



Effect of polyacrylic acid on direct aqueous mineral carbonation of flue gas desulfurization gypsum



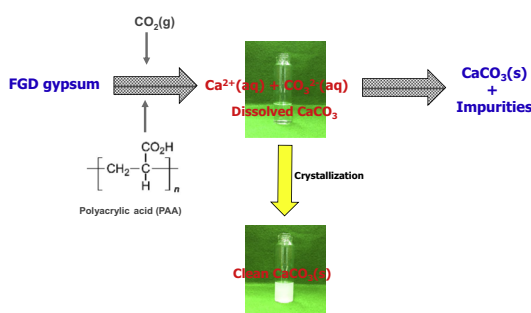
Kyungsun Song, Wonbaek Kim*, Sangwon Park, Jun-Hwan Bang, Chi Wan Jeon, Ji-Whan Ahn

Korea Institute of Geoscience & Mineral Resources (KIGAM), Gwahang-no 124, Yuseong-gu, Daejeon 305-350, Republic of Korea

HIGHLIGHTS

- Effect of PAA on carbonation of FGD gypsum was studied.
- PAA extended induction period to over 1.5 h.
- PAA increased Ca^{2+} in filtered solution to 60% of gypsum.
- In-situ liquid XRD revealed the crystallization sequence of calcite with time.
- Overall carbonation yield was reduced due to CO_2 emission.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 16 March 2016
Received in revised form 27 April 2016
Accepted 28 April 2016
Available online 29 April 2016

Keywords:

Mineral carbonation
Flue gas desulfurization (FGD) gypsum
Pure calcium carbonate
Polyacrylic acid (PAA)
Induction period

ABSTRACT

We have previously precipitated highly pure calcium carbonate (CaCO_3) crystals from a filtered solution extracted in the course of the direct mineral carbonation of flue gas desulfurization gypsum. However, the maximum amount of pure CaCO_3 obtained by the process was less than 5% of the gypsum. We thus attempted to manipulate the induction period by adding a polyacrylic acid (PAA), with the expectation of dissolving more Ca^{2+} in the solution. This was because it is known to inhibit the formation of CaCO_3 . The PAA was actually found to prolong the induction period to over 1.5 h, with the addition of 2.7 g/L PAA specifically increasing the amount of dissolved Ca^{2+} to 60% of the gypsum. It was also found that the addition of PAA lowered the overall carbonation yield via $\text{CO}_2(\text{g})$ emission, thus reducing the CO_2 dissolution. In addition, ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) was discovered to be usable for producing pure CaCO_3 in the presence of PAA. An in-situ liquid-phase X-ray diffraction of the filtered solution revealed the sequential formation of calcite crystals from the amorphous phase on exposure to air. The morphology of the obtained calcite comprised twinned pseudo-spherical or dumbbell-shaped crystals, unlike the typical rhombohedral calcite phase obtained without PAA. It is clearly demonstrated that the precipitation of clean CaCO_3 in direct mineral carbonation of FGD gypsum can be enhanced by additives as PAA for a better economic viability.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Mineral carbonation is one of the methods used for CO_2 sequestration processes that are based on natural weathering reactions,

wherein Ca- or Mg-bearing minerals are slowly carbonated in the presence of CO_2 [1]. The feedstocks used for the carbonation include industrial wastes that contain divalent cations such as Ca and Mg ions. However, compared to other strategies such as geological storage, the inherently slow kinetics of mineral carbonation makes it economically less competitive [2]. The dissolution step is known to primarily determine the overall rate of the mineral

* Corresponding author.

E-mail address: wbkim@kigam.re.kr (W. Kim).

carbonation process [3], and experiments using acidic extraction solvents have been performed to accelerate the dissolution of the reactive Ca or Mg component [4,5].

Likewise, organic additives have also been used to promote dissolution rate as weak acid extraction solutions or complexing agents for Ca or Mg [6–8]. Since the initial proposal of acetic acid (monocarboxylic acid) as a weak extraction solvent [6], mineral carbonation processes in which various carboxylic acids were used have been implemented [9–12]. However, carbonate precipitates are not always formed during the carbonation processes when the extraction is done using an organic acid [11,12]. For example, succinic acid (dicarboxylic acid) was found to form non-carbonate precipitates (calcium succinate), unlike the case of acetic acid, though it exhibited a high Ca-extraction efficiency [12]. In some cases, no detectable solid products were formed by the carbonation reaction of olivine using citrate (tricarboxylate) or ethylenediaminetetraacetic acid (EDTA). This has been attributed to the strong complexation ability with Mg [11].

Polycarboxylic acids, which are weak acids deprotonating at near-neutral pH, have the ability to form Ca/Mg-polycarboxylate complexes. The complexes are known to retard the crystallization of carbonate solid, and have been commercially used as CaCO₃ scale inhibitors in water systems [13]. The induction time is the period for solid particles to be observed, and that for CaCO₃ nucleation is altered by the presence of polycarboxylic acids [14]. Our previous studies [15,16] revealed that high-purity CaCO₃ could be obtained by manipulating the induction period of CaCO₃ nucleation via direct mineral carbonation of flue gas desulfurization (FGD) gypsum in an aqueous ammonia solution.

FGD gypsum is a by-product of the FGD process for removing sulfur oxides from flue gas in coal-fired power plants. Because FGD gypsum generally contains about 32.5 wt.% CaO, its CO₂ sequestration capacity is 0.26 ton per ton of FGD gypsum. The use of mineral carbonation of FGD gypsum for CO₂ sequestration has been proved to be technically feasible, with a high reactivity under ambient conditions [17]. Furthermore, the production of pure carbonated products has been highlighted in arguments for the economic competitiveness of mineral carbonation methods [18].

We have previously synthesized pure CaCO₃ by exploiting the induction period in the direct carbonation of FGD gypsum [15]. However, the amount of Ca²⁺ in the solution was small, being about 5% of the gypsum. Hence, in the present study, we investigated the use of polyacrylic acid (PAA) as an organic additive for enhancing the precipitation of high-purity carbonates. The effects of the PAA addition on the induction period, polymorph of CaCO₃, carbonation efficiency, and nucleation of CaCO₃ were examined.

2. Experimental

2.1. Materials

The utilized FGD gypsum was obtained from the Yeongheung Thermal Power Station, Incheon, Korea [15,16]. Its particle size distribution was measured using a laser scattering particle size analyzer (HELOS/RODOS & SUCCELL, Sympatec GmbH). The particle size of the sample ranged between 1 and 100 μm, with more than 80% of the particles smaller than 74 μm. The sample was used without pulverizing or any other form of grinding. Compositional analysis showed that impurities in the sample, such as Si and Fe, constituted <5 wt.% [15]. The mineral carbonation of FGD gypsum produces both calcium carbonate and ammonium sulfate, which is highly soluble in water (740 g/L at 20 °C) and is obtained as an aqueous solution, thus requiring an evaporation separation process [17]. Polyacrylic acid (PAA) with $M_w \approx 2000$ was chosen because it

has a low boiling point of 116 °C and can be recovered by an evaporation process.

2.2. Carbonation experiments

The carbonation experiment was performed by passing CO₂ gas (99.9 vol% pure) into ammonia solutions containing solid FGD gypsum particles with and without PAA, respectively, at atmospheric pressure. The CO₂ gas flow was controlled by an external mass flow controller (KRO-4000s, K.M.B Tech Co). The concentration of the ammonia solution was adjusted using a 25 wt.% ammonia solution with the density of 0.9 g/mL (NH₄OH, OCI Company Ltd.). PAA with $M_w \approx 2000$ in the form of an aqueous solution (50 wt.% in H₂O) was purchased from Sigma–Aldrich. The carbonation experiments were performed in a 1-L or 2-L three-neck double-jacketed Pyrex glass reactor. A mechanical stirrer (WiseStir® HT120DX, Daihan Scientific) was installed at the center of the reactor and used to mix the slurry. The ammonia solution containing FGD gypsum was stirred for 5 min at 250 rpm before injection of the CO₂ gas. The sampling continued until complete dissolution of the gypsum or the filtration could no longer proceed due to CaCO₃ colloid particles blocking the filter. The pH and temperature of the mixture was monitored by a pH meter (Orion 410A, Thermo Scientific).

The preliminary experiment considered a given range of PAA concentrations and was performed under the following conditions: mass of FGD gypsum: 200 g, concentration of aqueous PAA solution: 20 mL, CO₂ flow rate: 1 L/min, ammonia content: 3.9%, total liquid volume: 1.3 L. The employed ammonia content was 1.2 times the stoichiometric ratio, assuming complete reaction.

The experiments to examine the effect of PAA addition were performed under ambient conditions (without temperature or pressure control). PAA aqueous solutions of 2 and 5 mL (corresponding to 1.1 and 2.7 g/L if calculated as the amount of PAA) were respectively added to slurry containing 10 g FGD gypsum in 500 mL ammonia solution (2%, v/v). CO₂ gas was injected for 5 min at a flow rate of 0.3 L/min.

The possibility of precipitation of pure CaCO₃ at higher temperatures was examined, considering that a coal-fired power plant generally emits the flue gas from the FGD absorber at 50–80 °C [19]. In our previous study [15], pure CaCO₃ could not be produced by the carbonation of FGD gypsum at temperatures higher than 25 °C in the absence of PAA. Ammonium carbonate (ACS grade, Sigma–Aldrich) was also tested as the carbonate and ammonium source at 25, 35, and 45 °C, respectively, to investigate the effect of the temperature. The maintenance of a constant temperature was difficult with the ammonia solution because the sorption of CO₂(g) into aqueous ammonia is an exothermic process. The temperature of the reactor was maintained using an external circulating water bath (RW-1025, JEIL TECH).

The suspension was sampled at predetermined intervals using 20-mL portions. The filtration was performed using a 0.2-μm membrane filter (Nylon, Whatman™). A 1-mL filtered sample was acidified with instrumental-grade HNO₃ to 5% (v/v) to determine the total Ca concentration. For the crystallization of CaCO₃, the residual filtered solution was gently shaken in a closed sampling tube for 24 h at 60 rpm using a shaker (WiseShake® SHR-2D, Daihan Scientific). After the shaking, the solution was filtered again to determine the amount of dissolved calcium and sulfate. The concentration of the CaCO₃ precipitate was estimated from the difference between the total and dissolved concentrations of calcium. The calcium and sulfate ion contents were determined using an inductively coupled plasma-optical emission spectrometry (ICP-OES; Optima 5300DV, PerkinElmer) and ion chromatography (ICS-3000, Dionex), respectively. The impurities in the FGD gypsum were not detected in the filtered solutions. All the experiments

Download English Version:

<https://daneshyari.com/en/article/145378>

Download Persian Version:

<https://daneshyari.com/article/145378>

[Daneshyari.com](https://daneshyari.com)