

Polymorphs of pure calcium carbonate prepared by the mineral carbonation of flue gas desulfurization gypsum



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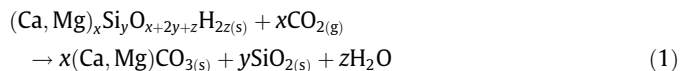
ABSTRACT

We previously developed a process for the precipitation of pure CaCO₃ by exploiting the induction period of one-step mineral carbonation of flue gas desulfurization gypsum. Herein, the process was further investigated to elucidate CaCO₃ polymorphism as a function of the addition of ammonia and ethanol using quantitative X-ray diffraction and field-emission scanning electron microscopy. Calcite, which was the dominant phase when using a stoichiometric amount of ammonia, was replaced by vaterite upon the addition of excess ammonia. Ethanol tends to induce vaterite and aragonite phases under stoichiometric and excess ammonia conditions, respectively. Thus, when using excess ammonia, single-phase aragonite was crystallized when the ethanol concentration exceeded 30 vol.%. Ethanol stabilized the vaterite phase, which otherwise transformed into superstructure calcite upon contact with water. This process offers a simple method for manipulating the phase and morphology of clean CaCO₃ produced using industrial by-products by mineral carbonation.

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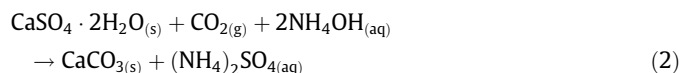
1. Introduction

Mineral carbonation is one of the methods for mitigating atmospheric CO₂ gas. This method mimics global silicate-weathering processes (Eq. (1)), wherein CO₂ is converted into inorganic carbonates using Ca/Mg-bearing minerals or industrial waste [1]. This method has attracted both industrial and academic interest because it enables the permanent storage of CO₂ without leakage. Nonetheless, some major issues such as high energy consumption and/or the disposal of carbonated products require resolution [2].



The reaction routes for mineral carbonation are divided into two major categories: direct and indirect processes [3]. Direct carbonation is carried out using a single process step and is usually employed to immobilize toxic elements in industrial materials. In contrast, in indirect carbonation the extraction and carbonation steps are performed separately. The indirect method has received more attention because it facilitates an increase in the carbonation rate or in the purity of the Ca/Mg carbonates produced. Recent research has focused on the feasibility of producing pure calcium carbonate (CaCO₃) during mineral carbonation using industrial wastes [4].

Flue gas desulfurization (FGD) gypsum is produced by the FGD process, which is the removal of sulfur oxides from flue gas in coal-fired power plants. Mineral carbonation of FGD gypsum is one of the methods that have been investigated for CO₂ sequestration [5]. Previously [6], we demonstrated the feasibility of producing high-purity CaCO₃ through the direct carbonation of FGD gypsum under ambient conditions, which can be described by the following reaction:



Pure CaCO₃ was successfully obtained during an induction period, in which CaCO₃ exists in the dissolved form wherein impurities were easily separated before precipitation [7].

CaCO₃ is one of the most important materials in polymer industry [8,9]. Various techniques have been developed to manipulate CaCO₃ using environmentally undesirable by-products [10,11]. It exists as three anhydrous crystalline polymorphs (calcite, aragonite, and vaterite), two hydrated metastable forms (monohydrocalcite and calcium carbonate hexahydrate), and one unstable amorphous phase. To the best of our knowledge, this is the first attempt to control the phase and/or morphology of pure CaCO₃ synthesized by using industrial by-products and greenhouse gas CO₂. Herein, we demonstrate the possibility of controlling which polymorph of pure CaCO₃ is obtained during the direct aqueous carbonation of FGD gypsum.

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2. Experimental

2.1. Materials

FGD gypsum was supplied by Yeongheung Thermal Power Plants, Incheon, Korea and was the same material as was used in our previous work [6,7]. It was used without performing a pulverizing or grinding process, because the particle size fraction of the sample was in the 1–100 μm range, which corresponds to the fraction generally employed in mineral carbonation [12]. The FGD gypsum was primarily composed of calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) with a purity of approximately 95%; Si, Al, and Fe were present as minor impurities.

Anhydrous ethanol and nitric acid were purchased from Sigma-Aldrich, and the deionized water used was purified using a Milli-Q 18 M Ω cm system (Millipore).

2.2. Preparation of pure CaCO_3 using ammonia and ethanol

Carbonation was carried out by injecting CO_2 gas (99.9 vol.% purity) into an aqueous ammonia solution containing solid particles of FGD gypsum. The amount of dissolved CaCO_3 was measured under the following conditions: CO_2 flow rate = 1 L/min, $[\text{NH}_3] = 0.5\text{--}25$ vol.%, and solid to liquid (s/l) ratio = 200 g/L. The suspension was filtered in approximately 20 mL portions at 5 min intervals during the carbonation. The solution containing dissolved CaCO_3 was initially transparent, but later turned into a milky-white suspension before the precipitation of CaCO_3 particles. The amount of CaCO_3 precipitated was estimated by measuring the Ca concentration in the solution before and after the precipitation. The Ca concentration in solution after the precipitation was <1.0 mM in all cases.

To investigate the effect of ammonia on CaCO_3 precipitation, carbonation was carried out under both stoichiometric and excess ammonia conditions. Under stoichiometric conditions (stoichiometric ratio of $\text{CO}_2/\text{NH}_3 = 2$), the sampling was performed after carbonation for 5 min under the following conditions: CO_2 flow rate = 0.3 L/min, total injected CO_2 volume = 1.5 L (approximately 0.06 mol), s/l ratio = 20 g/L (total Ca = approximately 0.1 mol/L), and $[\text{NH}_3] = 0.5$ vol.% (0.13 mol). Under excess ammonia conditions, the sampling was performed after carbonation for 20 min under the following conditions: CO_2 flow rate = 1 L/min, s/l ratio = 20 g/L, and $[\text{NH}_3] = 12$ vol.% (8.48 mol). For each condition, the sampling time was chosen to be when the dissolved CaCO_3 was maximum.

To evaluate the effect of ethanol on the CaCO_3 polymorphs formed, ethanol (10, 30, 50, 70, and 90 vol.%) was mixed with the solution extracted during the induction period in Nalgene bottles. After mixing, the solutions were gently shaken at 70 rpm using a digital reciprocating shaker (SHR-2D, DAIHAN Scientific). The stability of vaterite in the presence of water was assessed by soaking and shaking it in deionized water for two days.

All of the carbonation experiments were conducted under ambient conditions (room temperature and atmospheric pressure) while monitoring the temperature and pH (Orion 410A, Thermo Scientific). The solutions were filtered using a 0.2 μm membrane filter (Nylon, Sartorius). The calcium ion concentrations were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES; Optima 5300DV, PerkinElmer) after the acidification of the samples to pH 2 with instrumental-grade HNO_3 . All the precipitated CaCO_3 particles were washed with anhydrous ethanol or deionized water, and then dried either under vacuum or in air overnight at 30 $^\circ\text{C}$. The precipitated CaCO_3 particles were examined by X-ray diffraction (XRD; X'pert MPD, Philips

Analytical) and field-emission scanning electron microscopy (FE-SEM; S-4700, Hitachi).

2.3. Determination of phase composition by X-ray diffraction

The relative amounts (%) of the CaCO_3 crystalline phases, i.e., calcite, aragonite, and vaterite, were estimated using Eqs. (3) and (4), as proposed by Kontoyannis and Vagenas [13].

For a mixture of aragonite and calcite:

$$X_A = \frac{3.157I_{221A}}{I_{104C} + 3.157I_{221A}} \times 100, \quad X_C = 100 - X_A \quad (3)$$

and for a mixture of vaterite and calcite:

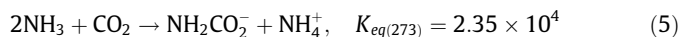
$$X_V = \frac{7.691I_{110V}}{I_{104C} + 7.691I_{110V}} \times 100, \quad X_C = 100 - X_V \quad (4)$$

where X_A , X_V , and X_C are the relative amount (%) of aragonite, vaterite, and calcite, respectively. I represents the integrated areas of the XRD peaks, and subscripts A, V, and C represent the aragonite, vaterite, and calcite phases, respectively, i.e., I_{221A} , I_{104C} , and I_{110V} are the areas of the (221), (104), and (110) peaks of aragonite, calcite, and vaterite, respectively.

3. Results and discussion

3.1. Effect of ammonia on the polymorphs of pure CaCO_3 precipitated from solution

In a slow precipitation process, CaCO_3 exists as a solvated pair (Ca^{2+} and CO_3^{2-}) before crystallization is induced [14]. The sequential formation of CaCO_3 during the direct aqueous carbonation of FGD gypsum has been described in detail in our previous study [6,7]. The amount of CaCO_3 dissolved in the solution was found to increase with increasing ammonia concentration. Fig. 1 shows the maximum amount of pure CaCO_3 (dissolved) at various ammonia concentrations (1.5, 4, 8, 12, and 25 vol.%). The pH was higher than 9.0 in each case. The ammonia tended to slow the carbonation rate, which prolonged the induction period, and accordingly increased the amount of pure CaCO_3 obtained. We attributed this effect to the formation of carbamate (NH_2CO_2^-) [7], which is the dominant species formed in the reaction between CO_2 and excess ammonia. The related reactions can be expressed as follows [15]:



The polymorphs of the precipitated CaCO_3 were examined after washing with anhydrous ethanol several times and drying under vacuum at 30 $^\circ\text{C}$ to prevent a possible transformation of

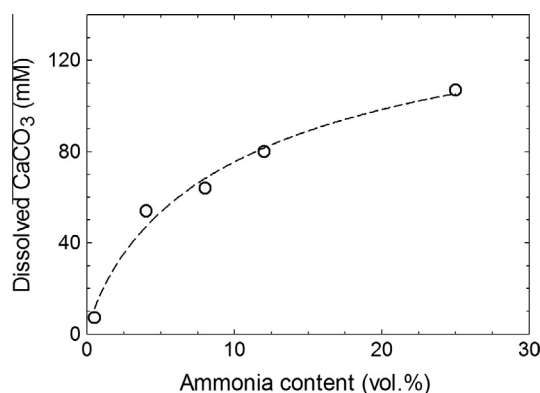


Fig. 1. Dissolved CaCO_3 (mM) as a function of ammonia concentration (vol.%).

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