

Absorption and Regeneration Studies for CO₂
Capture by Aqueous Ammonia

James T. Yeh and Henry W. Pennline
U.S. DOE – NETL

Kevin P. Resnik and Kathy Rygle
Parson Project Services, Inc.

P.O.Box 10940, Pittsburgh, PA 15236

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INTRODUCTION

The cost to capture CO₂ 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 CO₂ 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 CO₂ for the food processing and chemical manufacturing industries, they are considered to be too costly for the removal of CO₂ 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 operating costs by up to 40%. 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 CO₂ capture as compared to MEA.

The MEA process suffers the following disadvantages for CO₂ separation from flue gases: low carbon dioxide loading capacity (kg CO₂ absorbed per kg absorbent); high equipment corrosion rate; amine degradation by SO₂, NO₂, HCl and HF, and oxygen in flue gas which induces a high absorbent makeup rate; and high energy consumption during absorbent and regeneration. When capturing CO₂ from coal or petroleum-derived combustion flue gas, the MEA process requires that SO₂ be removed first from the flue gas stream, since MEA is degraded by SO₂ and oxygen, forming irreversible degradation products. The annual cost of MEA makeup is high because of degradation, even after most of the SO₂ is removed from the flue gas in an upstream flue gas desulfurization process. NO_x 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_x removal would occur upstream of the CO₂ absorber. Low NO_x burners and/or selective catalytic reduction would be required to reduce the NO_x level.

It is envisioned that the current widely utilized MEA Process could be replaced with the Aqua Ammonia Process to capture all three major acid gases (SO₂, NO_x, CO₂) plus HCl and HF, which may exist in the flue gas. Since SO₂ and NO_x emissions must comply with 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 CO₂, although a limit on CO₂ emission in the future may become a reality. Unlike the MEA Process, the Aqua Ammonia Process does not have absorbent degradation problems that are caused by sulfur dioxide and oxygen in flue gas and does not cause equipment corrosion. Recently, Powerspan, Corporation reported the application of ammonia for simultaneous reduction of SO₂, NO_x and mercury [3].

The major byproducts from the Aqua Ammonia Process include ammonium bicarbonate, ammonium nitrate, and ammonium sulfate. Ammonium sulfate and ammonium nitrate are well known fertilizers for certain crops. Ammonium bicarbonate has been utilized by certain developing countries as a crop fertilizer for over 30 years with proven results in farmland practice which enhanced crop root development and leaf growth [4].

Very few research reports in the usage of ammonia for CO₂ capture exist, but the most noted ones are from Bai and Yeh [5] and Yeh and Bai [6]. Bai's 1997 publication reported obtaining crystalline solids of NH₄HCO₃ by sparging CO₂ into ammonium hydroxide solution, and in the 1999 publication, data were published comparing maximum CO₂ loading capacity in MEA solution and in ammonium hydroxide solution on equal weight-of-absorbent basis. It was concluded that the maximum CO₂ removal efficiency by NH₃ absorbent can reach 99% and the CO₂ loading capacity can approach 1.20 kg CO₂/kg NH₃. On the other hand, the maximum CO₂ removal efficiency and loading capacity by MEA absorbent are 94% and 0.40 kg CO₂/kg MEA, respectively, under the same test conditions. In other words, ammonia's CO₂ loading is 3 times that of MEA's. Yeh et al. [6] plotted liquid absorbent temperature versus time during the CO₂ 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 NH₃ 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 CO₂ in a packed bed absorber produced similar CO₂ removal results [7] as compared to Yeh et al. [6].

The Aqua Ammonia Process seems to have avoided the shortcomings of the MEA process. In consideration, 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; and the energy requirement for absorbent regeneration is predicted to be much lower than in the MEA process. Prior to this study, it was estimated that thermal energy consumption for CO₂ regeneration using the Aqua Ammonia Process could be at least 75% less than if the MEA Process is used for CO₂ absorption and regeneration. The saleable, income-producing byproducts, ammonium sulfate and ammonium nitrate as fertilizer, will promote the burning of cheap and abundant high-sulfur coals. Higher sulfur content coals will generate higher income for the power plants and lower the cost of power generation. It is uncertain if there is market for ammonium bicarbonate fertilizer. As a technique to capture and sequester CO₂, the ammonium scrubbing process will produce ammonium bicarbonate that will be decomposed and ammonia will be recycled to the CO₂ capture system where carbon dioxide will be recovered and eventually sequestered.

PROCESS CHEMISTRY

Absorption

The absorption chemistry of CO₂ in aqueous solutions can be described by equations 1-4. The amount of CO₂ that can dissolve in the solution depends on the Henry's Law constant, and the pH of the solutions [8]. The Henry's Law constant of CO₂ decreases with the increase of the temperature and ionic strength of solutions. The absorbed CO₂ can dissociate to form bicarbonate, HCO₃⁻ and carbonate, CO₃²⁻ ions. The higher the pH the more effective the absorption of CO₂ will be. The equilibrium constants and the activity coefficients determine the concentration of species in solutions.



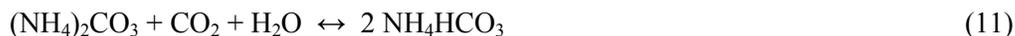
The desorption of ammonia from the solutions depends on the solution pH (Eq. 5 and 6).



In general, a high pH solution enables a high CO₂ absorption efficiency. However, the high pH solution would cause the ammonium ion to be lost as ammonia gas, resulting in lower absorbent concentration. A compromised pH of the solution must be established to allow an optimal point to be reached. Under certain conditions, a dilute ammonia solution will be more effective than a higher concentration solution for the capture of CO₂. The search for optimal point involves both thermodynamics and kinetics. For instance, at certain temperature, T, the NH₃ solution surface vapor pressure is so high that the NH₃ vapor loss rate is greater than the reaction kinetics of NH₃ and CO₂. As a result, less ammonium by-product will be formed at higher NH₃ concentration.

The absorption of CO₂ into an aqueous ammonia solution can produce the crystallization of CO₂-containing ammonium salts. These include ammonium bicarbonate (Eq. 8), ammonium carbonate (Eq. 10), and the co-crystallization of the those salts. These salts would crystallize once the concentrations reach their

corresponding solubility products. The concentration of ammonium ions, bicarbonate ions, carbonate ions, and CO₂, as well as the pH of the solutions influence the type of salt or salts produced.

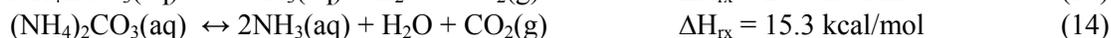
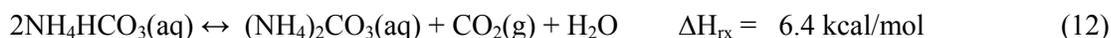


The formation of crystals in the scrubbing solution could cause scales on the walls or plugging of the pipes around the absorber system or other parts of a plant. If the by-product is intended for thermal regeneration, the regeneration should start before crystals could cause operational problem. Solution pH value's relationship to the degree of crystal formation is important.

Regeneration

In the regenerable aqueous ammonia process, the absorption by-products are thermally decomposed to release CO₂ from the solution of ammonium compounds.

Three potential reactions could be responsible for liberation of CO₂ during the thermal regeneration.



The heat of reaction for the MEA process has been reported to be 20.0kcal/mol [9].

From Eq. 12, it is shown that ammonium bicarbonate transforms into ammonium carbonate and CO₂. It has the lowest enthalpy of dissociation for CO₂ release. Ammonium carbonate can be further dissociated to release more CO₂, but at higher cost per mole CO₂ desorbed. Therefore, it would be beneficial to transfer ammonium carbonate solution from the regenerator to the absorber and use it as CO₂ absorbent, as shown in Eq. 11.

EXPERIMENTAL

CO₂ absorption and regeneration studies in aqueous ammonia were performed in a semi-continuous flow reactor as shown in Fig. 1. The simulated flue gas consists of 15%vol CO₂ and 85%vol N₂. The gases were supplied by compressed gas cylinders and the flow controlled by mass flow controllers. The CO₂ absorber was a 3-liter glass container filled with 1500-ml aqueous ammonia solution. Pressure was near atmospheric; total gas flow rate 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. In initial experimentation, the simulated flue gas entered the absorber through a sintered metal sparger (2 micron pore), but the sparger was constantly experiencing pore plugging problem from ammonium bicarbonate crystallization. The sintered metal sparger was later replaced with an open-tube CO₂ gas sparger and a mixer operating at 1600 rpm. Although the open tubing did not eliminate the plugging problem entirely, the plugging problem was reduced to manageable level, so that test results were not affected.

The vent gas from the absorber was sent to a reflux condenser, where the gas temperature was reduced to 10⁰F

to condense the vapor escaping from the absorber. The condensed vapor is continuously drained back to the reactor. The vent gas flow rate was measured by a flow meter. The gas from the flow meter was then analyzed for unreacted CO₂ gas before being vented. An Horiba Model VIA-510 CO₂ Analyzer gave continuous readings. The CO₂ concentration-versus-time data were used to calculate CO₂ absorption rates and to totalize the amount of CO₂ absorbed. Data was recorded every ten seconds for the duration of a test. The baseline condition for the tests was 80°F, utilizing a 14% ammonia solution.

Analysis of carbonation by-products

Carbonation of an aqueous ammonium solution forms complex ammonium and carbonate salts. The by-products are mixtures of ammonium bicarbonate, ammonium carbonate, complex salts of carbonate and bicarbonate, ammonium hydroxide, and other compounds. It is desirable to know the compound mix under various absorber conditions. In order to maximize the carbon dioxide loading with ammonium ion, it would be desirable to maximize ammonium bicarbonate formation, because one ammonium ion will combine with one mole of CO₂, whereas in ammonium carbonate formation, one ammonium ion only combines with ½ mole of CO₂.

A method was developed by Parsons Chemical Analysis Group at NETL to determine carbonate, bicarbonate and hydroxide quantitatively using phenolphthalein and total alkalinity titrimetric methods.

The wet methods of analysis are summarized as follows: Saturated barium chloride is added to an aliquot of a diluted sample to precipitate any carbonate. The development of a pink color upon addition of phenolphthalein indicates the presence of hydroxide. If present, the hydroxide is titrated with 0.1N HCl, giving hydroxide alkalinity. Bromocresol green indicator is added and titration continued to the endpoint for total alkalinity/carbonate alkalinity determination. This method presupposes the incompatibility of hydroxide and bicarbonate alkalinities (Method 2320B, Standard Methods for the Examination of Water and Wastewater, 18th edition, 1993).

If no pink color develops upon the addition of phenolphthalein indicator to a sample treated with barium chloride, the absence of hydroxide is indicated. The sample is then titrated to a bromocresol green endpoint with 0.1N hydrochloric acid for a total alkalinity measurement. A second volume of sample is treated with excess 0.1N sodium hydroxide to convert any bicarbonate to carbonate. All of the carbonate is precipitated with barium chloride. The excess sodium hydroxide is immediately titrated with 0.1N hydrochloric acid to determine the bicarbonate concentration. The carbonate concentration in the original sample (before the conversion step) is calculated from the total alkalinity and bicarbonate concentrations.

DISCUSSION OF RESULTS

Absorption cycle effect on CO₂ loading capacity

In order to measure CO₂ loading capacity change of an aqueous ammonia solution during repeated absorption and regeneration cycles, the following experiments were conducted [11].

Solutions of 7%, 10.5%, and 14% ammonia were used in cycling tests to determine the potential effective utilization rates available for the aqueous ammonia solutions. 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 utilized at 80°F (27°C). After the initial absorption test, the resultant solutions were thermally regenerated to 180°F (82°C). The absorption/regeneration cycle was repeated for a total of three cycles, anticipating that the amount of CO₂ absorbed in the absorption step and regenerated in the regeneration step would approach steady state condition in a flow reactor after a third cycle. CO₂ loading capacity (absorption capacity) versus test cycle number is plotted in Figure 2. The graphs show that there is a large drop in the loading capacity (g CO₂/g solution) between the first and the second

cycles, but little change thereafter. These results indicate that less than 100% regeneration of the initial aqueous ammonia solution is achieved. The loss in capacity is further compounded by the ammonia vapor lost during the test. Of the initial 198 g of ammonia in the 14% solution, 85.4 g (43%) was lost in the vent lines during the 3-cycle test, with 71.5 g being lost in the first absorption step. For the 10.5% and 7% solutions, 32% and 30% of the ammonia were vented, respectively, with similar proportions of ammonia released during the first absorption step.

Figure 2 displays the specific absorption capacity of the solutions for each cycle, also demonstrating that the experiments appear to have reached an equilibrium after the second absorption test. The results with aqueous ammonia are far from optimized with respect to the amount of CO₂ regenerated and the ammonia loss. The final measured specific absorption capacity is 0.068, 0.053, and 0.040 g CO₂/g solution for the 14%, 10.5%, and 7% ammonia solutions, respectively. This compares favorably to current MEA technology that has demonstrated a capacity of 0.036 g CO₂/g solution for a standard 20% MEA solution. The sensible heat of regeneration per mass of CO₂ is indirectly proportional to the loading and proportional to the temperature difference between the absorption and regeneration temperatures (131°F to 248°F for MEA, 80°F 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.

In addition to the sensible heat and heat of reaction (Eq. 12,13,14), a major contributor to the regenerator heat duty in an MEA process is the heat of vaporization to generate steam to carry the CO₂ overhead in the stripper. A reflux ratio of 2.0 moles of water per mole of CO₂ is common. The energy required to generate this amount of steam is an additional 18.9 kcal/mol of CO₂ evolved. Since the regeneration of the aqueous ammonia solutions was conducted without this steam requirement, an additional energy savings is 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					
Process	ΔH_{rx} (kcal/mol)	Sensible Heat* (kcal/mol)	Heat of vaporization (kcal/mol)	Total (kcal/mol)	% Reduction from MEA process
MEA	20.0	79.4	18.9	118.3	0
NH ₃ (eq. 1)	6.4	36.0	0	42.4	64
NH ₃ (eq. 2)	24.1	36.0	0	60.1	49
NH ₃ (eq. 3)	15.3	36.0	0	51.3	57
* Sensible heat = mass of solution (g)/mol CO ₂ * Cp (assume .001 kcal/g-°C) * ΔT (°C)					

Aqueous ammonia pH value effect

CO₂ solubility in the aqueous ammonia solution is determined by the pH value of the solution. As more CO₂ is absorbed into the solution, the acidity of the solution gradually increases, until a critical pH value is reached. At the critical point no more CO₂ can be absorbed. Changes in the pH of the solution were measured

during the cycling tests. The pH values of the solution oscillated between 8.8 and 9.6, as shown in Figure 3. The graph shows that to maximize CO₂ absorption capacity and the rate of absorption, the ammonia concentration should be as high as possible. The ammonia vapor loss and the subsequent vapor recovery at high ammonia concentration should determine the optimal ammonia solution's pH range. This is because at too high ammonia concentration, the solution ammonia slip will increase. Also, regeneration to ammonia requires either the reaction of equation 13 or equation 14, each of which has a higher heat of formation. Therefore, an optimal point must be found for economic reasons.

Effect of reaction temperature on absorption rate

Three reaction temperatures (60°F, 80°F, and 100°F) were tested at ammonia solution concentrations of 7%, 14%, and 21% [10]. Because the decomposition temperature of NH₄HCO₃ (s) is near 140°F, reactor temperatures above 100°F were not investigated. The net amount of CO₂ absorbed decreases with increasing temperature, and it may be favorable to operate the reactor at low temperatures. Yeh and Bai [6] reported that CO₂ absorption capacity of ammonia solution (28% concentration) decreased by 11% between reaction temperatures 50°F and 104°F. As the temperature approached the ammonium carbonate/bicarbonate decomposition temperature, the CO₂ absorption rate decrease is expected.

Regeneration of ammonium bicarbonate and ammonium carbonate

Figure 4 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 [10]. The dependent variable in Figure 4 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.

A CO₂ desorption history curve for the thermal decomposition of a typical mixture of ammonium bicarbonate and ammonium carbonate is shown in Figure 5. The crystal mix was mixed with water at 40°F to avoid the premature evolution of CO₂ before the reactor is sealed. This was necessary because these ammonium salts decompose in room temperature water. The solution temperature was gradually increased in stages. The temperature control at each level was predetermined. All released gases were mixed with a measured nitrogen sweep gas then flowed through a gas flow meter and a CO₂ analyzer; CO₂ and NH₃ were calculated. Total CO₂ flow was calculated from area integration. Each temperature level was held until there was no CO₂ evolved from the solution. Solution temperature was then advanced to the next level.

The analytical methods developed in-house, as described in the experimental section, to quantitatively analyze ammonium carbonate and ammonium bicarbonate was used to determine some absorption and regeneration test products. The sample aging effect was found to be as high as 24% after 11 days, with bicarbonate converting to carbonate. Therefore, samples should be analyzed shortly after they are taken.

ECONOMIC EVALUATION

Schematic flow diagrams of the Aqua Ammonia Process and the MEA Process are illustrated in Figure 6 and Figure 7 [12] respectively. Data from Table 1 and other related values from the cycling tests may be used to perform regeneration economic comparison between the Aqua Ammonia process and the MEA process. In Fig. 7, the flue gas enters at the bottom of the absorber with 15% CO₂ (dry basis). In the absorber CO₂ is absorbed by absorbent and the absorbent is recirculated back to the absorber from the regenerator.

In this sample calculation, the aqueous ammonia solution has 8% wt NH₃ equivalent. The solution lean loading is 0.08 lb CO₂ per lb solution from the regenerator. The rich CO₂ loading from the bottom of absorber is 0.15 lb CO₂ per lb solution. Therefore, approximately 50% of CO₂ in the ammonium solution is regenerated. The transfer capacity of ammonium solution is 0.07 lb CO₂ per lb NH₃ solution circulated.

Energy usage in ammonium solution regeneration is estimated at 1830 Btu per lb CO₂.

Figure 8 illustrates the MEA process. The sample calculation uses 20% wt MEA solution. The CO₂ lean loading is 0.022 lb CO₂ per lb MEA solution. The CO₂ rich loading is 0.058 lb CO₂ per lb MEA solution. The CO₂ transfer capacity is 0.036 lb CO₂ per lb MEA solution circulated. The thermal energy needed for regeneration is 4840 Btu per lb CO₂ regenerated. Approximately 38% CO₂ is regenerated per cycle.

The regeneration energy savings for the Aqua Ammonia process is approximately 62% compared with the MEA process. Only 8% ammonium is used in this sample calculation, higher ammonium solution will increase the ammonia process efficiency. Future work will test with a higher concentration of ammonia.

The economic advantage of aqua ammonia process will further improve when the saleable ammonium sulfate fertilizer by-product is included.

CONCLUSIONS

Thermal regeneration of standard solutions revealed that regeneration of up to 60% of the carbon in a bicarbonate solution may be regenerated. Ammonium carbonate solution resulted in approximately 38% carbon regeneration under the same temperature condition. Cycling test results demonstrated that a 62% 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 vaporization when compared to standard MEA solutions.

A flow system is being constructed for continuous operation absorption and regeneration steps. A parametric study will include temperature, ammonia concentration, CO₂ concentration, and flow rates of reactants. Future research work will additionally investigate removals of sulfur dioxide and nitric oxides with the ammonia solution.

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 favoring by the United States Department of Energy.

ACKNOWLEDGEMENT

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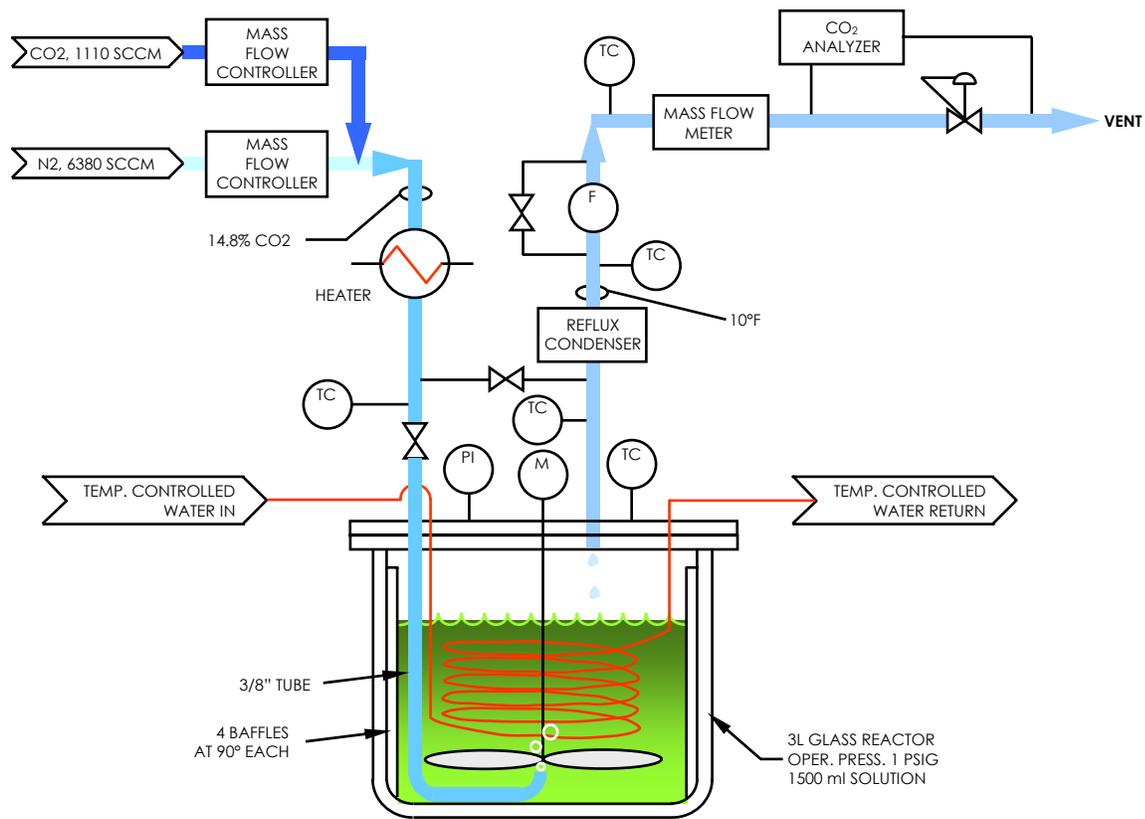


Fig. 1. Aqua Ammonia Semi-Continuous Reactor

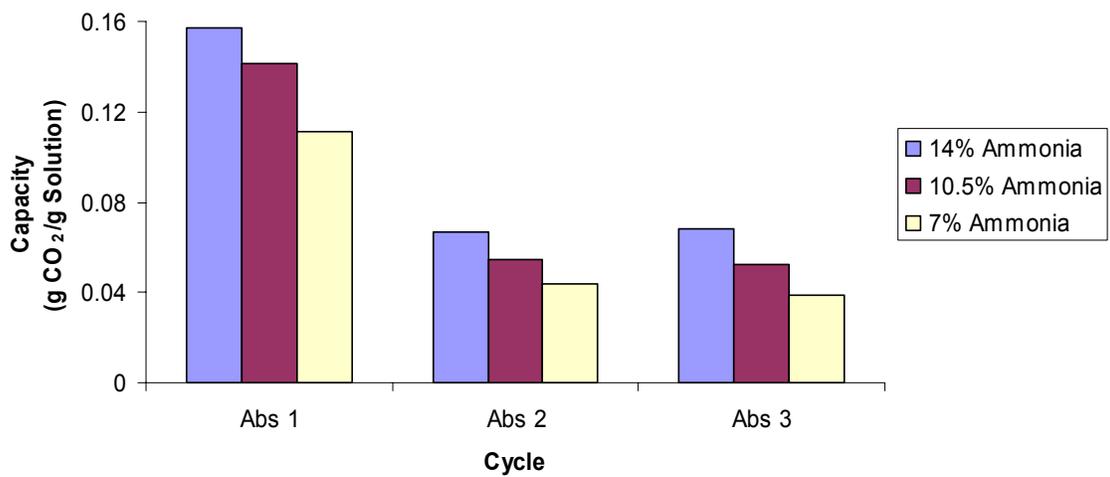


Fig. 2. Effect of Cycling on CO₂ Absorption Capacity

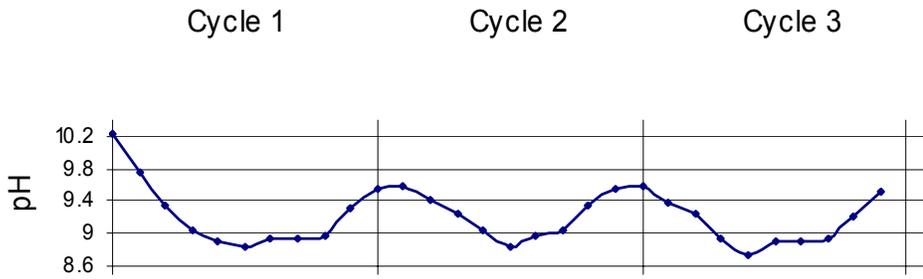


Fig. 3. NH₃ Solution pH Value Change Defines Absorption / Regeneration Cycle (7% NH₃, 80°F)

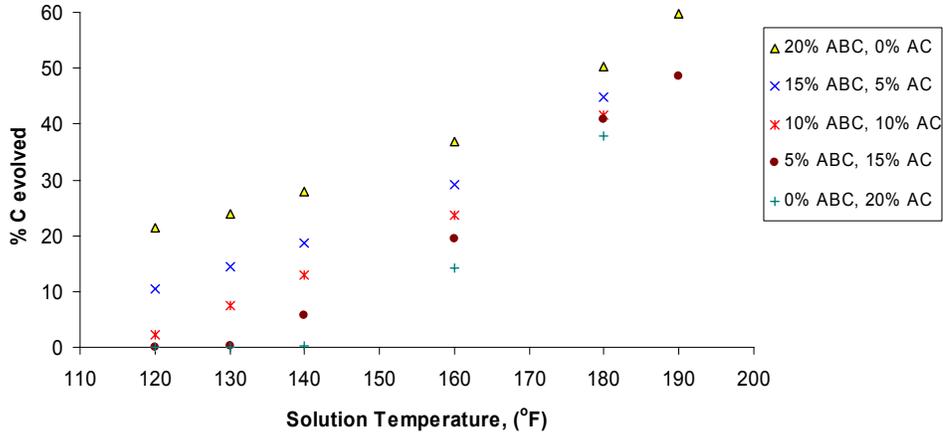


Fig. 4. Regeneration Test Summary

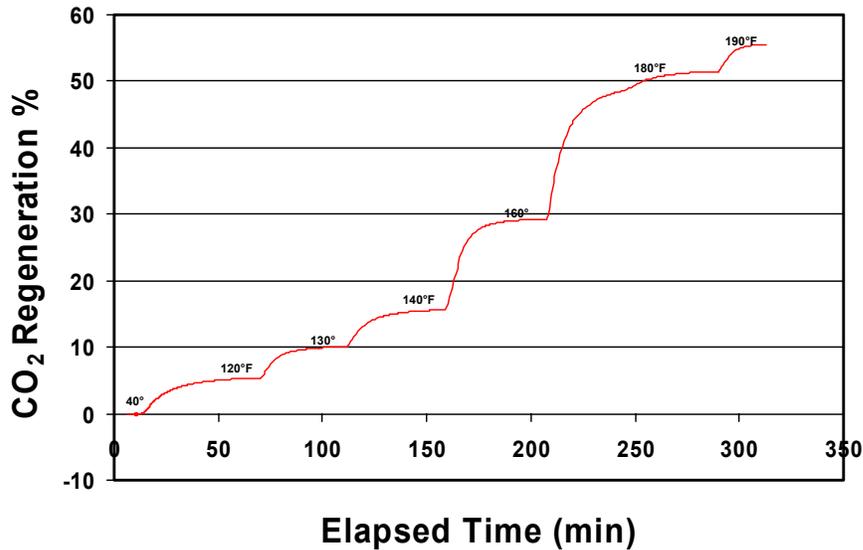
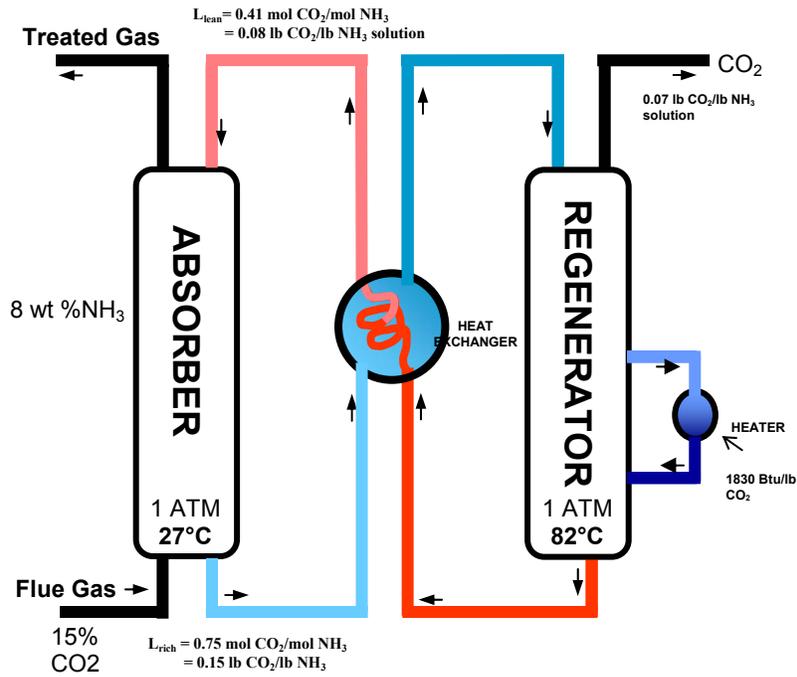
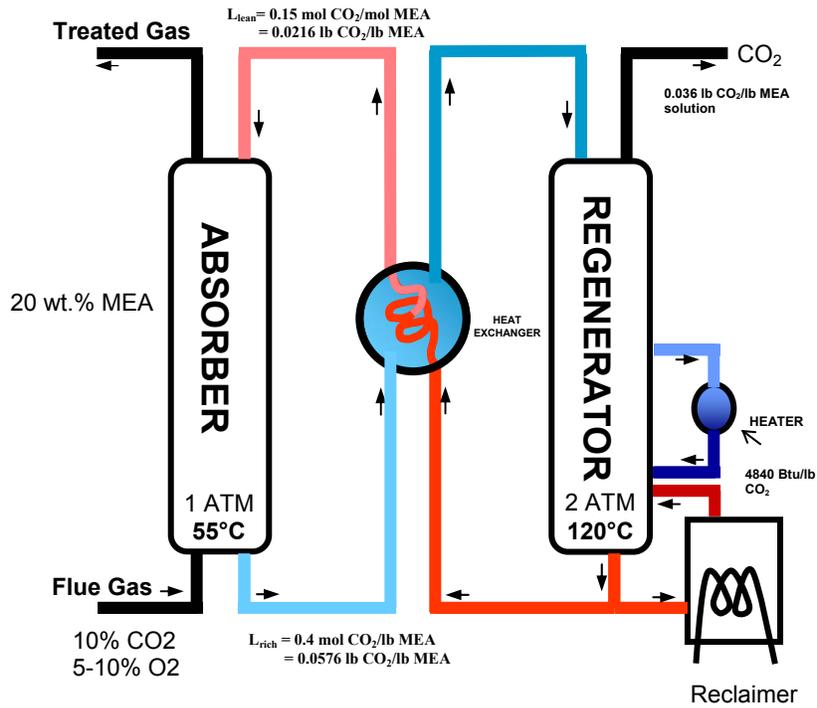


Fig. 5. CO₂ Desorption Curve of Ammonium



Process Flow Diagram for Aqua Ammonia CO₂ Capture Process
Fig. 6.



Process Flow Diagram for a Typical MEA CO₂ Capture Process
Fig. 7