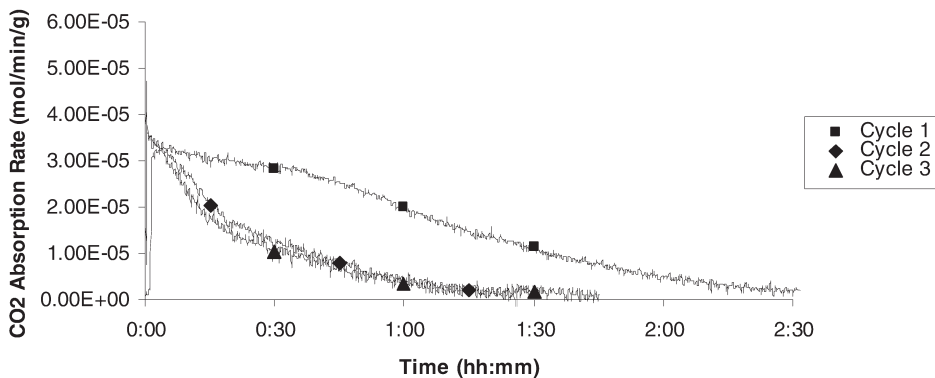
**Figure 7** Regeneration test summary

### 3.5 Cycling tests of aqueous ammonia solutions

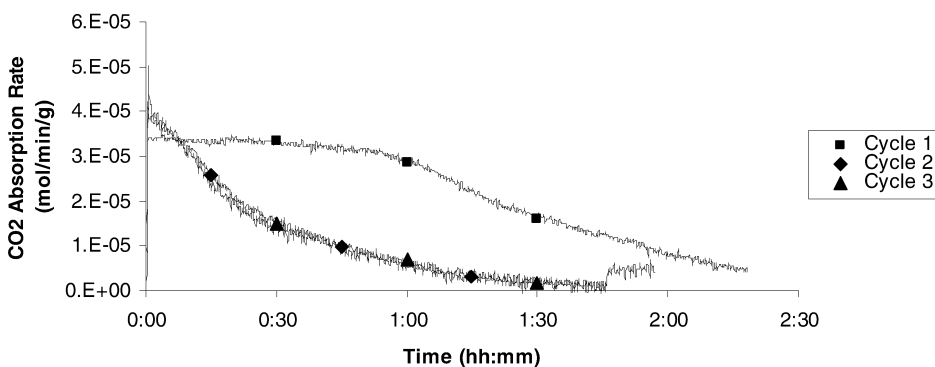
Figures 8–10 show the CO<sub>2</sub> absorption rate per gram of solution as a function of time for three cycles at 7, 10.5, and 14% aqueous ammonia solutions, respectively. The regeneration step heated the solution to 180°F. These graphs indicate that there is a dramatic change in the absorption capacity between the first and second cycles, but little change thereafter. These results indicate that less than 100% regeneration of the initial solution is achieved, and that significant evaporation of the ammonia is evident. Of the initial 198 g of ammonia in the 14% solutions, 85.4 g (43%) was lost in the vent lines during the cycling tests, with 71.5 g being lost in the first absorption step. For the 10.5 and 7% solutions, 32 and 30% of the ammonia was vented, respectively, with similar proportions of ammonia being released during the first absorption step. A large amount of ammonia is lost when a fresh ammonia solution is used for CO<sub>2</sub> capture in the impeller driven semi-continuous reactor. After the CO<sub>2</sub>-rich ammonia solution is regenerated by heating, the solution is a CO<sub>2</sub>-lean ammonia solution and it can be reused to capture CO<sub>2</sub>. The high loss of ammonia during the first absorption cycle is called the initial condition effect. There is very little additional ammonia lost during the second absorption and third absorption, as in a continuous process, where the ammonia vapour pressure would be much lower, because ammonia is being tied up with CO<sub>2</sub> to form ammonium carbonate and ammonium bicarbonate. The initial condition effect would be suppressed in a continuous process. Fresh ammonia solution would only be fed as a makeup solution. Little free ammonia is therefore present in the flow stream at any moment resulting in low NH<sub>3</sub> vapour pressure.

Figure 11 displays the specific absorption capacity of the solutions for each cycle, also demonstrating that the experiments appear to have reached equilibrium after the second absorption test. The results with aqueous ammonia are far from optimised with respect to the amount of CO<sub>2</sub> regenerated and the amount of ammonia lost. The final measured specific absorption capacity is 0.068, 0.053, and 0.040 g CO<sub>2</sub>/g solution for the 14, 10.5, and 7% ammonia solutions, respectively. This compares favourably to current MEA technology that has demonstrated a capacity of 0.036 g CO<sub>2</sub>/g solution for a standard

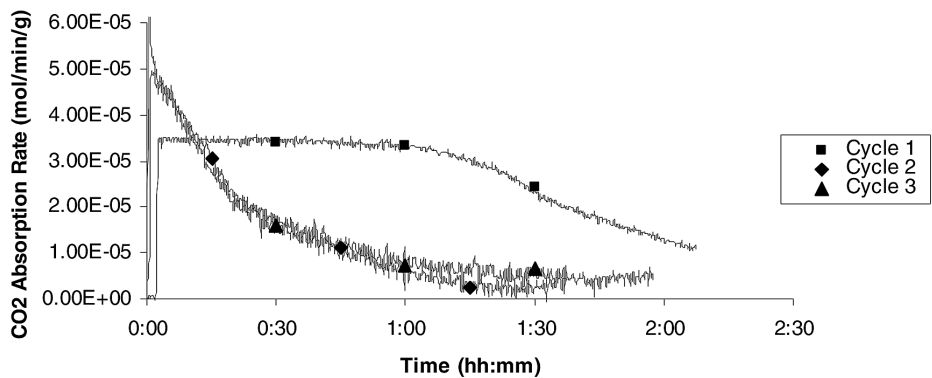
**Figure 8** 7% NH<sub>3</sub> CO<sub>2</sub> absorption rate



**Figure 9** 10.5% NH<sub>3</sub> CO<sub>2</sub> absorption rate

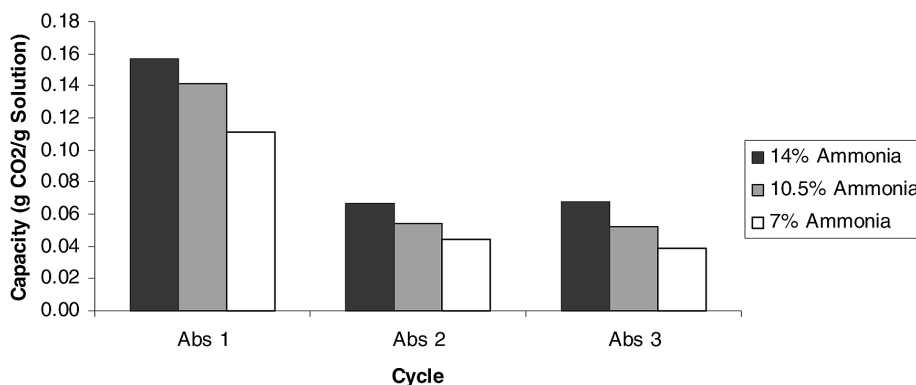


**Figure 10** 14% NH<sub>3</sub> CO<sub>2</sub> absorption rate

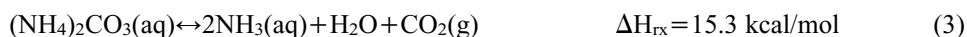
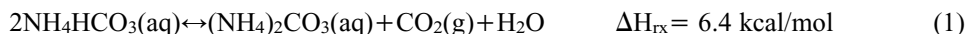


20% MEA solution [20]. The sensible heat of regeneration per mass of CO<sub>2</sub> is indirectly proportional to the loading and proportional to the temperature difference between the absorption and regeneration temperatures (131 to 248°F for MEA, 80 to 180°F for aqueous ammonia). Using the above absorption capacity data, the sensible heat of regeneration for the aqueous ammonia process may be as little as 45% that of the MEA process.

**Figure 11** Effect of cycling on CO<sub>2</sub> absorption capacity



Three potential reactions could be responsible for liberation of CO<sub>2</sub> during the thermal regeneration.



The heat of reaction for the MEA process has been reported to be 20.0 kcal/mol [7]. Regardless of the reaction which is occurring during regeneration, an energy savings for the heat of reaction is also realised.

In addition to the sensible heat and heat of reaction, a major contributor to the regenerator heat duty in an MEA process is the heat of vaporisation to generate steam to carry the CO<sub>2</sub> overhead in the stripper. A reflux ratio of 2.0 moles of water per mole of CO<sub>2</sub> is common [21]. The energy required to generate this amount of steam is an additional 18.9 kcal/mol of CO<sub>2</sub> evolved. Since the regeneration of the aqueous ammonia solutions was conducted without this steam requirement, additional energy savings are expected. Table 1 shows the relative contribution of these energy requirements, comparing the current MEA process to the proposed aqueous ammonia process.

**Table 1** Regeneration heat required. Comparison of a 14% aqueous ammonia solution to current MEA technology

<i>Process</i>	$\Delta H_{ix}$ (kcal/mol)	<i>Sensible heat*</i> (kcal/mol)	<i>Heat of vaporisation</i> (kcal/mol)	<i>Total</i> (kcal/mol)	<i>% Reduction from MEA process</i>
MEA	20.0	79.4	18.9	118.3	0
NH <sub>3</sub> (Eq. 1)	6.4	36.0	0	42.4	64
NH <sub>3</sub> (Eq. 2)	24.1	36.0	0	60.1	49
NH <sub>3</sub> (Eq. 3)	15.3	36.0	0	51.3	57

\*Sensible heat=mass of solution (g)/mol CO<sub>2</sub> \* Cp (assume 0.001 kcal/g-°C) \*  $\Delta T_{rx}$  (°C)

## 4 Conclusions

Rates of CO<sub>2</sub> absorption in aqueous ammonia solution were measured. The experiments took place in a semi-continuous reactor at controlled temperatures of 60, 80, and 100°F. Simulated flue gas at 15% vol CO<sub>2</sub> and 85% vol N<sub>2</sub> was fed into the aqueous ammonia solution through a sintered metal gas sparger to promote gas-liquid mixing. The liquid absorbent was not circulated. The rates of CO<sub>2</sub> absorption were measured at 7, 14, and 21% ammonia concentration by weight.

Thermal regeneration of standard solutions revealed that regeneration of up to 60% of the carbon in a bicarbonate solution may be regenerated. Cycling tests results demonstrated that a 64% reduction in regeneration energy is possible due to the higher loading capacity of an aqueous ammonia solution, the lower heat of reaction, and the lower heat of vaporisation when compared to standard MEA solutions.

Future research work will investigate removals of sulphur dioxide and nitric oxides in the ammonia solution. Work will also be conducted to determine the mechanism of the reactions involved in the absorption/regeneration reactions, in preparation for optimisation of the efficiency of the Aqua-Ammonia process for CO<sub>2</sub> separation.

## 5 Disclaimer

Reference in this report to any specific commercial process, product, or service is to facilitate understanding and does not necessarily imply its endorsement or favouring by the United States Department of Energy.

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