



Factors affecting the precipitation of pure calcium carbonate during the direct aqueous carbonation of flue gas desulfurization gypsum



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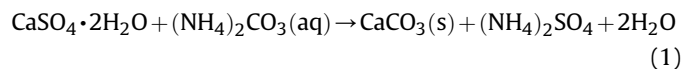
ABSTRACT

The mineral carbonation of FGD (flue gas desulfurization) gypsum was carried out through CO₂ sorption into ammonia solution containing FGD gypsum. High-purity calcium carbonate was precipitated from DCC (dissolved calcium carbonate) solution which was extracted during the induction period. The factors affecting the preparation of pure calcium carbonate were examined under the following conditions: CO₂ flow rate (1–3 L/min), ammonia content (4–12%), and S/L (solid-to-liquid) ratio (5–300 g/L). X-Ray diffraction study revealed that the PCC (precipitated calcium carbonate) was round-shaped vaterite. The induction time for PCC decreased as the CO₂ flow rate increased. The maximum formation efficiency for pure PCC was seen to increase linearly with the ammonia content. The formation efficiency for pure PCC was the highest (90%) for S/L ratio of 5 g/L but it decreased as S/L ratio increased. On the other hand, S/L ratio didn't affect the maximum solubility limit of DCC. It is believed that the pure PCC would add an economic value to the FGD gypsum carbonation for industrial CO₂ sequestration.

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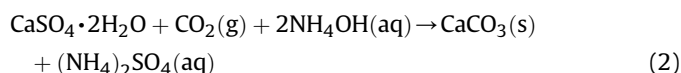
1. Introduction

FGD (flue gas desulfurization) gypsum (calcium sulfate dihydrate, CaSO₄·2H₂O) is the main product of desulfurization system for the removal of SO_x at fossil-fuel power plants. One of the well known application of waste gypsum is the production of the fertilizer ammonium sulfate ((NH₄)₂SO₄) [1–3]:



The reaction produces ammonium sulfate ((NH₄)₂SO₄) of high purity (up to 99%) and high yield, and the reaction rate increases with temperature [2,3]. Because of the high solubility of (NH₄)₂SO₄ (74 g/100 mL H₂O at 20 °C) [4], it can be separated easily from solid residues which consist of calcium carbonate as well as the insoluble impurities contained in FGD gypsum [3].

Recently, the direct mineral carbonation of FGD gypsum for CO₂ sequestration was performed; high carbonation reactivity under ambient conditions was observed [5,6]. The heat produced by CO₂ sorption into ammonia solution was utilized for the carbonation reaction. This process can be described by the following reaction:



The above reaction produces comparatively pure ammonium sulfate which can be commercially used. In contrast, the calcium carbonate product consisted of a mixture of the thermodynamically unstable vaterite and stable calcite phases containing impurities [5].

Calcium carbonate (CaCO₃) exists as a dissolved ion pair during the induction period [7]. An induction period was generally observed in the slow precipitation process, and its length depends on the reaction variables such as initial concentration, temperature, pH, and additives [8]. We previously reported that this induction period has the potential for the production of high-purity CaCO₃ during the direct carbonation of FGD gypsum [9].

PCC (precipitated calcium carbonate) refers to CaCO₃ synthesized in a controlled manner which is used in large quantities as a paper filler or in coatings [10]. The current synthesis method of PCC is environmentally disadvantageous because of lime calcination that releases CO₂, although CO₂ is bound during carbonation. Alternative carbonation processes for the synthesis of PCC have been suggested using other materials (i.e., wollastonite or slag) after dissolution treatments [10,11]. However, it may be difficult to obtain impurity-free PCC via indirect carbonation methods using

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acid-promoted dissolution, because other elements contained in the raw materials can also be dissolved.

Huijgen et al. (2007) [12] insisted that the production of useful carbonated products can strengthen the economic competitiveness of mineral carbonation methods compared to other CO₂ sequestration technologies. In this respect, we evaluated the effects of various experimental parameters on the precipitation of white, impurity-free calcium carbonate using the induction period in the direct mineral carbonation of FGD gypsum. The effects of the CO₂ flow rate, ammonia content, and S/L (solid-to-liquid) ratio were analyzed systematically monitoring the temperature and pH of the slurry.

2. Experimental

2.1. Materials

The FGD gypsum was obtained from the Yeongheung Thermal Power Station, Incheon, Korea [6,9]. The sample particle size ranged from 1 to 100 μm, with an average of 32.9 μm. Over 80% of the as-received particles were smaller than 74 μm without pulverizing or grinding processes. Based on the compositional analysis, the nominal purity of the CaSO₄·2H₂O was estimated to be 95–98%.

2.2. Carbonation experiments

The direct-carbonation experiment was carried out by flowing CO₂ gas (99.9 vol% purity) into an ammonia solution containing solid particles of FGD gypsum [6,9]. The characteristics of the DCC (dissolved calcium carbonate) were examined under the following conditions: CO₂ flow rate (1–3 L/min), ammonia content (4–12%), and S/L ratio (5–300 g/L). The suspension was sampled (in 20 mL portions) at predetermined intervals. Impurities in FGD gypsum were not detected in filtered solutions [9].

All experiments were performed under ambient conditions (room temperature and atmospheric pressure) while monitoring temperature and pH (Orion 410A, Thermo Scientific). Filtration was performed using a 0.2 μm membrane filter (cellulose acetate, Sartorius). Calcium ions were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES; Optima 5300DV, PerkinElmer) after acidification of the sample to pH 2 with instrumental grade HNO₃. Dissolved sulfate ions were quantified by ion chromatography (ICS-3000, Dionex) after filtering samples. Precipitated PCC particles were examined by XRD (X-ray diffraction; X'pert MPD, Philips Analytical) and FE-SEM (field-emission scanning electron microscopy; S-4700, Hitachi).

The formation efficiency for pure PCC (%) was calculated from the amount of PCC in a solution and the total input Ca concentration of the FGD gypsum. The latter can be determined from the total amount of dissolved sulfate after the termination of carbonation, because the stoichiometric ratio of Ca/SO₄ in CaSO₄·2H₂O is one. The efficiency can be expressed as:

PCC formation efficiency (%)

$$= \frac{(M_{\text{Ca-f}} - M_{\text{Ca-f'}})}{T_{\text{Ca-g}}} \times 100 \quad (3)$$

$$= \frac{(M_{\text{Ca-f}} - M_{\text{Ca-f'}})}{T_{\text{SO}_4\text{-g}}} \times 100 \quad (4)$$

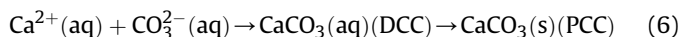
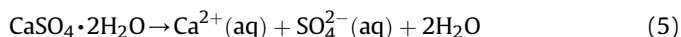
where $M_{\text{Ca-f}}$ is the total Ca concentration in filtered solutions at a specific time, $M_{\text{Ca-f'}}$ is the Ca concentration in the solution after the formation of pure PCC, $T_{\text{Ca-g}}$ is the total Ca concentration of FGD

gypsum used in the carbonation experiments, and $T_{\text{SO}_4\text{-g}}$ is the total SO₄ concentration. $T_{\text{SO}_4\text{-g}}$ is the dissolved SO₄ concentration in the final solution after the direct carbonation. It was almost identical to the calculated value based on the carbonation conversion yield (about 95%) of FGD gypsum [6].

3. Results and discussion

3.1. Scheme for pure PCC

As previously explained, pure ammonium sulfate can be separated relatively easily from the solid impurities in FGD gypsum because of its high solubility. However, this is not the case for PCC, because it forms as an admixture with solid impurities from which it cannot be easily separated. Our previous study [9] indicated that pure PCC can only be precipitated from a solution containing Ca²⁺ and CO₃²⁻ ions before the precipitation occurs to any significant extent, using the so-called “induction period”. The solvated ion pairs are termed the dissolved calcium carbonate (DCC), CaCO₃(aq). Once PCC is substantially formed, it would not be possible to separate it from the solid impurities of FGD gypsum. The DCC formed in the solution during the induction period can supposedly be precipitated to pure PCC. Calcium and carbonate ions are sourced from the FGD gypsum and CO₂(g) dissolution, respectively. Carbonate ions can be regarded to be instantly and excessively formed because of high pH. Main reactions for the formation of pure PCC can be expressed as follows:



In this study, we evaluated the experimental parameters to further take advantage of the induction period for the precipitation of pure PCC.

3.2. Polymorphs of pure PCC

Calcium carbonate exists as three anhydrous crystalline polymorphs (calcite, aragonite, and vaterite), two hydrated metastable forms (monohydrocalcite and calcium carbonate hexahydrate), and an unstable amorphous form. Among these, the ACC (amorphous calcium carbonate) is the most soluble form and the first detected form that precipitates ahead of the transformation to stable polymorphs under certain conditions (e.g., when magnesium ions are present at higher ratios compared to calcium ions) [13].

When the slurries were filtered at an early stage (i.e., induction time) during the direct carbonation of FGD gypsum, the clear filtered solutions were found to transform into a gelatinous state. Afterwards, white and pure crystalline PCC started to form after several minutes. This PCC was recovered by filtering and washing with anhydrous ethanol (a few mL), and then dried at room temperature to prevent the possible phase transformation. Polymorphic changes were not detected as a function of the carbonation conditions, such as ammonia content. The PCC particles were spherical (Fig. 1) and single-phase vaterite as confirmed by XRD diffraction (Fig. 2). This observation is consistent with the previous study [14] in which the formation of vaterite phase was favored under controlled pH conditions (7.5–9.5) using NH₃/NH₄Cl buffer.

3.3. Effect of CO₂ flow rate

The effect of the CO₂ flow rate on the formation efficiency for pure PCC was evaluated by varying the flow rates at 1, 2, or 3 L/min

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