The Regeneration of Ammonia Solution by Calcium Hydroxide for Carbon Dioxide Absorption from the Flue Gas

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Abstract: The tests of this study were conducted by the semi-continuous flow experiments to absorb the carbon dioxide (CO_2) gas in a bench-scale spraying column reactor. The absorption capacity and the regeneration efficiency of the absorbed ammonia (NH_3) solution were determined. In this study, the maximum regeneration efficiency is 68.4% as the concentration of NH_3 solution is 1% and the ratio of calcium hydroxide ($Ca(OH)_2$) and CO_2 is 1 as well. Furthermore, the absorption capacity of the NH_3 solution decreases from 1.67 to 0.27 kg-CO_2/kg-NH_3 after regenerating four times due to the 30-38% loss each time. Regarding the regeneration kinetics between absorbed products and $Ca(OH)_2$, the comparative degree of covered $Ca(OH)_2$ during the reaction was recognized after fitting by a surface coverage model. Finally, the ammonium bicarbonate (NH_4HCO_3) reduced by $Ca(OH)_2$ to calcium carbonate ($CaCO_3$) solid and NH_3 solution in the regeneration reactions was observed by scanning electron microscope (SEM), Energy-dispersive X-ray spectroscopy (EDS) pictures and X-Ray Diffraction (XRD) analyses. Although the NH_3 solution can be regenerated by $Ca(OH)_2$ effectively in this study, the overall benefit of this process should be estimated further in the energy aspect.

Keywords: Carbon dioxide, absorption, regeneration, ammonium solution, calcium hydroxide.

1. INTRODUCTION

Chemical absorption of carbon dioxide (CO_2) by ammonia (NH_3) solution is proven as an effective method for CO_2 elimination [1, 2]. Wang *et al.* (2007) concluded that NH_3 solution scrubbing is an effective way to reduce the anthropogenic CO_2 emissions *via* life cycle assessment [3]. The reactions between CO_2 and NH_3 solution have been conducted as equations (1) and (2) mainly [1, 2]. Several operating parameters were tested to determine the absorption kinetics of these two reactants [4]. The reaction between NH_3 solution and CO_2 from fossil fuel revealed more significant environmental beneficial than amine system while NH_4HCO_3 as synthetic N-fertilizer [5]. Furthermore, NH_3 solution could be obtained from NH_3 rich wastewaters and taken as a useful and free absorption solvent to capturing of CO_2 for upgrading biogas [6].

$$CO_{2(g)} + 2NH_{3(aq)} + H_2O_{(l)} \leftrightarrow (NH_4)_2CO_{3(S)(aq)} \tag{1}$$

$$CO_{2(g)} + NH_{3(aq)} + H_2O_{(l)} \leftrightarrow (NH_4)HCO_{3(S)(aq)} \tag{2}$$

Although ammonia bicarbonate is one of important synthetic N-fertilizer sources, however, the uncertain impurities of NH_4HCO_3 product is worthy to be concerned while the CO_2 comes from flue gas and/or NH_3 solution comes from wastewater. Therefore, the regeneration of reacted ammonia solution is one of important topics for promoting cost-down and avoiding secondary pollutions. The regeneration reactions in this study were conducted as equation from (3) and (5) [7, 8].

$$\begin{aligned} &Ca(OH)_{2(S)} + (NH_4)_2CO_{3(S)(aq)} \leftrightarrow \\ &CaCO_{3(S)} + 2NH_{3(aq)} + 2H_2O_{(l)} \end{aligned} \tag{3}$$

$$\begin{aligned} &Ca(OH)_{2(S)} + (NH_4)HCO_{3(S)(aq)} \leftrightarrow \\ &CaCO_{3(S)} + NH_{3(aq)} + 2H_2O_{(l)} \end{aligned} \tag{4}$$

$$Ca(OH)_{2(S)} + CO_{2(g)} \leftrightarrow CaCO_{3(S)} + 2H_2O_{(l)} \tag{5}$$

The target of this study is to investigate both absorption and regeneration capacities of NH_3 solution. In addition, the kinetic model and products for regeneration of NH_3 solution by $Ca(OH)_2$ were also estimated.

2. MATERIALS AND METHODS

All tests of this study were carried out in a bench-scale spraying column system shown in Figure **1**. The system was divided into three parts, including a flue gas simulation system, an absorption reactor, and a gas sampling and analyzing system (Figure **2**). Flow rates of pure N_2 and pure CO_2 (San Fu) were controlled by mass flow meters. CO_2 was diluted by N_2 in a plug flow mixer and further diluted by the mass flow-controlled compressed air in another plug flow mixer to the desired concentrations and O_2 contents. The

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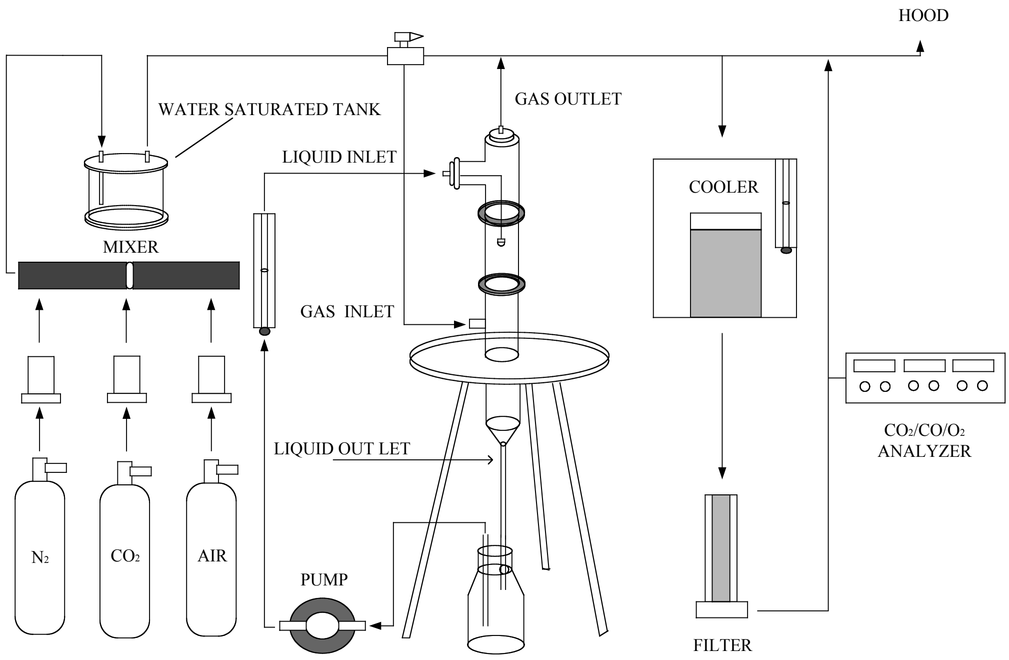

Figure 1: Diagram of bench-scale experimental setup.

simulated flue gas was then heated to 50°C by an electrical heating tape before entering into the absorption reactor.

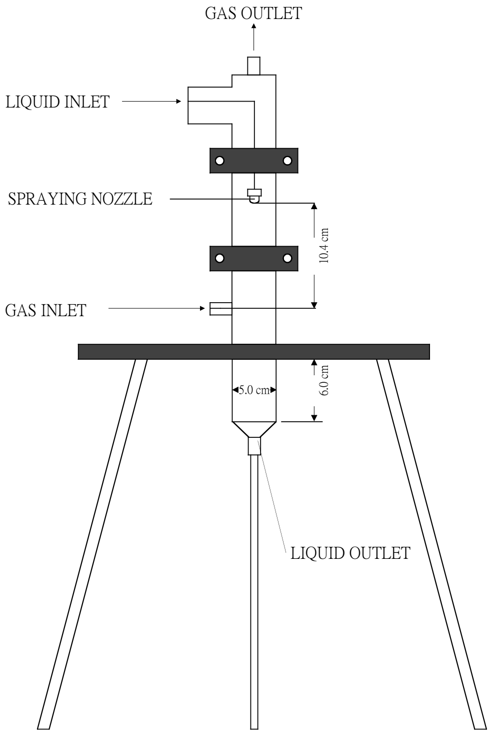

Figure 2: Bench-scale absorption reactor.

The heated simulation flue gas entered a saturator first to make sure it was saturated with water vapor. Then the simulated flue gases were flow through the absorption reactor or bypass to be analyzed by the CO_2/CO/O_2 analyzer (California Analytical Instrument, Inc., Model 300 type).

The NH_3(aq) (Merck, purity 25%) were used to prepare the scrubbing liquor. The $Ca(OH)_2$ (J.T. Baker, purity >98%) and CaO (J.T. Baker, purity >98%) were added into CO_2-saturated scrubbing liquor to regenerate the ammonia.

The reactor that performed the scrubbing liquor regeneration tests was the same as the apparatus used in our previous study [4]. The crystalline solids in the solutions for absorbent regeneration experiments were determined by scanning electron microscope (SEM), Energy-dispersive X-ray spectroscopy (EDS) pictures and X-Ray Diffraction (XRD) analyses [1].

The operating conditions are listed in Table **1** and Table **2** in details.

Table 1: Operating Conditions of Absorption Experiments

Parameters	**Values**
CO_2 concentration in the simulated flue gas (%)	15
The flowrate of simulated flue gas (L/min)	4
The temperature of simulated flue gas (°C)	50
NH_3 (aq) concentration (%)	1, 3, 5
The flowrate of scrubbing liquor (mL/min)	200
The temperature of scrubbing liquor (°C)	35

Table 2: Operating Conditions of Regeneration Experiments

Set	CO_2 (%)	NH_3(aq)	Stoichiometric ratio	Regeneration time
1	15	1	1/1	100 sec ~ 100 min.
2	15	1, 3, 5	1/1	20 min.
3	15	1	0.75/1, 1/1, 1.5/1	20 min.
4	15	1	1/1	Regeneration cycles (1~4)

3. RESULTS AND DISCUSSION

The definitions of absorption capacity (AC), regeneration efficiency (RE), and relative regeneration efficiency (RRE) are listed as below.

$$\mathrm{AC\ (kg\ CO_2/kg\ NH_3)} = \frac{\mathrm{CO_2\ absorbed}}{\mathrm{NH_3\ added\ in\ the\ absorption\ solution}} \quad (6)$$

$$\mathrm{RE\ (\%)} = \frac{\mathrm{CO_2\ Absorption\ Capacity\ of\ regenerated\ absorbent}}{\mathrm{CO_2\ Absorption\ Capacity\ of\ fresh\ absorbent}} \quad (7)$$

$$\mathrm{RRE\ (\%)} = \frac{\mathrm{AC_{i+1}}}{\mathrm{AC_i}} \qquad i = 0, 1, 2, 3 \quad (8)$$

3.1. Effect of Ammonium Concentration

As shown in Figure **3**, the regeneration efficiency decreases when ammonia concentration increases. It may result from the irreversible reactions exist and ammonia volatilizes from absorption solution in the duration of absorption and regeneration tests. Except the ammonium carbonate and ammonium bicarbonate, the reaction between CO_2 and ammonium solutions also may produce ammonium carbamate (NH_2COONH_4) according to Eq. (9). Song *et al*. (2014) indicated that the concentration of ammonium carbamate increases as the ammonia concentration increases at a given inlet CO_2 concentration [9]. If ammonium carbamate cannot be regenerated by $Ca(OH)_2$ to ammonia, the regenerated ammonium solutions will lose some CO_2 absorption capacity.

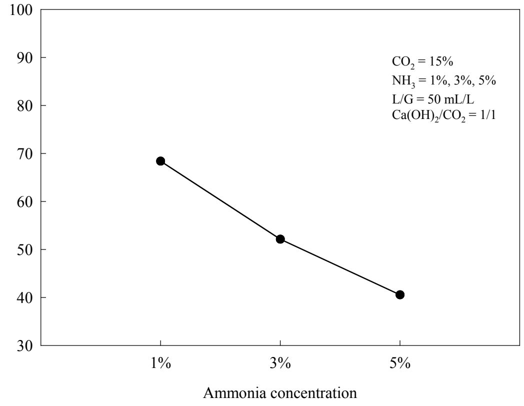

Figure 3: Effect of ammonia concentration on regeneration efficiency.

$$CO_{2(g)} + 2NH_{3(aq)} \rightarrow NH_4^+ + NH_2COO^-_{(aq)} \quad (9)$$

In fact, ammonium carbamate is approved for use as an inert ingredient in aluminum phosphide pesticide formulations and used in the aluminum phosphide formulation to reduce the potential fire hazard of the phosphine in US Environmental Protection Agency (EPA) [10]. This approval induces ammonium carbamate reusable if it can be purified further.

3.2. Effect of $Ca(OH)_2/CO_2$ Stoichiometric Ratio

As shown in Figure **4**, the regeneration efficiency is better as $Ca(OH)_2/CO_2$ is 1 than 0.75. However, the regeneration efficiency decreases as $Ca(OH)_2/CO_2$ increases from 1 to 1.5. It probably results from the increase of masked reaction surface and limitation of mass transfer after adding excessive calcium hydroxide. Furthermore, the amounts of calcium hydroxide added into the solutions increase as the ammonium concentration increases from 1% to 5% if $Ca(OH)_2/CO_2$ ratio is the same, the mask effect also becomes more significant due to the limitation of mass transfer. In addition, the existence of irreversible reactants is probably another barrier for generation at higher $Ca(OH)_2/CO_2$ Stoichiometric Ratio (ex. 1.5). Consequently, the overall effect of irreversible reactants, masked reaction surface and limitation of mass transfer results in the regeneration performance.

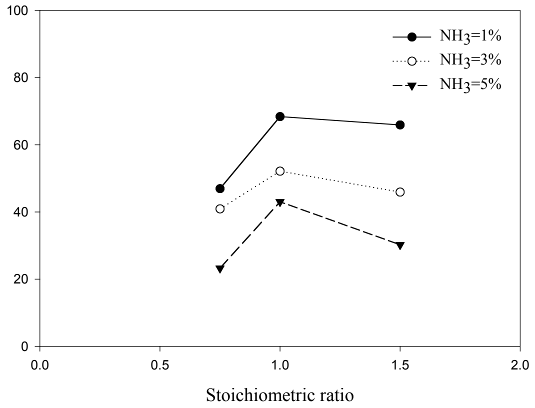

Figure 4: Effect of stoichiometric ratio on the regeneration efficiency.

(CO_2 = 15%, NH_3 = 1%/3%/5%, L/G = 50 mL/L, $Ca(OH)_2/CO_2$ = 1.5/1、1/1、0.75/1)

3.3. Effect of Regeneration Cycles

The relative regeneration efficiencies are in the range of 62-70% as shown in Figure **5**. It indicates that the reactive ammonium in the solution will lose about 30-38% in each regeneration process partly due to the production of irreversible reactants and the volatilization of ammonia probably. The regeneration efficiencies seem to be a constant. Therefore, the percentage of reactants that cannot be regenerated by $Ca(OH)_2$ might be given. If ammonium carbamate is one of the reactants that cannot be regenerated by $Ca(OH)_2$, the proportion of Eq. (9) of the reactions between ammonia solution and carbon dioxide should be no more than 35%. If ammonium carbamate is the major irreversible reactant, it is worthy to be regenerated for CO_2 absorption further by other methods if the energy consumption is low enough [11].

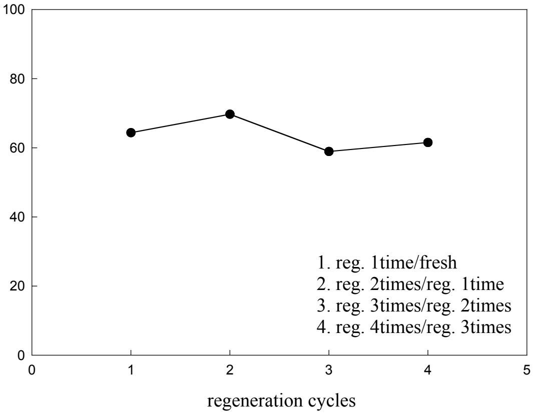

Figure 5: Effect of regeneration cycles on regeneration efficiency.

(CO_2 = 15%, NH_3 = 1%, L/G = 50 mL/L, $Ca(OH)_2/CO_2$ = 1/1)

3.4. Kinetic Analysis

According to the assumption of surface coverage model [7], when the carbonation of hydrated lime is controlled by surface reaction and that the surface reaction only takes place on the reactive surface which is not covered by product, the relation between conversion and time can be expressed as:

$$X = \frac{\left[1 - \exp\left(-k_1 k_2 t\right)\right]}{k_2} \quad \text{for } n = 1 \qquad (10)$$

$$X = \frac{\left[\ln\left(1 + k_1 k_2 t\right)\right]}{k_2} \quad \text{for n = 2} \qquad (11)$$

$$X = \frac{\left\{1 - \left[1 - \left(1 - n\right) k_1 k_2 t\right]^{(2-n)/(1-n)}\right\}}{\left[\left(2 - n\right) k_2\right]} \quad \text{for n} \neq 1, 2 \qquad (12)$$

where k_1 and k_2 represent the rate constant and mass transfer between $Ca(OH)_2$ and CO_2, respectively.

Shih *et al.* (1999) had published the detailed development of Eqs (10) to (12) [7]. After comparing these three equations, Li (1996) and Shih *et al*. (1999) found that Eq (10) is the simplest to use and predict the final conversion directly by the reciprocal of k_2 [7, 8].

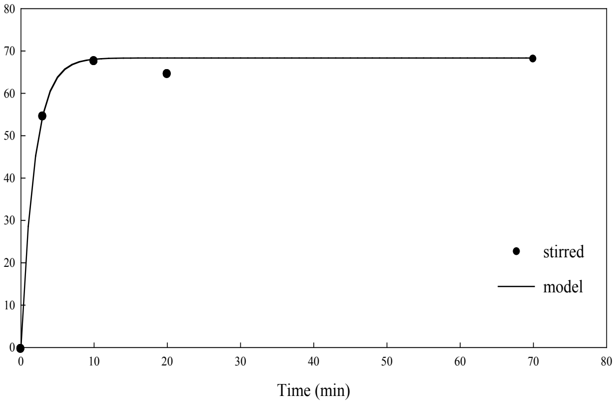

Figure 6: Difference between experimental data and the predicted value of surface coverage model.

(CO_2 = 15%, NH_3 = 1%, L/G = 50 mL/L, $Ca(OH)_2/CO_2$ = 1/1).

Using the Eq. (10) to predict the tested results in this study, the predicted values fitted with the experimental data very well as shown in Figure **6**. The k_1 and k_2 values obtained in this study and the previous study [7] are listed in Table **3**. The k_1 value obtained in this study is higher than that of the previous study [7]. It results from the differences of free energy and equilibrium constant's values listed in Table **4** between Eqs. (3) to (5). The k_2 values obtained in this study was lower than that of the previous study [7]. In the previous study [7], the gas-solid phase reaction between CO_2 and $Ca(OH)_2$ as Eq. (5) was conducted in a differential fixed bed reactor. The surface of unreacted $Ca(OH)_2$ was easily masked by the reaction product in this type of reactor. Therefore, according to the definition of k_2, its surface area of unreacted $Ca(OH)_2$ decreased with the reaction. In this study, we conducted the liquid-solid reaction between $(NH_4)HCO_3/(NH4)_2CO_3$ and $Ca(OH)_2$ as Eqs. (3) and (4) in a stirred tank. The surface area seems to be not masked significantly relatively since the k_2 in this study is lower than that of the previous study.

Table 3: Differences of k_1 and k_2 Values Between this Study and the Previous Study [8]

	This study	The previous study [8]
k_1	0.37	0.01
k_2	1.463	3.03

Table 4: Comparison of Thermal Dynamics Constants

	Eq. (1)	Eq. (3)	Eq. (4)	Eq. (5)
ΔG° (kJ/mol)	-2.2	-79	-72.8	-25.4
K	2.43	6.93×10^{13}	5.68×10^{12}	2.83×10^{4}

3.5. Identification of Reaction Products

According to equations. (1) and (2), the reaction products between CO_2 and ammonia solution should be $(NH_4)_2CO_3$ and NH_4HCO_3 in the majority. The initial pH values of 1%, 3% and 5% ammonia solutions were 11.07, 11.56 and 11.66, respectively. After absorbing the 15% CO_2, the final pH values of 1%, 3% and 5% ammonia solutions dropped down to 8.22, 8.43, 8.48, respectively (Figure **7**). In this pH range, the predominant speciation in CO_2-HCO_3-H_2CO_3 system is bicarbonate. The main reaction product in the absorption solution should be NH_4HCO_3. Bai & Yeh (1997) and Chen *et al*. (2012) also indicated that the predominant reaction product of CO_2 absorption by ammonium solutions is NH_4HCO_3 [1, 12]. The crystalline solids in the solutions for absorbent regeneration experiments were determined by SEM, EDS and XRD analyses.

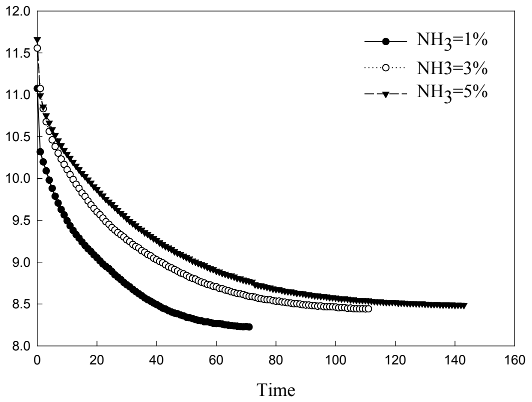

Figure 7: pH variance of ammonium solutions.

As shown in Figure **8** and **9**, the SEM and EDS pictures reveal that the reaction product has a surface structure similar to that of standard carbon carbonate ($CaCO_3$) powders. The EDS analysis reveals that the main elements in the solid-phase reaction product are carbon, oxygen, and calcium. It is similar to the prediction of regeneration reaction mechanism (Eqs. (3) to (5)). Furthermore, the nitrogen element is none in the solid-phase product *via* EDS analysis. It reveals that the NH_4HCO_3 should have been reduced to $CaCO_3$ solid and NH_3 solution during the regeneration reaction. Finally, the XRD pattern of the reaction products is also compared to standard compounds and identified to be $CaCO_3$ and unreacted carbon hydroxide (Figure **10**).

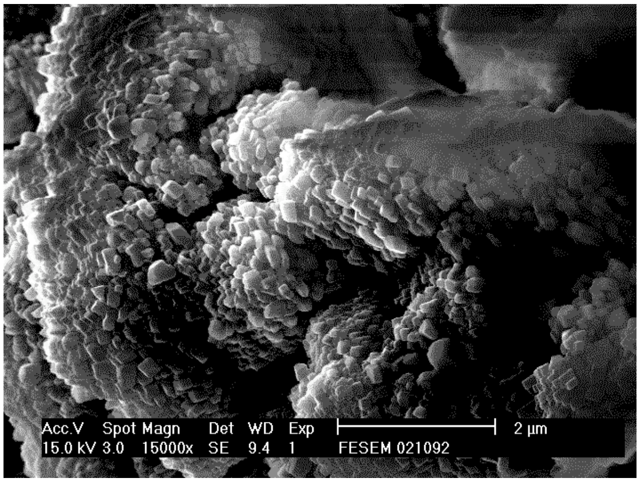

Figure 8: SEM of solid-phase reaction product.
(CO_2=15%, NH_3=1%, L/G=50mL/L, CaO/CO_2=1/1).

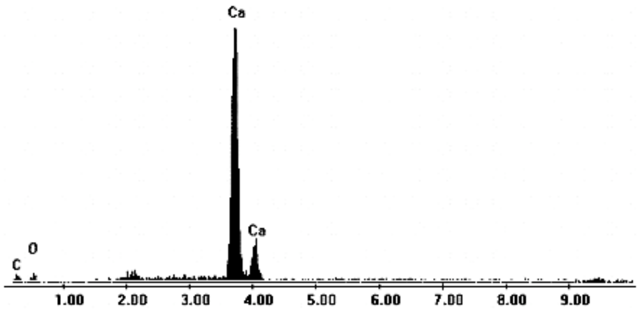

Figure 9: The EDS of solid-phase reaction product.
(CO_2=15%, NH_3=1%, L/G=50 mL/L, CaO/CO_2=1/1).

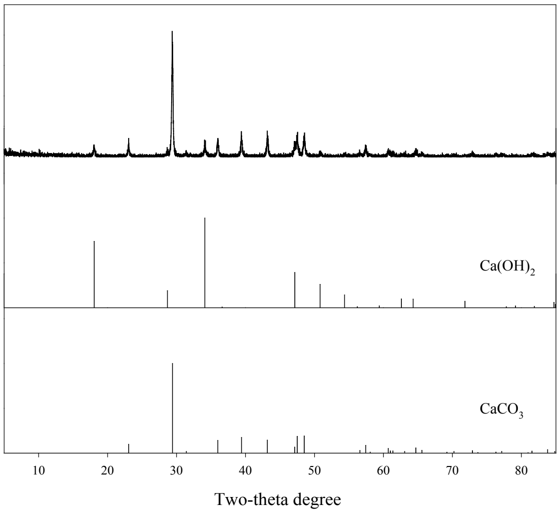

Figure 10: XRD of solid-phase reaction product.
(CO_2=15%, NH_3=1%, L/G=50 mL/L, CaO/CO_2=1/1).

4. CONCLUSIONS

In this study, the absorption capacity and the regeneration efficiency of the absorbed NH_3 solution were determined *via* the semi-continuous flow experiments to absorb the CO_2 gas in a bench-scale spraying column reactor. The maximum regeneration efficiency, 68.4% was achieved and the absorption capacity of the NH_3 solution decreases from 1.67 to 0.27 kg-CO_2/kg-NH_3 after regenerating four times due to the 30-38% loss each time. The comparative degree of covered $Ca(OH)_2$ during the reaction was recognized and reveals that regeneration loss no more than 35% may arise from the production of irreversible byproducts. The comparative degree of covered $Ca(OH)_2$ during the reaction between absorbed products and $Ca(OH)_2$ was recognized after fitting by a surface coverage model. The regeneration products identified by SEM, EDS pictures and XRD analyses were $CaCO_3$ solid and NH_3 solution in the majority.

ACKNOWLEDGMENT

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NOMENCLATURE

k_s = initial reaction rate of solid, mol/(min m^2)

$k_1 = k_s S_g M$, min^{-1}

$k_2 = k_p/(S_g M)$

n = constant defined by Eqs. (6) to (8)

S_g = initial specific surface area of solid, m^2/g

T = reaction temperature, K

t = time, min

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