EXPERIMENTAL STUDY ON SEQUESTRATING OF CO_2 IN THE TRUE FLUE GAS BY AMMONIA SPRAY AND PRODUCING NH_4HCO_3

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ABSTRACT

Carbon dioxide, a major greenhouse gas, need to removed from flue gas produced by combustion of fossil fuels. Under the international cooperation with U.S. DOE, the National Power Plant Combustion Engineering Technology Research Center (NPCC) in P.R. China has designed and built an absorption facility in which the spraying aqueous ammonia was injected in order to sequestrate CO_2 flue gas. The flue gas used is the actual flue gas produced by the coal-fired Combustion Research Facility (CRF) during a series of tests. The experiments were specified under different conditions of concentrations of ammonia solution from the nozzle. It is concluded that: spraying ammonia not can only capture CO_2 but also SO_2 and NO_X from the flue gas. Absorption efficiencies of both CO_2 and SO_2 are ascended with increasing in the ammonia concentration. The reacted ammonia solution after absorbing CO_2, SO_2 and NO_X contains NH_4HCO_3, $(NH_4)_2SO_4$ and NH_4NO_3. Based on the chemical thermodynamics, the calculated Gibbs free energy change showed and confirmed that the three products above found in the liquid phase will be obtained simultaneously.

Keywords: flue gas, CO_2, sequestrate, aqueous ammonia, NH_4HCO_3

INTRODUCTION

It is well known that carbon dioxide is a major greenhouse. Coal is the main energy of the world and the flue gas produced by combusting coal is the primary source of CO_2 emission. This condition will keep several decades. International society has already been aware of the serious consequences of global climate change owing to greenhouse. Many programs for CO_2 emission control are been researched an explored widely.

The method to capture CO_2 by spraying aqueous ammonia into flue gas from the boiler in coal-fired power plant was inspired by one of working procedures, called as carbonization, of the synthetic ammonia production in China. From the period of 60's of last century, Chinese chemical fertilizer industry utilizes water-gas-shift reaction to produce a synthesis mixed gas containing hydrogen and nitrogen, further produces synthesis ammonia as the main end product. The raw synthesis gas contains amount of CO_2, CO and others as impurities. These impurities must be removed for NH_3 composing. Therefore, the part of formed aqueous ammonia is re-injected back to remove CO_2 and other acid gases in order to purify the mixed gas. CO_2 will react with the aqueous ammonia and form the ammonium-bicarbonate, which is a nitrogen fertilizer as a by-product of this technology. Figure 1 show the flow chart that used in China. By feeding a certain particular size anthracite coal or coke into a fixed bed gasifier, and alternatively supplying air and steam into the bed, the synthesis gas is produced. After cooling down, it is pumped to a storage bank. Then by removing the dust, it is pressured and sent into desulfuration system. The sulfur-free synthesis gas further compressed and pumped into a scrubber system to remove most of CO by shift reaction. The gas, then enters the carbonization reactor system to remove CO_2.The semi-clean and CO_2-free synthesis is pressured again and enters the $CuSO_4$ washing tower to remove the residual CO. After above treatments, the synthesis gas becomes pure and the amount of $CO+CO_2$ is lower than 20×10^{-6}. The clean synthesis gas then is pressured to 32MPa and NH_3 composition is obtained as the main product of this method. A part of the main product NH_3 is re-fed into the loop removing CO_2 and producing the NH_4HCO_3 as a by-product.

The National Energy Technology Laboratory (NETL) in the United States and the National Power Plant Combustion Engineering Technology Research Center (NPCC) in P.R. China have begun a cooperative project. This cooperation is under Annex Ⅳ-A: Energy and Environmental Technologies of the Fossil 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). This paper is done by NPCC of China and focused on the preliminary experimental study of CO_2 sequestration in flue gas from coal-fired facility by spray aqueous ammonia.

This process is a complicated chemical gas-liquid reaction. The general chemical reaction expression is as follow:

$$NH_3 + H_2O + CO_2 = NH_4HCO_3 \qquad (R1)$$

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

$$NH_3 + CO_2 = NH_2COONH_4 \qquad (R2)$$

NH_2COONH_4 hydrolyzes into NH_4HCO_3:

$$NH_2COONH_4 + H_2O = NH_4HCO_3 + NH_3 \qquad (R3)$$

Also, ammonia can react with H_2O to create NH_4OH:

$$NH_3 + H_2O = NH_4OH \qquad (R4)$$

NH_4HCO_3 produced by hydrolytic reaction will react with H_2O to create $(NH_4)_2CO_3$:

$$NH_4HCO_3 + NH_4OH = (NH_4)_2CO_3 + H_2O \qquad (R5)$$

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

$$(NH_4)_2CO_3 + H_2O + CO_2 = 2NH_4HCO_3 \qquad (R6)$$

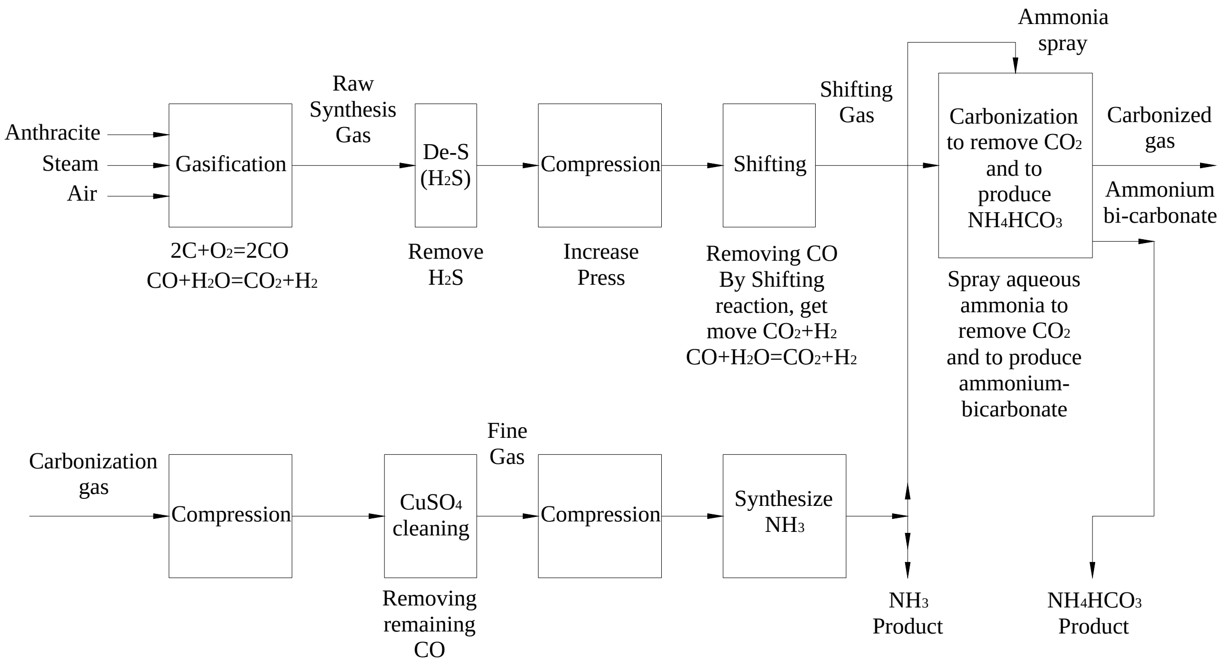
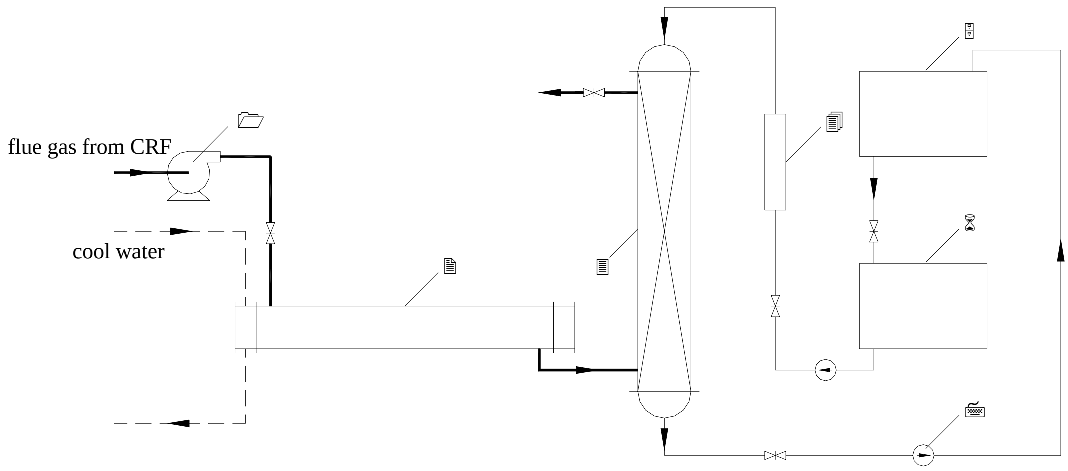


Fig.1　Flow Chart of Synthesis Ammonia by Coal Gasification

RESEARCH FACILITY AND EXPERIMENTAL METHOD

The experimental study was conducted at Combustion Research Facility (CRF) in NPCC. This facility can be used for studying characteristics of combustion of coal, oil, gas, civic garbage and so on at a maximum heating rate of 640MJ/h. The test equipment consists of five parts, which are coal grinding and pneumatic conveying system, combustion system, data acquisition and control system, compressing air and cooling system. The furnace is a cylindrical chamber, it is 4.2m high, and 0.4m in diameter. 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.

Following the carbonization step of the China's chemical fertilizer production of NH_4HCO_3, a CO_2 absorption facility after the electrostatic precipitator of CRF was designed and established in NPCC. The absorption facility consists of a packed absorb tower (250 mm in inner diameter, 2000 mm in height), a flue gas sampling and analysis system, along with ancillary equipment such as a forced fan and cooler (see figure 2).



1. Forced fan　2. Cooler　3. Absorber　4. Flow gauge　5. No.2 Ammonia Pot
6. No.1 Ammonia Pot　7. Pump

Fig.2　Sketch of the Flow Sheet for Absorption Test of CO_2 from Flue Gas

During the experiment, a part of flue gas produced from the coal-fired CRF enters cooler(a heat exchanger) for temperature control. Then, flue gas enters the absorber packed with certain height of some ceramic rings from the bottom. The concentrated aqueous ammonia from No. 1 ammonia pot enters the absorber from the top of the absorber through a spray nozzle. The flue gas and the aqueous ammonia will flow counter-current-wise in tower. Then, some contents of the flue gas will react with aqueous ammonia in the absorb tower. After reaction, flue gas exhausts into atmosphere from the top of the absorber while the mixed ammonia solution flows into No. 2 ammonia pot from the bottom of the absorber. During the test, data acquisition and control system is used to measure the component 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, data on concentrations of substances in the mixed aqueous ammonia solution can be acquired.

The experimental aqueous ammonia was used repeatedly. After each run of tests, the aqueous ammonia in No. 2 ammonia pot flows into No. 1 ammonia pot for the next test. So, the aqueous ammonia used for the next run contains a certain amount of products of last run. Therefore, the concentration of aqueous ammonia for spray will descend run by run.

TEST RESULT AND ANALYSIS

A kind of South China bituminous coal was burned in CRF in NPCC during the period of CO2 capture tests in 2002. Table 1 shows the analytical result of the components of the coal.

Table 1 The components of the experimental coal

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

The absorber was filled with structured packing (25 mm in outer diameter and 25 mm in height of ceramic rings), with packing height 800 mm. Flue gas comes from CRF and then goes through the heat exchanger, which has the temperature of 35 and flow rate of 70 m^3/h, enters the absorber from the bottom, and aqueous ammonia enters the absorber from the top at the flow rate of 200 l/h.

CO_2 Absorption Efficiency

Tests were conducted under different conditions with different concentrations of ammonia in the nozzle. During the test, data acquisition and control system is used to measure the component of O_2 and CO_2 in inlet and outlet of the gas flow of the absorber. The measuring result is shown in Table 2.

Table 2 Tests measuring result

Absorber Inlet					
Operating conditions	1	2	3	4	5
O_2 %	5.7	5.24	5.02	5.74	6.10
CO_2 %	11.25	11.04	10.88	11.12	10.96
Absorber Outlet					
Operating conditions	1	2	3	4	5
O_2 %	11.12	10.95	10.70	11.25	11.66
CO_2 %	0.6	0.7	0.9	1.3	1.6

The measuring data of CO_2 percent were transferred and normalized to the same condition of O_2 concentration of the flue gas. Normalization was used with the following equation:

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

where $[CO_2]$ —— corrected data of CO_2 , %
$[CO_2]_o$ —— measuring data of CO_2, %
x —— the same condition of O_2 concentration, % (assumed x=6)
O_2 —— measuring data of O_2, %

The normalized result is shown in Table 3.

Table 3 The normalized CO_2 concentration

Absorber Inlet					
Operating conditions	1	2	3	4	5
CO_2 %	10.90	10.51	10.21	10.93	11.03
Absorber Outlet					
Operating conditions	1	2	3	4	5
CO_2 %	0.9	1.04	1.3	2.0	2.6

By chemical acid-base titration method, the concentration of the ammonia solution sampled at the inlet and outlet of the liquid flow in absorber during the tests can be acquired. Then, the data of CO_2 absorption efficiency can be obtained under the different mole ratio of NH_3 / CO_2. The test results are shown in Table 4 and figure 3.

Table 4 Absorptive efficiency and molar ratio of NH_3/ CO_2

	Test 1	Test 2	Test 3	Test 4	Test 5
Molar ratio	1.40	1.35	1.3	1.28	1.25
Efficiency %	91.7	90.1	87.3	81.7	76.4

Absorber temp: 35℃ packing height: 800mm
Molar ratio: moles of ammonia (absorbent) at liquid inlet/moles of CO_2 at gas inlet

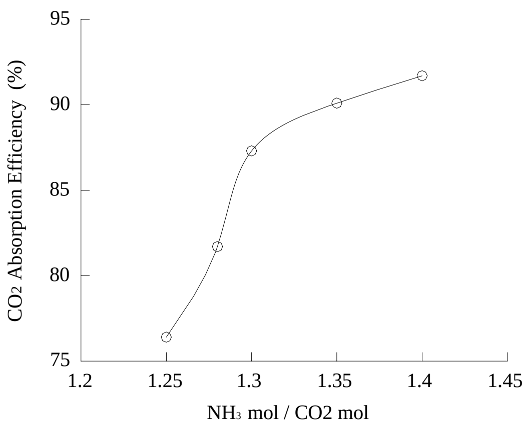


Fig.3 CO_2 absorption efficiency dependence of the NH_3/ CO_2 molar ratio

According to the test results, absorption efficiency of CO_2 was ascended with increase of the molar ratio of NH_3/CO_2. The highest CO_2 absorb efficiency is near 92%. Comparing with that in the carbonization working procedures of the synthetic ammonia production in China, the CO2 concentration decreases from 29.60% at the inlet of gas to 0.30% at the outlet, the efficiency is 99%[3], the CO_2 absorb efficiency of our facility seems to be lower. The reasons may be that working pressure in the synthetic ammonia production is much higher, which is 12 atm, 11 times higher than it of our testing condition; And the CO_2 concentration at the inlet of gas is different: the former is almost 30%, the latter is lower than 12%. As a matter of fact, 90% of CO_2 capture from flue gas is very high efficiency which people never think of before.

Analysis of the mixed ammonia solutions

The mixed ammonia solutions produced contains OH^-, HCO_3^-, CO_3^{-2}, SO_4^{-2} and NO_3^- negative ions. Based on the alkalinity of OH^-, HCO_3^-, 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 can be determined. According to the results of SO_4^{-2} and NO_3^- measured by colorimetry, data on concentrations of the $(NH_4)_2SO_4$ 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.

It is seen in Figure 4 that the carbon in the mixed ammonia solution have two form: HCO_3^- and CO_3^{-2}. The content of HCO_3^- in solution was increased and the content of CO_3^{-2} was decreased, simultaneously, when the NH_3 / CO_2 molar ratio is decreasing. For a certain mole ratio of NH_3 / CO_2, there are a set of the concentration that can be considered of the balance concentrations between NH_4HCO_3 and $(NH_4)_2CO_3$ shown in reaction (R5) in the mixed ammonia solution produced. From the chemical kinetics point of view, when the concentration of NH_4OH was increased, the reaction (R5) would moves toward right. Then, more CO_3^{-2},namely $(NH_4)_2CO_3$) in the solution could be found. Namely, the concentration of HCO_3^- (NH_4HCO_3) would be decreased. On 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 got from the bottom of the tower could be increased. It means that the balance of react equation (R6) will move toward right in order to get more NH_4HCO_3.

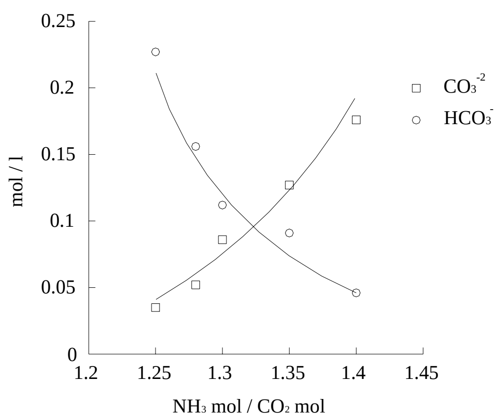


Fig.4 Relation of concentrations of HCO_3^- and CO_3^{-2} in produced ammonia solutions to NH_3/CO_2 molar ratio

From the measuring results of SO_4^{-2} (in Table 5), one may see that the mixed ammonia solution contains a small quantity of SO_4^{-2}. The absorption efficiency of SO_2 (SO_4^{-2}.in solution) was ascended with increase of the NH^3 / CO_2 molar ratio.

Table 5 The concentrations of SO_4^{-2} in solution while different NH_3/CO_2 molar ratio

	1	2	3	4	5
NH^3 / CO_2 molar ratio	1.40	1.35	1.3	1.28	1.25
SO_4^{-2} $\times 10^3$ mol	0.863	0.538	0.450	0.275	0.150

And from our measure result, the content of NO_3^- is less then 1mg/l which is the lower limit of the examination of the measuring equipment. So, spraying aqueous ammonia can capture both SO_2 and NO_2. The absorption efficiency of SO_2 and NO_2 will be analyzed in the further experiments.

Analysis of the chemical thermodynamics

According the date of chemical thermodynamics, the standard of Gibbs free energy change (ΔG^0) of NH_4HCO_3, $(NH_4)_2SO_4$ and NH_4NO_3 products are -159.23kcal/mol, -215.77kcal/mol and -45.58kcal/mol, respectively. Because the tests were processed under the conditions of 35℃ and 1 atmosphere which is close to the standard condition (25℃ and 1 atmosphere), the actual Gibbs free energy changes of above products is very close to the standard, respectively.

According to the principle of the chemical thermodynamics, the bigger the negative standard Gibbs free energy, the more favorable the chemical reaction more takes place. Thus, it can be seen that the order of the reaction with aqueous ammonia should be SO_2 first, CO_2 the second, NO_2 is the last. But from the results of tests, the amount of SO_4^{-2} is small. The reason is that the sulfur content in testing coal is small(0.34%). So the quantity of SO_2 produced by combusting coal is few. And so is the $(NH_4)_2SO_4$ (SO_4^{-2}) produced by reacting ammonia with SO_2 (SO_3).

In addition to very small absolute figure of the standard Gibbs free energy change, the total content of nitrogen in the coal is few (1.16%) And only the organic nitrogen can produce NOx (NO and NO_2)during the coal combustion. NO accounts for more per cent (say, 70%) of NO_X while NO_2 less. And only the latter can solve in water. Then, the concentration of NH_4NO_3 (NO_3^-) is tiny.

CONCLUSTIONS

1) Spraying aqueous ammonia into actual flue gas produced by a coal-fired facility not only captures CO_2 but also absorbs SO_2 and NO_2 from the flue gas. SO_2 reacts favorably with ammonia, then CO_2, NO_2 is last.
2) Absorption efficiency of CO_2 and SO_2 in actual flue gas from coal-fired facility is ascended with increase of the concentration of aqueous ammonia.
3) The absorbed CO_2 in the aqueous ammonia is in the form of HCO_3^- and CO_3^{-2}. For a certain molar ratio of NH_3/CO_2, there are balance concentrations between HCO_3^- and CO_3^{-2} in the mixed ammonia solution produced. By using the mixed ammonia solution spray into flue gas containing CO_2, more NH_4HCO_3 content (higher HCO_3^- concentration) in mixed solution can be obtained.

REFERENCES

1.Presentation in Office of Fossil Energy of U.S.DOE:A Win-Win Proposal for CO_2 Sequestration Via Aqua Ammonia Scrubbing, July 1999

2.Shi-xiang WANG, Bao-he YANG:The Technology and Operation of the Small Synthetic Ammonia Factory, Chemical Industry Publishing Company of China, 1994(in Chinese)

3.The Jilin University:The essential theory of physical chemistry, Higher Education Press, 1995(in Chinese)

4.Zhen-zhong LI, et al:A New CO2 Sequestration Technology for Fossil Fuel Power Generation, Preprint Proceedings of the 1st U.S.-China Symposium on CO_2 Emission Control Science & Technology, pp.75-82, Hangzhou, China, August 22-24, 2001