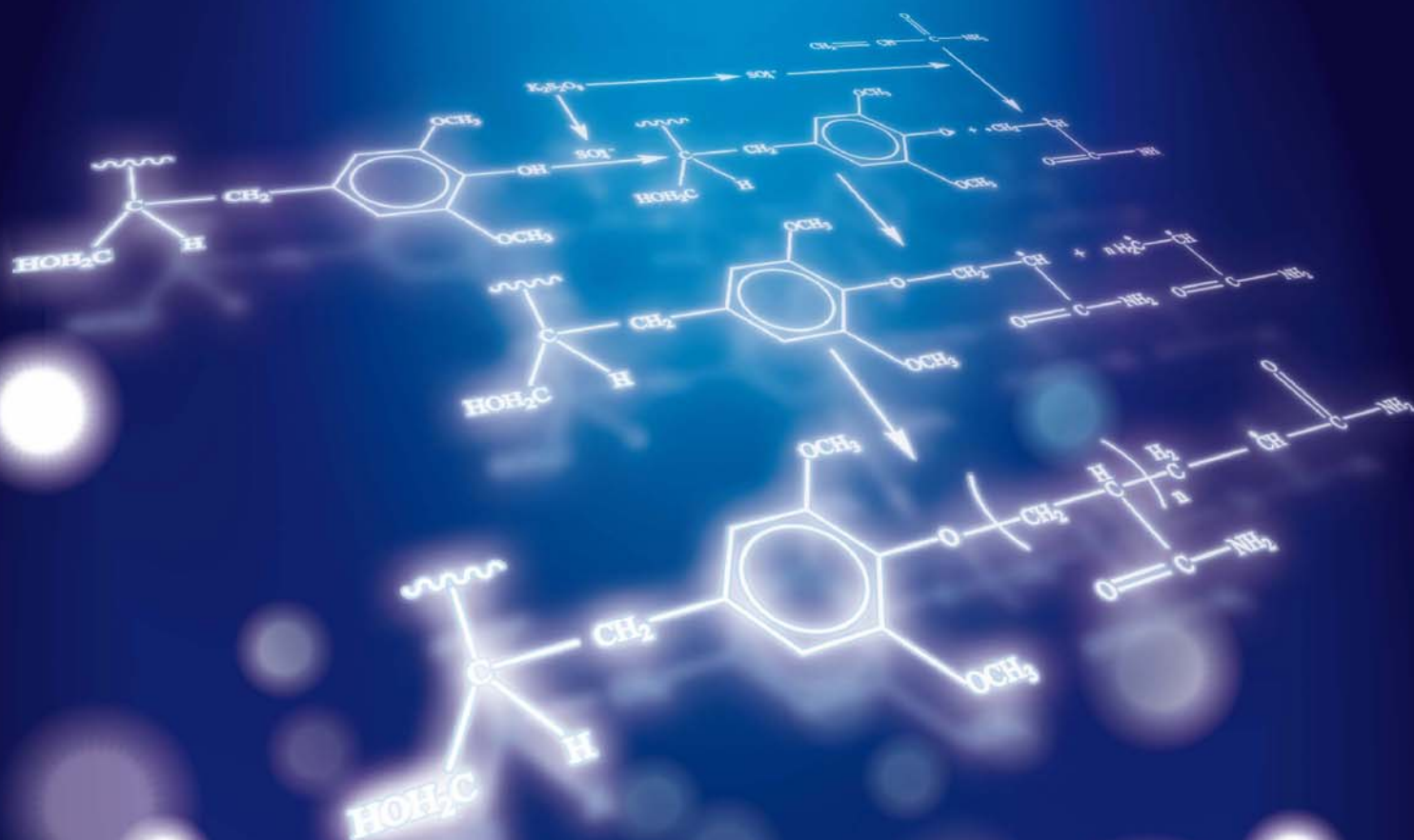


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## Effects of amine, amine salt and amide on the behaviour of carbon dioxide absorption into calcium hydroxide suspension to precipitate calcium carbonate

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Yoshiki Wakimoto<sup>3</sup>, Yoshiaki Fukushima<sup>1,2</sup>

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### Abstract

The amount of carbon dioxide (CO<sub>2</sub>) absorption and calcium ion (Ca<sup>2+</sup>) concentration besides the pH of aqueous solution were observed during the CO<sub>2</sub> absorption to precipitate calcium carbonate (CaCO<sub>3</sub>) from calcium hydroxide (Ca(OH)<sub>2</sub>). A reaction rate-limiting effect of an amount of CO<sub>2</sub> absorption without any organic additives in the early stage of the precipitation was observed, which was attributed to an interruption effect of bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) on the precipitation of CaCO<sub>3</sub>. The improvement for the reaction rate was achieved not only by amine additives but also by neutral additives such as ε-caprolactam or amine salt. When the hexamethylene diamine was dissolved in the solution, successive change of crystal forms of CaCO<sub>3</sub> aragonite to calcite in aqueous suspensions, confirmed by Ca<sup>2+</sup> concentration change and X-ray diffraction, was concluded that a local environment around the amine group in aqueous solution and an interaction of the diamine with precipitated CaCO<sub>3</sub> particles were important factors for these reactions.

**Key words:** carbon dioxide absorption; calcium carbonate precipitation; local functional group interaction

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### Introduction

The present technique to separate CO<sub>2</sub> from an exhausted gas before releasing to the atmosphere is divided in two steps. The first step uses an amine as alkali, to capture CO<sub>2</sub> from the exhausted gas. Then the captured CO<sub>2</sub> is separated from the solvent by the temperature or pressure swing. In the final step, the concentrated CO<sub>2</sub> gas is pressurized to be a supercritical CO<sub>2</sub> liquid disposed in some deep geological areas (D'Alessandro et al., 2010; Huang et al., 2001) or it is converted to be a carbonate salt such as calcium carbonate (CaCO<sub>3</sub>) which is ensured that CO<sub>2</sub> is fixed safely and environmentally in long term.

Efforts towards finding the inexpensive, energy-saved, quick and simple processes for converting carbonate minerals have been developed by using various reactants and processes. For example Nelson (2004), Krevor and Lackner (2011) and Lackner et al. (1995) investigated the CO<sub>2</sub> sequestration by a natural and artificial rock such as wollastonite, forsterite and lizardite based on the rock weathering reaction. While other researchers proposed

waste cement (Iizuka et al., 2004; Kodama et al., 2008; Yamasaki et al., 2000), slag from steel making (Kodama et al., 2008; Tsuneo et al., 2001; Yogo et al., 2004) and brine (Liu et al., 2005) as an alkaline earth metal source in the mineral carbonation.

In order to improve the reaction rate of the mineral carbonation, a mechanochemical method that is a grinding of alkaline mineral to proper size under gaseous CO<sub>2</sub> (Nelson, 2004) and a surface activation of a raw mineral surface (Maroto-Valera et al., 2005) have been proposed. A bio-mimetic method in which an enzyme is added in an aqueous process of the carbonate formation (Liu et al., 2005) has been also reported.

The fixed calcium carbonates have been found generally as shells, corals or other structural materials in nature. Calcium salts formation process in natural shells or bones have been studied for bio-mimetic composite materials (Lin and Meyers, 2005; Hu et al., 2011; Fu et al., 2005), besides the CO<sub>2</sub> captures. Additives for control or promoting the carbonate formation were proposed (Bentov et al., 2010; Kim and Park, 2010; Wang et al., 2010) and processes of the absorption of CO<sub>2</sub> into aqueous solutions followed by the precipitation were analyzed (Chen et al.,

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1997). However, the complicated interactions between water ( $\text{H}_2\text{O}$ ), hydronium ion ( $\text{H}_3\text{O}^+$ ), hydroxide ion ( $\text{OH}^-$ ),  $\text{CO}_2$ ,  $\text{HCO}_3^-$ , carbonate ion ( $\text{CO}_3^{2-}$ ),  $\text{Ca}^{2+}$  and other ions due to additives, have been still blocked to understand. When organic or inorganic additional ions are coexisted in the solutions, the interactions of the additive ions with surfaces of precipitated carbonate particles should affect the precipitation reactions, apart from the complicated interaction between the ions in aqueous solutions.

In this study, an amount of  $\text{CO}_2$  absorption and  $\text{Ca}^{2+}$  concentration change during the process were monitored besides the pH change and the analysis of precipitated powder was conducted. Information of  $\text{CO}_2$  absorption amount should be useful to discuss the effect of additives during the  $\text{CO}_2$  absorption. In order to observe an equilibrium of the solid  $\text{Ca}(\text{OH})_2$  in aqueous suspensions with various polymorphs of  $\text{CaCO}_3$ ; calcite (solubility product:  $\log K_{\text{sp}} = -8.48$ ), aragonite (solubility product:  $\log K_{\text{sp}} = -8.33$ ) and vaterite (solubility product:  $\log K_{\text{sp}} = -7.92$ ) (Visscher and Vanderdeelen, 2003),  $\text{Ca}^{2+}$  change monitoring was employed. This information should be an important factor to control the precipitation process whereas a limited information is available.

The authors picked out hexamethylene diamine-adipic acid salt (nylon 6-6 salt) and  $\epsilon$ -caprolactam, which were related compounds with natural amino acids in biomineralization process, they are expected to be useful as a monomer of polyamide and to promote the  $\text{CO}_2$  absorption due to the basic properties around the amine group. Effects of hydrophilic amine group to the carbamate formation from the view point of ionic arrangement in aqueous solutions and the effect of hydrophobic groups in these molecules from the view point of the surface of solid precipitates are discussed in comparison of diamine, amine salts and lactam.

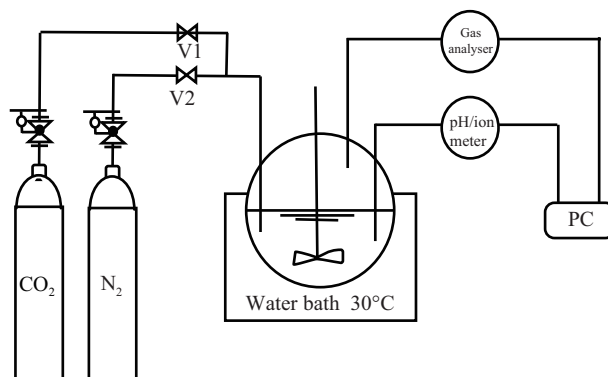
## 1 Materials and methods

### 1.1 Chemicals

Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ , assay 96%, Wako), hexamethylene diamine ( $\text{C}_6\text{H}_{16}\text{N}_2$ , assay 96%, Sigma-Aldrich), adipic acid ( $\text{C}_6\text{H}_{10}\text{O}_4$ , assay 99.5%, Wako) and  $\epsilon$ -caprolactam ( $\text{C}_6\text{H}_{11}\text{NO}$ , assay 99.7%, Wako) were used in this study and the deionization water was employed to prepare a suspension. The samples were prepared on a mass base with a balance precision of  $\pm 1 \times 10^{-4}$  g. The aqueous suspensions with 500 mL of water containing the listed components in **Table 1** were prepared.

### 1.2 Observation of $\text{CO}_2$ absorption process

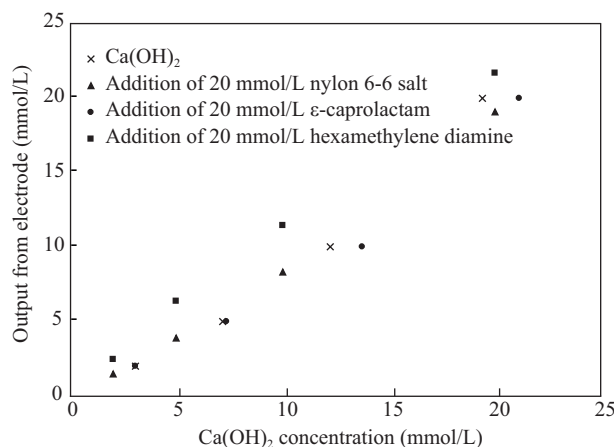
A schematic diagram of the  $\text{CO}_2$  absorption experiment is shown in **Fig. 1**. The suspensions with the components listed in **Table 1** were kept at  $30^\circ\text{C}$ , by using a water bath. The mixed gas  $\text{CO}_2$  with  $\text{N}_2$  ( $\text{N}_2:\text{CO}_2 = 95:5$  vol.%) was bubbled into the suspensions in the glass flask with



**Fig. 1** Schematic diagram of the stirred reactor set-up.

total flow rate at 1 L/min. The pH and  $\text{Ca}^{2+}$  concentration change was monitored by using a pH electrode (9678-10D, Horiba, Japan) and  $\text{Ca}^{2+}$  selective electrode (6583-10C, Horiba, Japan) with ion/pH meter (D-53, Horiba, Japan). As the output from  $\text{Ca}^{2+}$  selective electrode was strongly affected by the coexisting ions as amine, we checked the relation between the electrode output and the  $\text{Ca}^{2+}$  concentration, which was confirmed by ion-chromatography, and the calibration curves were obtained as shown in **Fig. 2**. In order to collect the data to the computer, the Horiba data navi software was used by setting the sampling at every 3 sec.

Concentration of  $\text{CO}_2$  in the exhausted gas was monitored by gas analyzer (350-s, Testo, Germany) using infrared gas sensor at pump flow rate 1.23 L/min at every 3 sec. The data were collected and recorded to the computer by software (Testo easy emission V.2.5 SP.1., Testo, Germany). The total amount of  $\text{CO}_2$  absorption was estimated by differences between the total amount of  $\text{CO}_2$  in the inlet gas and the exhausted gas. The monitoring was continued until no change was found in the pH,  $\text{Ca}^{2+}$  concentration and the amount of  $\text{CO}_2$ . The precipitated  $\text{CaCO}_3$  was collected by a filtration. The  $\text{CaCO}_3$  precipitation yield and  $\text{CO}_2$  conversion to  $\text{CaCO}_3$  were calculated based on the



**Fig. 2** Calibration curves of selective  $\text{Ca}^{2+}$  electrode.



**Table 1** Chemical components used in the experiment

Sample		Ca(OH) <sub>2</sub>	Organic additive		
			Hexamethylene diamine(mmol/L)	Adipic acid (mmol/L)	ε-Caprolactam (mmol/L)
1	Without additive	20	–	–	–
2	Hexamethylene diamine	20	5	–	–
3	5 mmol/L	20	10	–	–
4	10 mmol/L	20	20	–	–
5	200 mmol/L	20	200	–	–
6	Nylon 6-6 salt	20	5	5	–
7	5 mmol/L	20	10	10	–
8	10 mmol/L	20	20	20	–
9	200 mmol/L	20	200	200	–
10	ε-Caprolactam	20	–	–	5
11	5 mmol/L	20	–	–	10
12	10 mmol/L	20	–	–	20
13	200 mmol/L	20	–	–	200

following Eqs. (1) and (2).

$$Y_{\text{CaCO}_3} = \frac{M_{\text{CaCO}_3}}{M_{\text{Ca(OH)}_2}} \times 100\% \quad (1)$$

$$Y_{\text{CO}_2} = \frac{M_{\text{CaCO}_3}}{A_{\text{CO}_2}} \times 100\% \quad (2)$$

where,  $Y_{\text{CaCO}_3}$  is  $\text{CaCO}_3$  precipitation yield,  $M_{\text{CaCO}_3}$  is mole of precipitated  $\text{CaCO}_3$ ,  $M_{\text{Ca(OH)}_2}$  is mole of  $\text{Ca(OH)}_2$ .  $Y_{\text{CO}_2}$  is  $\text{CO}_2$  conversion to  $\text{CaCO}_3$ , and  $A_{\text{CO}_2}$  is total amount of  $\text{CO}_2$  absorption.

### 1.3 Analysis of precipitates

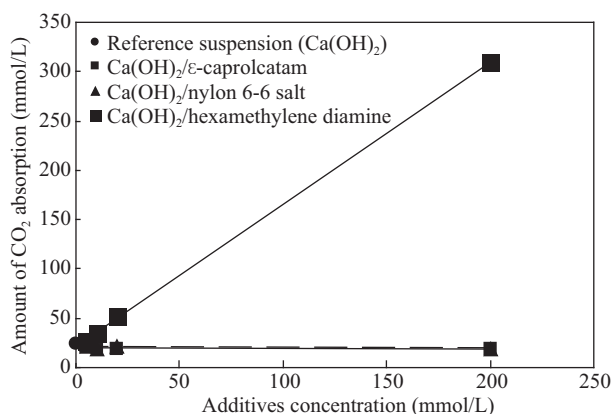
The precipitated samples were collected by filtration, drying at 55°C and analyzed by X-ray diffraction (XRD, RINT-2200, Rigaku, Japan). The analysis was performed by using 0.3 mm slit and  $\text{CuK}\alpha$  with wave length of 0.154 nm under 40 kV and 30 mA as an X-ray source.

## 2 Results

### 2.1 Amount of $\text{CO}_2$ absorption and $\text{CaCO}_3$ precipitation yield

**Table 2** lists the amount of  $\text{CO}_2$  absorption and  $\text{CaCO}_3$  precipitation from the  $\text{Ca(OH)}_2$  suspensions with different concentrations and additives. As some amount of  $\text{Ca}^{2+}$  in the initial suspensions and  $\text{CO}_2$  absorbed in the suspensions were not used to form  $\text{CaCO}_3$ , but they remained in the final suspensions, thus the  $\text{CaCO}_3$  precipitation yield and the  $\text{CO}_2$  conversion values in **Table 2** that were not 100%.

**Table 2** shows that the initial pH of the suspensions was not affected by the additives except the samples 6–9 affected by the neutralization of adipic acid. Most of the final pH of the samples were neutral, except the samples 2–5 due to the strong base effect of hexamethylene diamine.



**Fig. 3** Correlation between the amount of  $\text{CO}_2$  absorption and the additives.

The  $\text{CO}_2$  absorption amount was increased proportionally with hexamethylene diamine concentration increase, in contrast, other additives did not increase the  $\text{CO}_2$  absorption amount as shown in **Fig. 3**.

The hexamethylene diamine could promote the yield of precipitation whilst the hexamethylene diamine neutralized by the adipic acid was unfavorable to the precipitation yield. As regards the effect of ε-caprolactam, it did not show a significant effect on the precipitation yield.

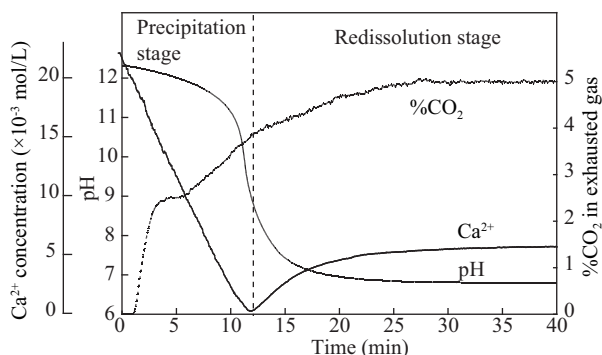
The absorbed  $\text{CO}_2$  was not only used for making  $\text{CaCO}_3$  precipitates but also for making equilibrium with  $\text{Ca}^{2+}$  or organic amine ions as a form of  $\text{CO}_3^{2-}$  or  $\text{HCO}_3^-$ . A high % $\text{CO}_2$  conversion to  $\text{CaCO}_3$  showed the absorbed  $\text{CO}_2$  presented in  $\text{CaCO}_3$  form, less  $\text{CO}_3^{2-}$  or  $\text{HCO}_3^-$  were remained in the solution for the samples coexisted with ε-caprolactam or diamine adipic acid salts.

### 2.2 Changing of pH, % $\text{CO}_2$ in exhausted gas and $\text{Ca}^{2+}$ concentration in $\text{Ca(OH)}_2$ without additive

The changing of pH, % $\text{CO}_2$  in the exhausted gas and the  $\text{Ca}^{2+}$  concentration in sample 1 can be divided in two

**Table 2** Amount of CO<sub>2</sub> absorption and CaCO<sub>3</sub> precipitation yield from the different concentration and types of additives

Sample		Initial pH	Final pH	CO <sub>2</sub> absorption (mmol/L)	CaCO <sub>3</sub> precipitation (mmol/L)	CaCO <sub>3</sub> precipitation Yield	%CO <sub>2</sub> conversion to CaCO <sub>3</sub>
1	Without additive	12.4	6.9	24	15.4	77%	62%
2	Hexamethylene diamine						
3	5 mmol/L	12.3	7.0	26	17.4	87 %	66%
4	10 mmol/L	12.3	7.3	34	18.2	91%	52%
5	20 mmol/L	12.3	7.5	52	18.4	92%	34%
6	200 mmol/L	12.5	8.3	310	18.4	92%	6%
7	Nylon 6-6 salt						
8	5 mmol/L	12.2	7.0	20	14.4	72%	69%
9	10 mmol/L	12.0	6.9	20	15.0	75%	78%
10	20 mmol/L	11.2	6.9	22	12.8	64%	58%
11	200 mmol/L	9.3	7.0	20	10.0	50%	51%
12	ε-Caprolactam						
13	5 mmol/L	12.3	6.9	22	15.2	76%	71%
14	10 mmol/L	12.3	6.9	20	15.2	76%	74%
15	20 mmol/L	12.3	6.9	20	15.6	78%	81%
16	200 mmol/L	12.3	6.9	20	18.6	93%	97%

**Fig. 4** Changing of Ca<sup>2+</sup> concentration, pH and %CO<sub>2</sub> in the exhausted gas in the sample 1 in Table 2 (Ca(OH)<sub>2</sub> suspension without additive).

stages as shown in Fig. 4.

In pH change and Ca<sup>2+</sup> concentration curve, the process was divided into two stages. The precipitation stage, the Ca<sup>2+</sup> concentration was drastically decreased to the minimum point and the pH was decreased, which would be resulted in the rapid hydrolysis reaction of CO<sub>2</sub> with excess OH<sup>-</sup> promoting the CO<sub>2</sub> dissolution and the CaCO<sub>3</sub> precipitation.

The CO<sub>2</sub> concentration in the exhausted gas was steeply increased, then it showed a plateau, that would be attributed to the reaction rate limit. With relate to the pH changing, at the beginning period, the pH was slightly changed because the amount of OH<sup>-</sup> could neutralize the H<sub>3</sub>O<sup>+</sup> from the CO<sub>2</sub> dissolution which was the acid-base reaction.

In the redissolution stage, the Ca<sup>2+</sup> concentration was gradually increased again because the pH value was low enough to dissolve the CaCO<sub>3</sub> particles to be calcium bicarbonate (Ca(HCO<sub>3</sub>)<sub>2</sub>), as discussed by Uebo et al. (1992). During this stage, gradual decrease of the pH and CO<sub>2</sub> absorption were continued to reach the equilibrium at

pH 7 to the same value of CO<sub>2</sub> in the inlet gas (5 vol.%).

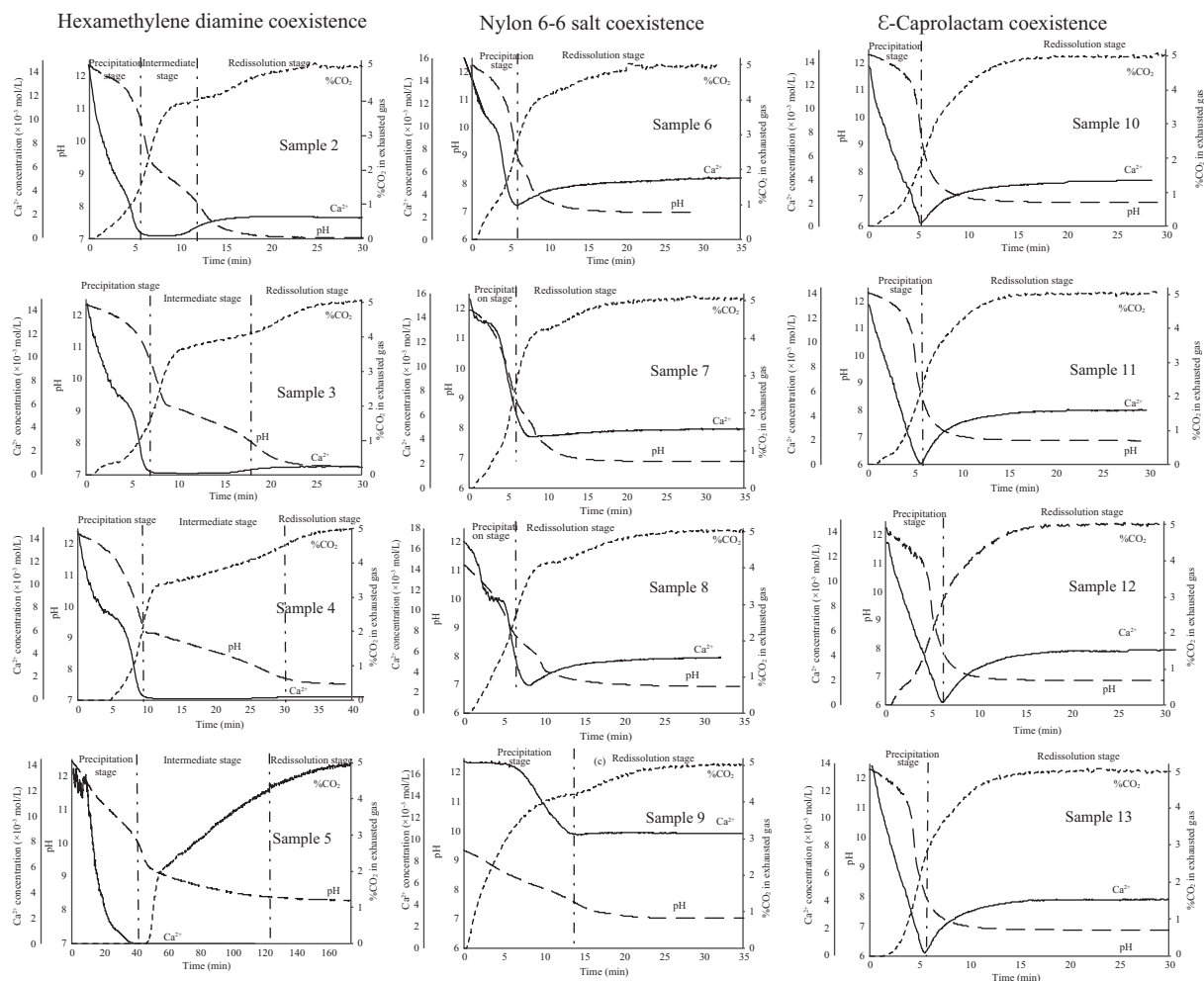
### 2.3 Variation of pH, %CO<sub>2</sub> in exhausted gas and Ca<sup>2+</sup> concentration in Ca(OH)<sub>2</sub> with coexisted materials

The experimental results with coexisted hexamethylene diamine showed the changing in three stages, while nylon 6-6 salt and ε-caprolactam salt showed two stages as shown in Fig. 5.

When the hexamethylene diamine was dissolved in the aqueous solution, additional stage was observed between the precipitation stage and the redissolution stage observed in Fig. 4 for samples without additives. In the intermediate stage, Ca<sup>2+</sup> concentration was not changed at almost zero but the gradual change in pH and CO<sub>2</sub> absorption amounts were continued. The results suggested the neutralization equilibrium among basic amine ions, acid CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> ions in the aqueous systems was continued before the redissolution of CaCO<sub>3</sub> until the CO<sub>2</sub> absorption was saturated.

When the adipic acid was coexisted in the solutions (Fig. 5 samples 6–9), the intermediate stage of the samples only with the hexamethylene diamine was not found but the Ca<sup>2+</sup> ions were still detected in the solutions even after the CO<sub>2</sub> absorption was saturated. The stepwise change in Ca<sup>2+</sup> concentration in the precipitation stage, which was observed in the sample with hexamethylene diamine, was also observed.

The CO<sub>2</sub> absorption curves shown in Fig. 5 (samples 10–13) resembled to that without any additives shown in Fig. 4, except Ca<sup>2+</sup> concentration change in the precipitation stage which was high reaction rate. Although it took about 30 min to absorb CO<sub>2</sub> to precipitate CaCO<sub>3</sub> for the sample without additives shown in Fig. 4, almost half time was necessary for the reaction when ε-caprolactam was coexisted in the suspension under the condition in



**Fig. 5** Changing of  $\text{Ca}^{2+}$  concentration, pH and  $\%\text{CO}_2$  in the exhausted gas for the  $\text{Ca}(\text{OH})_2$  suspension with coexistence of hexamethylene diamine, nylon 6-6 salt and  $\epsilon$ -caprolactam respectively. Samples 2–13 refer to Table 2.

this work. Little concentration dependence in the range between 5 and 200 mmol/L  $\epsilon$ -caprolactam in aqueous solutions was observed.

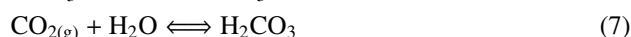
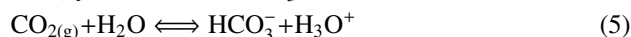
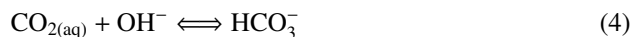
#### 2.4 Results of X-ray diffraction of precipitated $\text{CaCO}_3$

The results of XRD in Fig. 6, showed mostly the obtained  $\text{CaCO}_3$  precipitates were calcite except the precipitates from the suspensions using 200 and 20 mmol/L hexamethylene diamine aqueous solution. The XRD for precipitates collected during the precipitation stage at the point of pH = 10 to 11 without additives (sample 1) and with 20 mmol/L of hexamethylene diamine (sample 4), nylon 6-6 salts (sample 8) and  $\epsilon$ -caprolactam (sample 12) are also shown in Fig. 7. The precipitates in the precipitation stage without additive and with  $\epsilon$ -caprolactam were calcite, which suggested that the calcite crystal had grown in the early stage during the precipitation reaction. On the other hand, vaterite and aragonite were also observed for the precipitates collected at the plateau in the  $\text{Ca}^{2+}$  concentration curves shown in Fig. 5 with 20 mmol/L hexamethylene diamine and nylon 6-6 salt (hexamethylene diamine + adipic acid).

### 3 Discussion

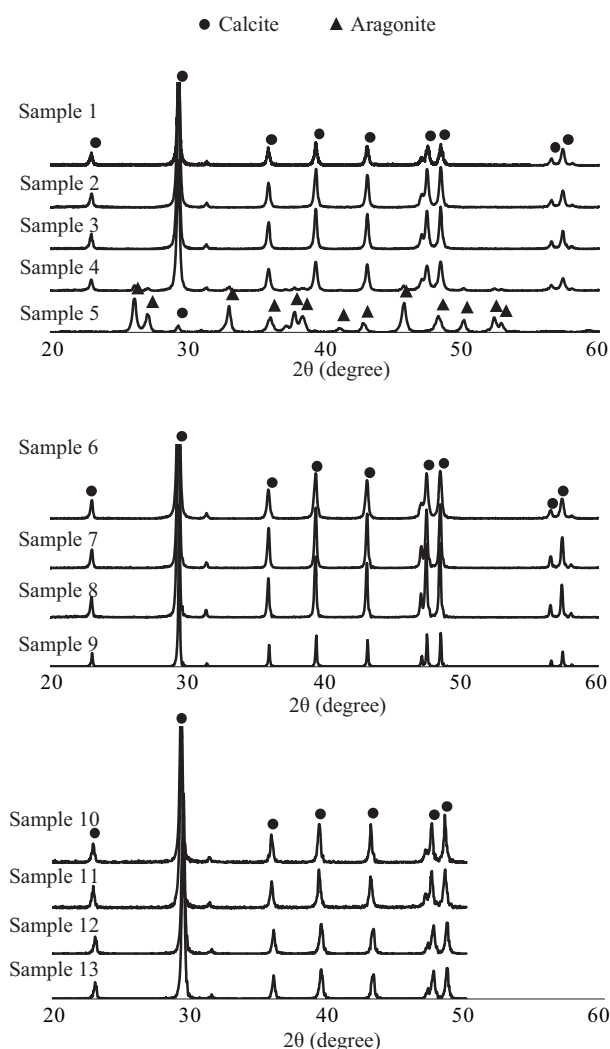
#### 3.1 $\text{CO}_2$ absorption and precipitation of $\text{CaCO}_3$ without additives

When the  $\text{CO}_2$  gas dissolved into water, it formed  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{H}_2\text{CO}_3$  as the following reactions.



Above pH 11, the hydration reaction was relatively rapid as  $\text{CO}_2$  reacted directly with  $\text{OH}^-$  to form  $\text{HCO}_3^-$  as Reaction (4). Then the hydration reaction of  $\text{CO}_2$  was slow to reach the equilibrium until pH=8 in the pure systems (Burau and Zasoski, 2002).

During  $\text{CO}_2$  absorption, the precipitation of  $\text{CaCO}_3$  was occurred following the reaction:



**Fig. 6** X-ray diffraction pattern of the precipitate from different samples. Samples refer to **Table 2**.



However,  $\text{Ca}(\text{HCO}_3)_2$  formation also occurred along with  $\text{CaCO}_3$  precipitation. In particular,  $\text{Ca}(\text{HCO}_3)_2$  was dominant within pH 6.4–10.3. The reaction of  $\text{Ca}(\text{HCO}_3)_2$  formation is shown as below:



The  $\text{CO}_2$  absorption and  $\text{Ca}^{2+}$  concentration curve in **Fig. 4** should be useful information for the reaction process. The  $\text{Ca}^{2+}$  curve in the first precipitation stage suggested that the precipitation of  $\text{CaCO}_3$  started at the beginning of the reaction and continued until the end of this stage. However, the  $\text{CO}_2$  absorption curve revealed that at the early stage, most  $\text{CO}_2$  gas soon dissolved into  $\text{Ca}(\text{OH})_2$  aqueous suspension but following absorption of  $\text{CO}_2$  was interrupted by  $\text{HCO}_3^-$  in the solution under the equilibrium of Reactions (3) and (5). The steep increase of

$\text{CO}_2$  concentration in the first precipitation stage without additives shown in **Fig. 4** should be attributable to the temporal block effect of the following  $\text{CO}_2$  absorption by the successive Reactions (3), (5), (6) and (8) proceeded the precipitations that was confirmed by the  $\text{Ca}^{2+}$  concentration curve. Continuous bubbling of  $\text{CO}_2$  gas produced  $\text{HCO}_3^-$  ions followed by supplying the  $\text{CO}_3^{2-}$  and proceeded the  $\text{CaCO}_3$  precipitation accompanied with the  $\text{CO}_2$  absorption,  $\text{Ca}^{2+}$  concentration and pH decrease.

Any additives which consist  $-\text{NH}$  or  $-\text{NH}_2$  groups could trap  $\text{HCO}_3^-$  by forming carbamate intermediate molecule (Caplow, 1968). This formation leads to speeding up the absorption of  $\text{CO}_2$  gas. The steep increase in  $\text{CO}_2$  concentration in the exhausted gas was not observed for the sample with additives in this study, which suggested that neutral additives of nylon 6-6 salts and  $\epsilon$ -caprolactam besides the base hexamethylene diamine also promoted the  $\text{CO}_2$  absorption into aqueous solutions. However, excess base additives inhibited the calcium carbonate precipitation as discussed in the following sections.

### 3.2 Effect of additives on $\text{CO}_2$ absorption

Reaction behaviour of absorption of  $\text{CO}_2$  to precipitate calcium carbonates for high concentration; 200 mmol/L, was different from other lower concentration samples with all additives except  $\epsilon$ -caprolactam. Without any additives, solubility of  $\text{Ca}(\text{OH})_2$  and  $\text{CO}_2$  into water at  $25^\circ\text{C}$  are 1.7 g/L; 23 mmol/L, and 1.45 g/L; 33 mmol/L respectively. At high concentration, before and during the bubbling the gases with  $\text{CO}_2$ , main ions in the aqueous solutions were additives. On the other hand, the samples with lower concentrations; 20, 10 and 5 mmol/L, there were no main ions in the aqueous solutions because the concentration of constitution as additive,  $\text{CO}_2$ ,  $\text{Ca}^{2+}$  and their related ions were comparable.

In early stage of the precipitation stage for the sample with 200 mmol/L hexamethylene diamine shown in **Fig. 5** sample 5, almost all  $\text{CO}_2$  gas was absorbed with a little decrease of pH and no  $\text{Ca}^{2+}$  concentration change. As diamine kept pH of aqueous solution higher level, the absorbed  $\text{CO}_2$  would be combined with  $\text{OH}^-$  near the diamine ions to make  $\text{CO}_3^{2-}$  followed by the reaction with  $\text{Ca}^{2+}$  cation to precipitate  $\text{CaCO}_3$ . As  $\text{OH}^-$  were supplied enough in the aqueous solutions of hexamethylene diamine even in lower concentration, only a little plateau region was observed in  $\text{CO}_2$  concentration curve in **Fig. 5** samples 2, 3 and 4. It was reconfirmed that the addition of alkaline additives such as amine promotes the dissolving  $\text{CO}_2$  into aqueous systems.

It took about 40 min for the first stage to complete the precipitation for the sample with 200 mmol/L diamine and the required times for the absorption and precipitation were decreased with the lower additive concentration and the time was less than that without additive ions shown in **Fig. 4**. These results suggested that the excess amine was



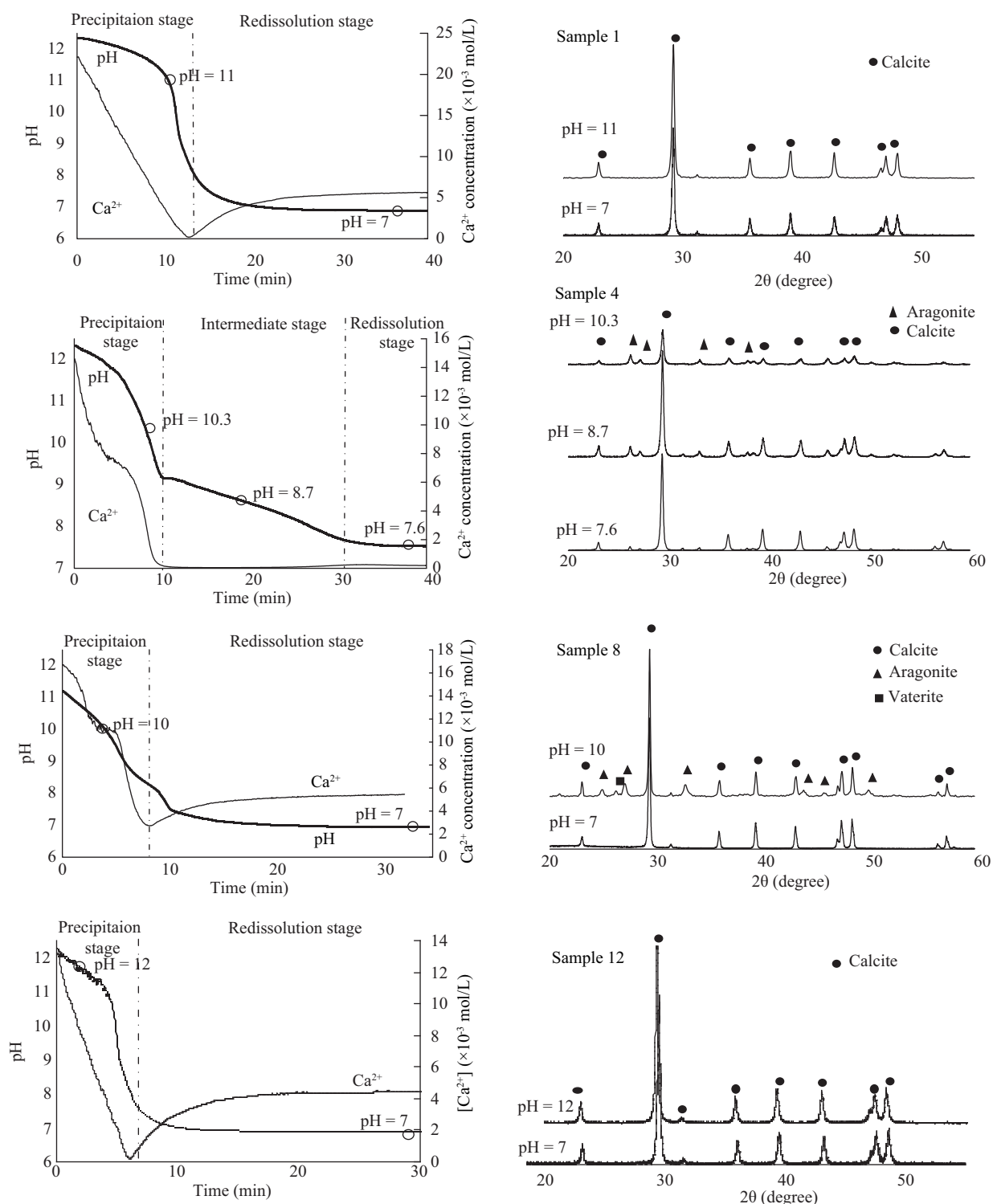


Fig. 7 Sampling points and X-ray diffraction pattern of the precipitate samples at different pH values.

as an interception for the reaction of  $\text{CO}_3^{2-}$  with  $\text{Ca}^{2+}$  to form  $\text{CaCO}_3$ .

The steep increase in  $\text{CO}_2$  concentration curve in the first precipitation stage was not observed for the samples with additives in this experiment and the precipitation reaction was promoted by the additives except for that with higher concentration of hexamethylene diamine. These

results suggested that the molecules with  $-\text{NH}$  or  $-\text{NH}_2$  groups played some effects on the  $\text{CO}_2$  absorption and  $\text{CaCO}_3$  precipitation processes, even when counter groups such as  $\text{COOH}$  or  $\text{CO}$  were coexisted.

Since the acid dissociation constants,  $\text{p}K_a$ 's around  $-\text{NH}$  or  $-\text{NH}_2$  groups are about 10–12, which are smaller than 12.5 for  $\text{Ca}(\text{OH})_2$  but larger than 9 for  $\text{CaCO}_3$ , hexam-

ethylene diamine and  $\epsilon$ -caprolactam would not affect the  $\text{CO}_2$  absorption behaviour in the initial stage but make significant effect on the precipitation of  $\text{CaCO}_3$ . Even when the  $\text{HCO}_3^-$  was existed in the aqueous solution, interaction with  $-\text{NH}$  or  $-\text{NH}_2$  groups blocked the influence on the precipitation reaction. It is interesting that the effect was also observed in the system coexisting of  $\text{COO}^-$  group in adipic acid and  $\text{CO}^{\delta-}$  group in  $\epsilon$ -caprolactam. A local environment around the groups of additives would play an important role on reaction rate including gas-liquid solution phases. These results were confirmed by the observation of amount of  $\text{CO}_2$  absorption in this paper.

### 3.3 Effect of additives on $\text{CaCO}_3$ precipitation

The precipitation of  $\text{CaCO}_3$  was inhibited by the interactions between amine and  $\text{CO}_3^{2-}$  or  $\text{HCO}_3^-$  to stabilize the aqueous solutions of  $\text{CO}_3^{2-}$  anions, that was confirmed by the results for the sample with only hexamethylene diamine as an additive. It was also confirmed that the co-existence of counter anions such as  $\text{COO}^-$  would mitigate the effects of the amines.

Addition of hexamethylene diamine and hexamethylene diamine adipic acid salt obstructed the  $\text{Ca}^{2+}$  concentration decrease to precipitate the calcium carbonate powders which presented as a plateau in the  $\text{Ca}^{2+}$  concentration curves. The results of the XRD for the samples collected at earlier stage of the precipitation confirmed that the plateau in  $\text{Ca}^{2+}$  concentration curves attributed to the transformation of aragonite to calcite in the aqueous suspensions. The behaviour was observed not only for the samples with hexamethylene diamine but also for nylon 6-6 salt. The successive change of crystal structure was not the simple effect of base additives. The behaviour was not observed for the sample with  $\epsilon$ -caprolactam even for the high concentration condition, which suggested the effect would not be simple organic additive effect. The successive changes of crystal structure; amorphous, vaterite, aragonite and calcite, in the process of the precipitation of calcium carbonates was reported (Uebo et al., 1992; Naka et al., 2006). They also proposed that the crystal structure change was occurred through the dissolution and recrystallization process. The dissolution was hindered by the adsorption of organic molecules on the surface of the calcium carbonate crystals. The resemblance result for hexamethylene diamine was observed here. It was confirmed that the successive phase transformation of  $\text{CaCO}_3$  could be monitored by  $\text{Ca}^{2+}$  concentration change during the precipitation reaction. It is interesting that the effect was only for hexamethylene diamine but not for  $\epsilon$ -caprolactam. Balance between hydrophobic and hydrophilic groups or molecular shape would affect these behaviours. Comparison with water soluble macromolecules or other organic small molecules should be necessary to understand the mechanism to control the crystal structure and morphology of  $\text{CaCO}_3$  precipitates.

## 4 Conclusions

We examined the effect of hexamethylene diamine, amine salt (hexamethylene diamine-adipic acid salt), and amide ( $\epsilon$ -caprolactam) on  $\text{CO}_2$  absorption into  $\text{Ca}(\text{OH})_2$  suspension to precipitate  $\text{CaCO}_3$  by the observation of pH,  $\text{Ca}^{2+}$  concentration and  $\%\text{CO}_2$  in exhausted gas. We confirmed the  $\%\text{CO}_2$  in exhausted gas monitoring during the reaction besides the pH measurement was useful to understand the  $\text{CO}_2$  absorption process and reconfirmed the rate-limiting process due to the  $\text{HCO}_3^-$  formation in the aqueous solutions accompanied by the  $\text{CaCO}_3$  precipitation, which was improved by the amine additives. The analysis confirmed that the improvement for the reaction rate was not only achieved by the base amine additives but also by the addition of neutral additives such as  $\epsilon$ -caprolactam or amine salt.

Observation of  $\text{Ca}^{2+}$  concentration change and XRD analysis of the precipitates during the reaction showed the successive change of crystal forms of calcium carbonates. It was confirmed first time that only when the hexamethylene diamine was added to the aqueous solution, the successive transformation from aragonite to calcite occurred even coexistence of adipic acid.

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