Preliminary Study to Capture CO_2 in Flue Gas by Spraying Aqueous Ammonia to Produce NH_4HCO_3

ZHANG Yun, LI Zhen-zhong, LI Xin, DONG Jiang-xun, and WANG Yang
National Power Plant Combustion Engineering Technology Research Center,
Shenyang, P.R. China

Scott M. Smouse and James M. Ekmann
U.S. Department of Energy
National Energy Technology Laboratory
Pittsburgh, PA, USA.

ABSTRACT

To address climate change, many believe that the carbon dioxide (CO_2) produced from using fossil fuels for power generation will need to be captured and sequestered to allow the continued long-term use of these resources. At the National Power Plant Combustion Engineering Technology Research Center (NPCC) in P.R. China, an experimental facility has been designed and erected in an existing coal-fired research facility to evaluate the ability of aqueous ammonia to absorb CO_2. A series of experiments to evaluate the capture of CO_2, along with sulfur dioxide (SO_2) and nitrogen oxides (NO_x), by spraying aqueous ammonia in a pilot-scale absorption tower have been conducted. The following conclusions were reached: (1) Spraying aqueous ammonia into actual flue gas produced from coal combustion, i.e., not simulated flue gas, can not only capture CO_2, but also SO_2 and NO_x. (2) The absorption efficiency of CO_2 was found to increase with an increase in the NH_3/CO_2 molar ratio. (3) The ammonia solution after absorption was found to contain ammonium bicarbonate [NH_4HCO_3], ammonium sulfate [$(NH_4)_2SO_4$], and ammonium nitrate [NH_4NO_3], which constitute a compound fertilizer. (4) In addition, from the chemical thermodynamics point of view, the calculated Gibbs free energy change showed and confirmed that the three products found above in the liquid phase will be obtained simultaneously.

INTRODUCTION

In spring 2002, the National Power Plant Combustion Engineering Technology Research Center (NPCC) in Shenyang, Liaoning Province, P.R. China began cooperating with the U.S. Department of Energy's National Energy Technology Laboratory (DOE/NETL) on a project entitled "Study of CO_2 Sequestration by Spraying Concentrated Aqueous NH_3 and Production of a Modified NH_4HCO_3 Fertilizer." This project is being implemented under Annex IV: Energy and Environmental Technologies of the Protocol for Cooperation in the Field of Fossil Energy Technology Development and Utilization between the U.S. Department of Energy (DOE) and P.R. China's Ministry of Science and Technology (MOST). NPCC's work to date has focused on experiments in a pilot-scale CO_2 absorptive facility using actual flue gas from an existing coal-fired research facility to produce a modified ammonium bicarbonate (ABC) fertilizer. NETL has been developing a thermal regeneration process for the NH_4HCO_3 product that yields a concentrated stream of CO_2 that could be sequestrated. The initial results of NETL's laboratory-scale research are reported elsewhere at this conference along with a preliminary analysis of the projected economics of the process.

NPCC's interest in the project is driven by the fact that agriculture holds a leading position in the national economy of most developing countries, including P.R. China. China feeds about 22% of the world's population with only 7% of the world's arable land. Crop production is obviously influenced by weather, which is driven by global climate change. Chinese agricultural experts have indicated that a change in the weather, caused by the increase of CO_2 content in the atmosphere, would cause water to evaporate faster from the soil. Thus, the production of paddy, wheat, and cotton, which are major agricultural products in P.R. China, may be reduced. Development of a process to capture CO_2 before it enters the atmosphere and subsequently sequester it in the soil would appear to offer benefits (short term if the carbon doesn't stay in the soil for long periods of time or long term if it does). Furthermore, development of a low-cost process to regenerate the ammonium bicarbonate product and produce a concentrated stream of CO_2 that could be sequestered would expand the basic process concept should future reductions of CO_2 emissions from fossil fuel combustion be required to address climate change.

The method of capturing CO_2 by spraying aqueous ammonia into the flue gas from coal-fired power plants was inspired by one of working processes, called as carbonization, of synthetic ammonia production in China[1]. The mixed gas, containing hydrogen and nitrogen, generated from coal gasification has been used to produce ammonia in the Chinese chemical industry since 1960s. The impurities in the mixed gas, which include CO_2 and CO, must be eliminated. By spraying aqueous ammonia into the syngas, CO_2 is absorbed and a byproduct, NH_4HCO_3, is produced, which is widely used as fertilizer in China.

The process involves a complicated chemical gas-liquid reaction[1], whose general chemical reaction expression follows:

$$NH_3 + H_2O + CO_2 \rightarrow NH_4HCO_3 \qquad (1)$$

In fact, there are a series of middle reaction processes included:

$$NH_3 + CO_2 \rightarrow NH_2COONH_4 \qquad (2)$$

NH_2COONH_4 hydrolyzes into NH_4HCO_3:

$$NH_2COONH_4 + H_2O \rightarrow NH_4HCO_3 + NH_3 \qquad (3)$$

Also, ammonia can react with H_2O to create NH_4OH:

$$NH_3 + H_2O \rightarrow NH_4OH \qquad (4)$$

NH_4HCO_3 produced by hydrolytic reaction will react with NH_4OH to create $(NH_4)_2CO_3$:

$$NH_4HCO_3 + NH_4OH \rightarrow (NH_4)_2CO_3 + H_2O \qquad (5)$$

$(NH_4)_2CO_3$ absorbs CO_2 and creates NH_4HCO_3:

$$(NH_4)_2CO_3 + H_2O + CO_2 \rightarrow 2NH_4HCO_3 \qquad (6)$$

RESEARCH FACILITY AND EXPERIMENT

The experimental study was conducted in NPCC's Combustion Research Facility (CRF), which can be used to study the combustion characteristics of coal, lignite, oil, gas, garbage, and other fuels. The test facility, which is designed for a maximum coal firing rate of 20 kg/h of bituminous coal, or 640 MJ/h (0.607 million Btu/h), consists of five major components: (1) coal grinding and pneumatic conveying system, (2) combustion system, (3) gas treatment systems, (4) compressed air and cooling systems, and (5) data acquisition and control system (see Figure 1). The combustion system consists of a furnace (4.2-m high and 0.4-m diameter), a swirl burner, electrostatic precipitator, and other process equipment. The data acquisition and control system can measure the concentration of O_2, CO_2, CO, SO_2 and NO_x in flue gas from the facility continuously and simultaneously.

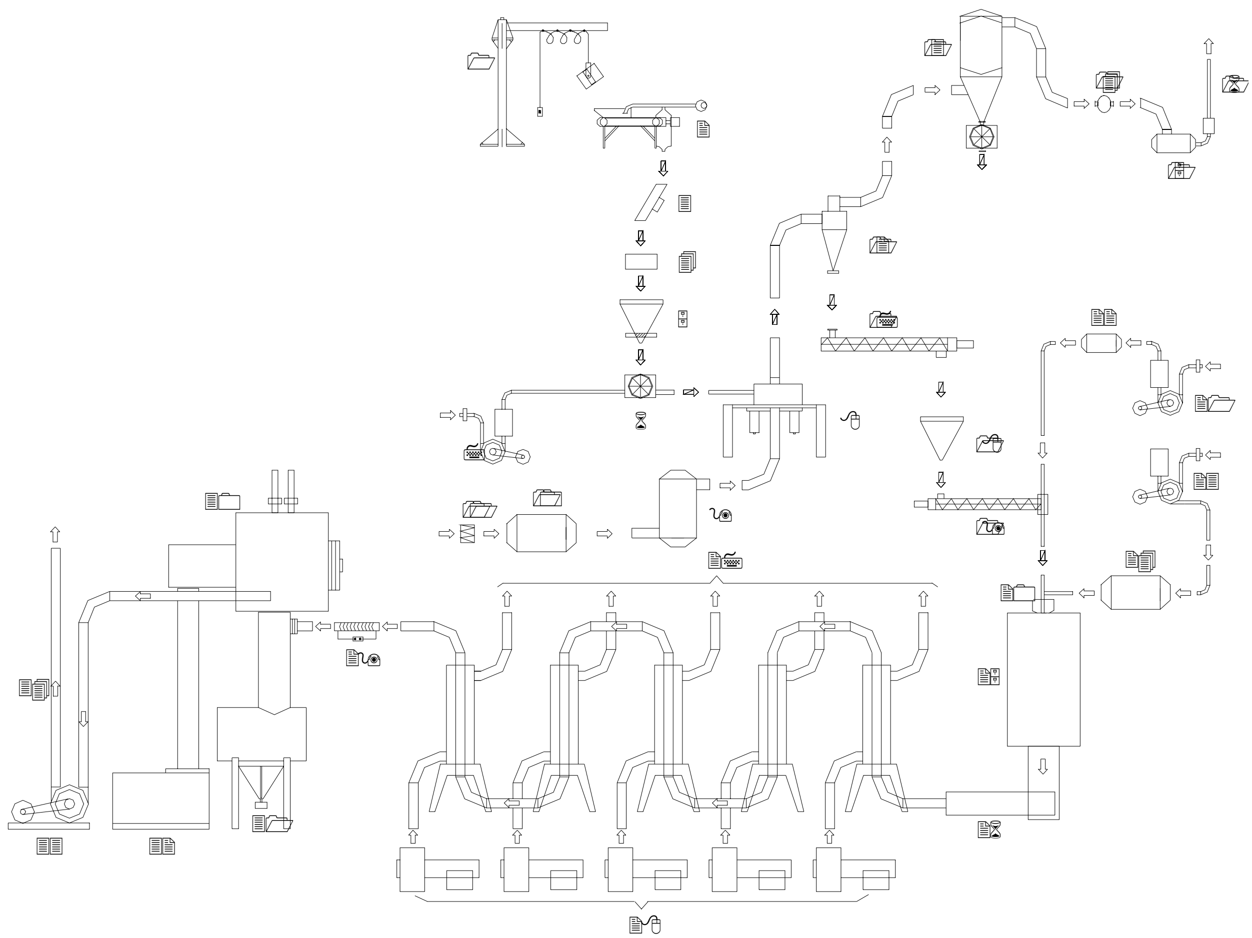

Figure 1. Flow Sheet of CRF System

1. Crane 2. Belt Conveyor 3. Magnet 4. Roller Crusher 5. Crusher coal feed hopper
6. Variable Speed Blower 7. Air Pump 8. Coal Pulverizer 9. Silencer 10. Air Heater
11. Filter 12. Cyclone 13. Pulsed Jet Collector 14. Explosion Barrier 15. Vacuum Pump
16. Vent to Atmosphere 17. Screw Conveyor 18. Coal Hopper 19. Volumetric Screw Feeder
20. Burner 21. Primary Air Blower 22. Primary Air Heater 23. Secondary Air Blower
24. Secondary Air Heater 25. Furnace 26. Flue Gas Sample 27. Air-Cooled Heat Exchanger
28. Cool Air Blower 29. Flue Gas Trace Heater 30. Electrostatic Precipitator
31. Fly Ash Hopper 32. Transformer 33. Exhaust Gas Blower 34. Chimney

NPCC designed and erected a CO_2 absorption facility after the electrostatic precipitator of CRF in 2002. The absorption facility consists of a packed absorb tower (250-mm inner diameter x 2000-mm height), a flue gas sampling and analysis system, along with ancillary equipment, such as a forced draft fan and cooler (see Figure 2).

During the experiment, a part of flue gas produced from the coal-fired CRF enters the cooler (i.e., heat exchanger) for temperature control. The flue gas then enters the absorber, which is packed with ceramic rings, from the bottom. Concentrated aqueous ammonia from the No. 1 ammonia pot enters the absorber from the top of the tower through a spray nozzle. The flue gas and the aqueous ammonia flow counter-current-wise in the tower, causing reaction between the flue gas components and the aqueous ammonia. The flue gas exhausts into atmosphere from the top of the absorber while the mixed ammonia solution flows into the No. 2 ammonia pot from the bottom of the absorber. During testing, the data acquisition and control system measures the concentration of O_2, CO_2, SO_2, and NO_x in flue gas at the inlet and outlet of absorber. By chemical analysis of the mixed ammonia solution before and after each test, the concentration of substances in the mixed aqueous ammonia solution can be acquired.

The aqueous ammonia used in the experiment was reused. After each series of tests, the aqueous ammonia in the No. 2 ammonia pot flows into the No. 1 ammonia pot for the next test. Therefore, the aqueous ammonia used for a subsequent run contains some products of the previous run. Therefore, the concentration of aqueous ammonia for spray decreases for each subsequent test.

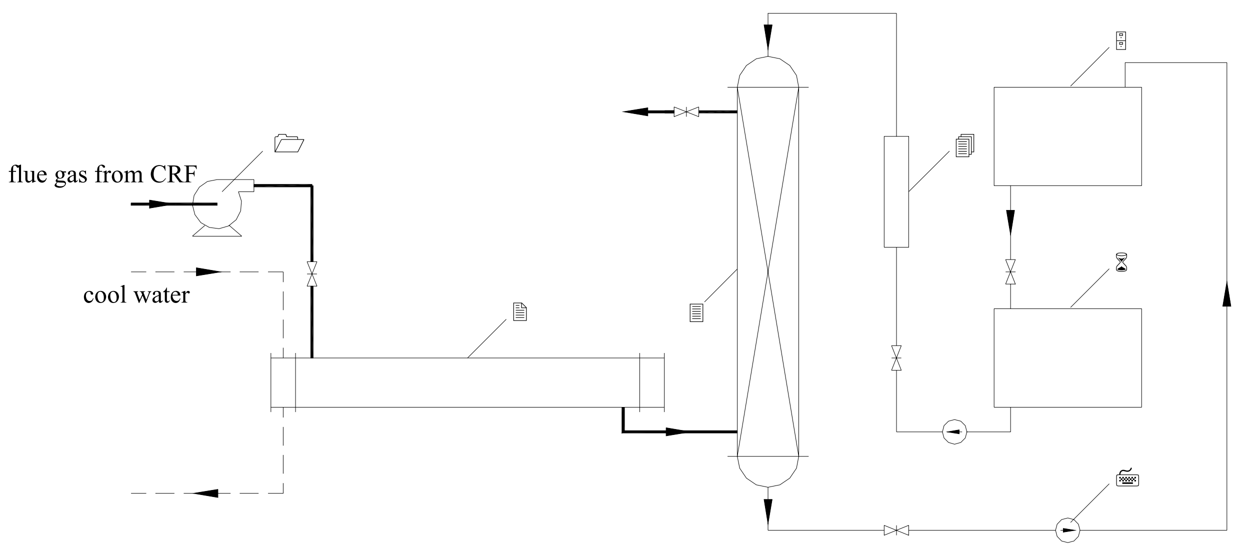

Figure 2. Flow Sheet for Absorption of CO_2 from Flue Gas in CRC
1. Forced Fan 2. Cooler 3. Absorber 4. Flow Gauge 5. No. 2 Ammonia Pot
6. No. 1 Ammonia Pot 7. Pump

TEST RESULT AND ANALYSIS

South China bituminous coal (analysis in Table 1) was burned in the CRF during the CO_2 capture tests conducted in 2002.

Table 1. South China Coal Analysis

C_{ar} %	H_{ar} %	O_{ar} %	N_{ar} %	S_{ar} %	M_{ar} %	A_{ar} %
57.76	4.14	6.99	1.16	0.34	4.90	24.71

During the tests, the absorber was filled with structured packing (25-mm outer diameter x 25-mm high ceramic rings) to a height of 800 mm. Flue gas from the CRF flows through the heat exchanger and enters the absorber from the bottom at 70 m^3/h and 35°C. Aqueous ammonia enters the absorber from the top at 200 l/h.

CO_2 Absorption Efficiency

Tests were conducted under a number of conditions with varying concentrations of ammonia. During the tests, the data acquisition system measured the concentration of O_2 and CO_2 at the inlet and outlet of the absorber. The measured results are given in Table 2.

Table 2. Initial Tests Results

	Absorber Inlet					Absorber Outlet				
	1		2		3		4		5	
NH_3/CO_2 Molar Ratio	1.40		1.35		1.30		1.28		1.25	
Gas Conc., %	**O_2**	**CO_2**	**O_2**	**CO_2**	**O_2**	**CO_2**	**O_2**	**CO_2**	**O_2**	**CO_2**
Absorber Inlet	5.70	11.25	5.24	11.04	5.02	10.88	5.74	11.12	6.10	10.96
Absorber Outlet	11.12	0.60	10.95	0.70	10.70	0.90	11.25	1.30	11.66	1.60

The measured CO_2 concentrations were subsequently normalized to the same concentration of O_2 of the flue gas using the following equation:

$$[CO_2] = [CO_2]_0 \frac{21 - x}{21 - O_2}$$

where

$[CO_2]$ is the corrected CO_2 concentration, %

$[CO_2]_o$ is the measured CO_2 concentration, %

x is the normalized O_2 concentration, % (assumed x = 6)

O_2 is the measured O_2 concentration, %

The normalized test results are presented in Table 3.

Table 3. Normalized CO_2 Concentrations

	Test Number				
	1	**2**	**3**	**4**	**5**
NH_3/CO_2 Molar Ratio	1.40	1.35	1.30	1.28	1.25
CO_2, % Absorber Inlet	10.90	10.51	10.21	10.93	11.03
CO_2, % Absorber Outlet	0.90	1.04	1.30	2.00	2.60

By chemical acid-base titration method, the concentration of ammonia solution sampled at the inlet and outlet of the liquid flow of the absorber during the tests can be determined. The resulting CO_2 absorption efficiency was calculated for the different mole ratios of NH_3/CO_2 that were tested, as shown in Table 4 and Figure 3.

Table 4. CO_2 Absorption Efficiency vs. Molar Ratio of NH_3/CO_2

	Test Number				
	1	**2**	**3**	**4**	**5**
NH_3/CO_2 Molar Ratio	1.40	1.35	1.30	1.28	1.25
CO_2 Absorption Efficiency, %	91.7	90.1	87.3	81.7	76.4

Absorber Temperature: 35°C Packing Height: 800mm

Molar Ratio: moles of ammonia (absorbent) at liquid inlet/moles of CO_2 at gas inlet

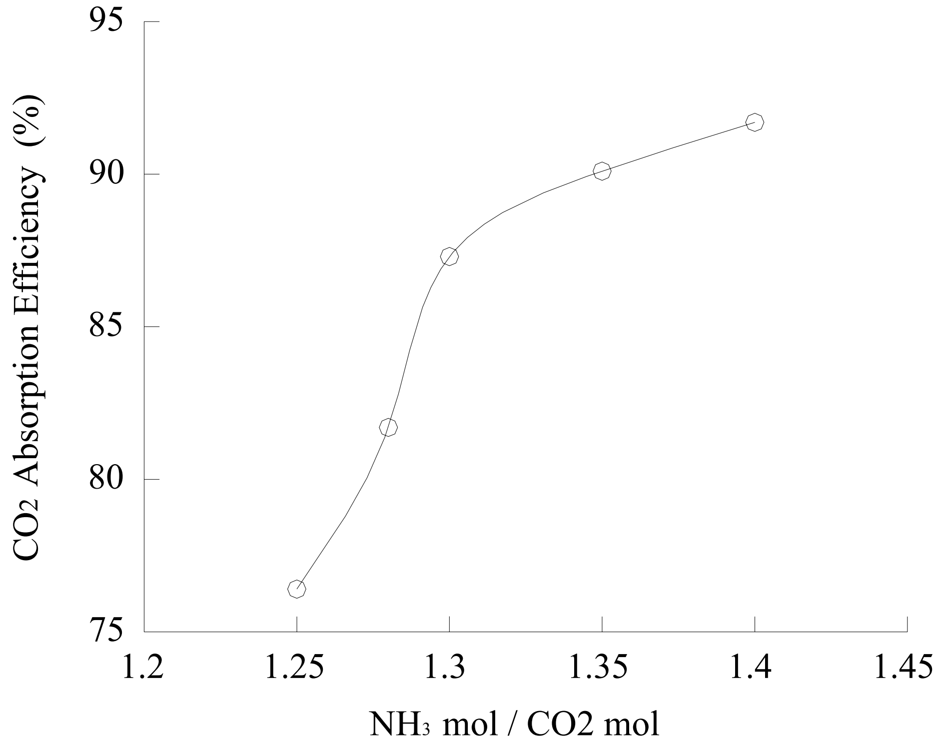

Figure 3. CO_2 Absorption Efficiency Dependence of the NH_3/CO_2 Molar Ratio

According to the test results, the absorption efficiency of CO_2 increased with an increase in the molar ratio of NH_3/CO_2. At about a NH_3/CO_2 molar ratio of about 1.4, the highest CO_2 absorption efficiency was measured at about 92%. Compared to that in the carbonization process used in synthetic ammonia production in China, which is 99%[2], the CO_2 absorption efficiency in these tests seems comparatively low. The reason for this is that the working pressure used in synthetic ammonia production is much higher, 12 atm[1], which is 11 times higher than that in the combustion test facility. However, capturing 90% of the CO_2 in the flue gas from actual coal combustion is a significant achievement in these initial tests, showing that the process offers promise should the overall process economics proved attractive compared other CO_2 capture processes.

Analysis of the Mixed Ammonia Solutions

The mixed ammonia solution produced in the tower contains OH^-, HCO_3^-, CO_3^{-2}, SO_4^{-2}, and NO_3^- ions. Based on the alkalinity of OH^-, HCO_3^-, and CO_3^{-2} by using the method of hydrochloric acid neutralization, the concentrations of NH_4OH, NH_4HCO_3, and $(NH_4)_2CO_3$ in the ammonia solutions were determined. According to the results of SO_4^{-2} and NO_3^- measured by colorimetry, the concentrations of $(NH_4)_2SO_4$ and NH_4NO_3 can also be obtained, respectively.

The concentrations of HCO_3^- and CO_3^{-2} in the mixed ammonia solution produced are shown in Figure 4.

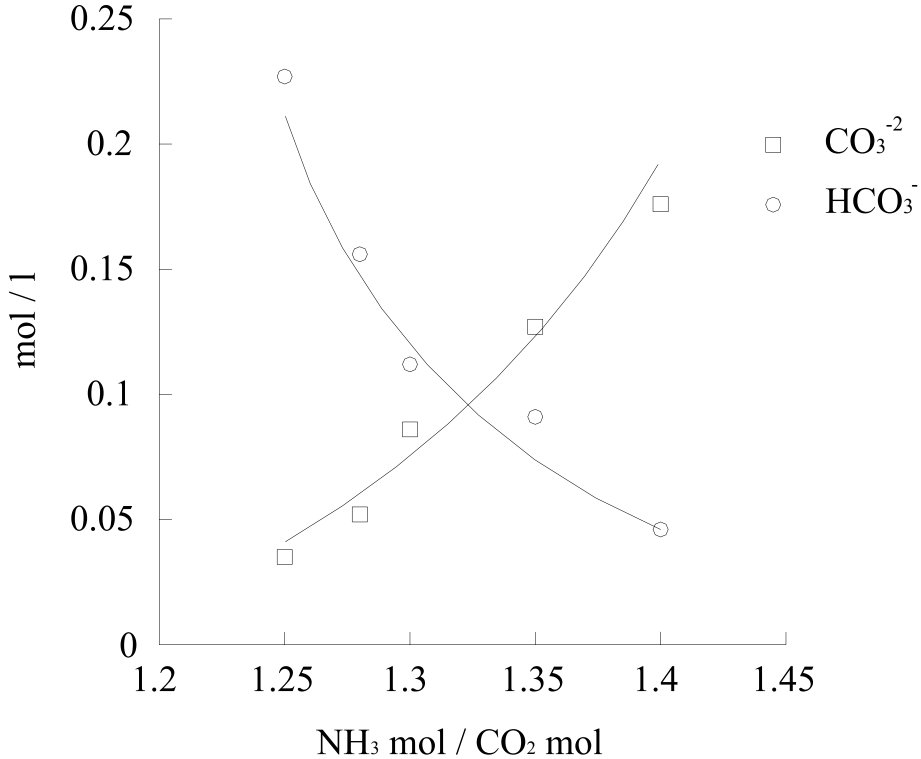

Figure 4. Relation of Concentrations of HCO_3^- and CO_3^{-2} Ions in the Produced Ammonia Solutions to NH_3/CO_2 Molar Ratio

It is seen in Figure 4 that the carbon in the mixed ammonia solution has two forms: HCO_3^- and CO_3^{-2}. The concentration of HCO_3^- in solution increases and the concentration of CO_3^{-2} decreases when the NH_3/CO_2 molar ratio decreases. At a mole ratio of NH_3/CO_2 around 1.30-1.35, there is a balance between the concentrations NH_4HCO_3 and $(NH_4)_2CO_3$ in the mixed ammonia solution produced as shown in reaction (5). From the chemical thermodynamics point of view, when the concentration of NH_4OH increases, reaction (5) moves toward the right and more CO_3^{-2} ($(NH_4)_2CO_3$) is found in the solution and the concentration of HCO_3^- (NH_4HCO_3) decreases. Other the other hand, when the mixed solution spray, which contains ammonia, was used repeatedly to absorb CO_2 in flue gas, the concentration of NH_4HCO_3 in the mixed solution from the bottom of the tower increases. This means that the balance of reaction equation (6) will move towards the right to produce more NH_4HCO_3.

From the measured results of SO_4^{-2}, the mixed ammonia solution contains a small quantity of SO_4^{-2}. The absorption efficiency of SO_2 increased with an increase of the NH_3/CO_2 molar ratio (seen in Table 5).

Table 5. Measured Concentrations of SO_4^{-2} in Solution for Different NH_3/CO_2 Molar Ratios

	Test Number				
	1	**2**	**3**	**4**	**5**
NH_3/CO_2 Molar Ratio	1.40	1.35	1.30	1.28	1.25
$SO_4^{-2}\times10^3$ mol	0.863	0.538	0.450	0.275	0.150

From the measured results, the concentration of NO_3^- is less than 1 mg/l in the reaction solution, which is the lower detection limit of the measuring equipment. Therefore, spraying aqueous ammonia into flue gas can capture both SO_2 and NO_2. The absorption efficiency of SO_2 and NO_2 will be analyzed in the future experiments.

Chemical Thermodynamic Analysis

The standard Gibbs free energy change for the NH_4HCO_3, $(NH_4)_2SO_4$, and NH_4NO_3 products are -159.23 kcal/mol, -215.77 kcal/mol, and -45.58 kcal/mol, respectively[2]. Because the tests were conducted under at 35°C and 1 atmosphere, which are close to the standard conditions of 25°C and 1 atmosphere, the actual Gibbs free energy changes of these products are very close to the standard.

According to the principles of chemical thermodynamics, the more favorable chemical reaction occurs for the more negative standard Gibbs free energy. Thus, the order of the reaction with aqueous ammonia should be SO_2 first, CO_2 second, and NO_x last. However, in actual testing, the amount of measured SO_4^{-2} is small because the sulfur content in the test coal is low (0.34%) and relatively little SO_2 is produced in the combustion of the coal. Therefore, the amount of $(NH_4)_2SO_4$ (i.e, SO_4^{-2}) produced by reacting ammonia with SO_2 (i.e., SO_3) is also low. In addition to small absolute figure of the standard Gibbs free energy change for NH_4NO_3, the nitrogen content of the test coal is also relatively low (1.16%). NO accounts for the majority of the NO_x emissions produced from coal combustion. Thus, the concentration of NH_4NO_3 (i.e., NO_3^-) measured in the mixed ammonia solution is also low.

FUTURE WORK

Plans are being made to improve the CRC's capabilities for on-line measurement of the gas species of interest and post-test chemical analysis of the reaction solution. NPCC and NETL are developing a plan for future cooperation, which will include reciprocal visits by researchers from both organizations. Future cooperation may also include pilot-scale regeneration experiments at NPCC and additional technical and economic analyses of the modified NH_4HCO_3 fertilizer process.

CONCLUSIONS

(1) Spraying aqueous ammonia into actual flue gas produced by a coal-fired facility can not only capture CO_2 but also absorb SO_2 and NO_x from the flue gas.

(2) The absorption efficiency of CO_2, SO_2, and NO_x in actual flue gas from a coal-fired facility varies depending on the reaction conditions. The absorption efficiency of CO_2 and SO_2 was found to increase with an increase in the concentration of aqueous ammonia. Over the NH_3/CO_2 molar ratio of 1.25 to 1.40 that was tested, the CO_2capture efficiency was measured at 76.4% to 91.7% at 35°C. Further analysis is needed to quantify the capture efficiency of SO_2 and NO_x.

(3) The aqueous ammonia absorption solution was found to contain a mixed crystalline of ammonium bicarbonate [NH_4HCO_3], ammonium sulfate [$(NH_4)_2SO_4$], and ammonium nitrate [NH_4NO_3]–the main components of a compound fertilizer. The absorbed CO_2 in the aqueous ammonia solution is in the form of HCO_3^- and CO_3^{-2}. For a certain molar ratio of NH_3/CO_2, there is a balanced concentration of HCO_3^- and CO_3^{-2} in the mixed ammonia solution. By spraying the mixed ammonia solution into flue gas containing CO_2, higher NH_4HCO_3 content (higher HCO_3^- concentration) in mixed solution can be obtained.

(4) From the chemical thermodynamics point of view, the calculated Gibbs free energy change showed and confirmed that the three above products found in the liquid phase will be obtained simultaneously. SO_2 should react favorably with ammonia, and then CO_2, and NO_x last.

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