



Effect of experimental parameters on the carbonate mineralization with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ using CO_2 microbubbles



Jun-Hwan Bang^a, Wonbaek Kim^{b,*}, Kyung Sun Song^a, Chi Wan Jeon^a, Soo Chun Chae^a,
Hwan-Joo Cho^a, Young Nam Jang^a, So-Jin Park^c

^aGeologic Environmental Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Gwahang-no 92, Yuseong-gu, Daejeon 305-350, Republic of Korea

^bMineral Resource Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Gwahang-no 92, Yuseong-gu, Daejeon 305-350, Republic of Korea

^cDepartment of Chemical Engineering, Chungnam National University, Daejeon 305-764, Republic of Korea

HIGHLIGHTS

- Carbonate mineralization fixes CO_2 as CaCO_3 with CaSO_4 without pH swing.
- Ratio of $[\text{OH}^-]/[\text{Ca}^{2+}]$ affects the CO_2 fixation efficiency.
- CO_2 microbubble enhances the CO_2 fixation efficiency.

ARTICLE INFO

Article history:

Received 4 November 2013

Received in revised form 22 January 2014

Accepted 24 January 2014

Available online 4 February 2014

Keywords:

Carbon dioxide
Carbonate mineralization
Carbon dioxide fixation
Microbubble
Calcium carbonate
Calcium sulfate

ABSTRACT

Carbonate mineralization fixes CO_2 as carbonate minerals such as CaCO_3 mitigating anthropogenic CO_2 related problems. However, studies on the carbonate mineralization using $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ have not been made widely, even though it is a good source of Ca^{2+} . In this study, the CO_2 fixation using $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was investigated without swinging pH. In addition, the effect of using microbubbles was evaluated and compared with the conventional CO_2 bubbles. We injected CO_2 microbubbles into the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ suspension in which the NaOH solution added to maintain alkaline pH. The development of the carbonation reaction was considered by quantitative analysis of the solid phases using an X-ray diffraction technique. The phase composition study revealed that the efficiency of the carbonate mineralization changes with the concentration ratio ($[\text{OH}^-]/[\text{Ca}^{2+}]$). The condition for 100% CaCO_3 was achieved when the concentration ratio was chosen to be between 2 and 3. We also suggested the transformation pathways of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to CaCO_3 in terms of the concentration ratio. We believe that the result in this study would be helpful to find the optimal reaction conditions for the CO_2 fixing carbonate mineralization when calcium source was chosen from various materials.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The reduction of anthropogenic CO_2 causing global warming has been needed more than ever. Various technologies have been suggested to accomplish this assignment. Among them, carbonate mineralization is practical and already commercialized because it uses the well-known reaction of precipitating carbonate minerals [1,2]. It is possible to obtain useful minerals such as CaCO_3 from the reaction of CO_2 and $\text{Ca}(\text{OH})_2$ or CaO [3]. In any case, the dissolution of CO_2 in an aqueous phase is most important to form CO_3^{2-}

at above pH 10.3 for the carbonate mineralization. Generally, pressurization and/or cooling the water increase the solubility of the gaseous phase by Henry's law. Nevertheless, these processes consume large energy and thus are not suitable for the CO_2 fixation.

Microbubbles (MBs) refer to tiny bubbles the diameter of which is typically smaller than $50 \mu\text{m}$ [4]. They are produced by a microbubble generator (MBG). MBs can be generated by many ways. They used fluid dynamics such as venturi [5] and ejector [6], membranes [7], electrolysis [8], and ultrasonic [9]. The physical properties of MBs are quite different from those of the ordinary bubbles due to the tiny bubble size. The high surface tension and small buoyancy of MBs lead to extended retention time in an aqueous phase [10]. In addition, large surface area can be supplied by the unit volume of a gas [9,11]. Above mentioned properties will

Abbreviations: MBG, microbubble generator; MB, microbubble; AD, air diffuser.

* Corresponding author. Tel.: +82 42 868 3659; fax: +82 42 861 9720.

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

increase the solubility of gaseous CO_2 in a Ca^{2+} supplying aqueous phase so that CaCO_3 can be formed faster than when the ordinary bubbles were used. In our previous work [12], the effect of MBs was demonstrated in precipitating CaCO_3 at room temperature and atmospheric pressure.

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was not mainly used to precipitate CaCO_3 since its solubility is lower than that of CaO or $\text{Ca}(\text{OH})_2$. Additionally, the solubility of the mineral is not fully understood as Yuan et al. pointed out [13]. When $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was used instead of CaO or $\text{Ca}(\text{OH})_2$, acid digestion is required: the pH swing from acidic to alkaline pH is required [14]. In this case, the large quantity of the agents may harm the environment and increase of operation cost for the carbonate mineralization. However, CaO or $\text{Ca}(\text{OH})_2$ is not suitable for the supply of Ca^{2+} for CO_2 reduction, because they are obtained by thermal decomposing of naturally mined CaCO_3 at 900 °C. For the practical application of mineral carbonation for CO_2 reduction, diversification of Ca^{2+} containing raw materials including $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ are necessary.

In this study, we used the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ suspension to demonstrate that the Ca^{2+} sources for the carbonate mineralization could be diverse. Our previous study [15] described the carbonate mineralization utilizing FGD gypsum and ammonia solution. This study concentrates on the fundamental aspect of the reaction pathway and the process optimization. The extraction of Ca^{2+} and the precipitation of CaCO_3 were carried out under alkaline conditions without swinging pH of the suspension. The injection rate of CO_2 MBs, and the concentrations of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and NaOH in the suspension were varied. The CO_2 fixation efficiency to CaCO_3 was investigated in terms of the concentration ratio of OH^- to Ca^{2+} and compared with that of an ordinary air diffuser (AD). It is expected that this study would help to enhance and optimize the mineral carbonation using various industrial wastes containing Ca^{2+} .

2. Materials and methods

2.1. Raw materials

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Junsei Chemicals, 96%, without any treatment) was suspended in 1 L of deionized water (Milli-Q Advantage A 10, Millipore) at 0.05, 0.1, 0.3, and 0.5 M. The concentration of NaOH (Samchun Chemicals, 97%) stock solution was 6 M in deionized water. 25, 50, 75, and 100 mL of the solution was added in the suspensions to maintain strong alkalinity. The purity of CO_2 gas was 99.9%.

2.2. MBG system

The MBG used in this study was originally used in the polluted water treatment. An ordinary centrifugal pump was reconstructed for this system. It was consisted of two major parts: an inlet line for the injection of gases, and a specially made nozzle for the outlet of gas and liquid. The “pump” vigorously mixed the gas and the aqueous phase, and flowed out the mixed substance accompanying MBs through the nozzle.

When MBG started to operate, CO_2 at 0.4, 0.8, and 1.0 L/min and the Ca^{2+} source suspension of 1 L containing the NaOH solution flowed into the MBG to be mixed. CO_2 MBs were generated as the mixture discharged, and then it flowed into the double jacketed glass container in which the suspension was initially stored. Coolant at 277 K circulated through within the jacket wall to eliminate heat from MBG but the removal was not mandatory for the carbonate mineralization. All experiments were performed at ambient temperature and pressure. The schematic diagram of circulation of the mixture is shown in Fig. 1 (A) [12]. The pH and the temperature of the suspension were measured (Orion 3 star, Thermo Scientific)

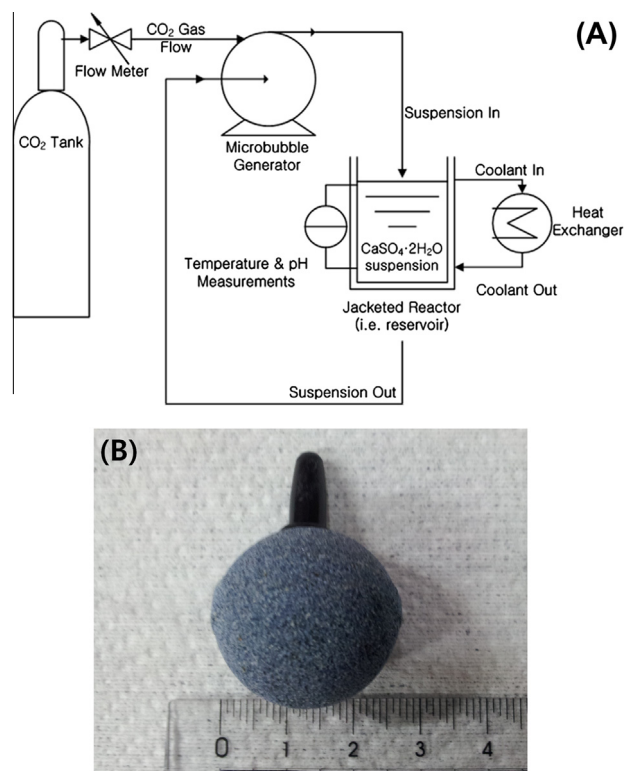


Fig. 1. (A) Process diagram for CO_2 mineralization based on a CO_2 MBG [12] and (B) an air diffuser used for the control experiments.

every 30 s during the MBG operation. CO_2 injection and MBG operation were continued to the near-neutral-steady state pH. All experiments were repeated at least twice. The total volume of the suspensions was maintained throughout the experiments.

2.3. Phase composition analysis by XRD

After the MBG operation, the suspension was filtered by a nylon membrane (0.2 μm pore, Whatman). The particles were dried in an oven at 303 K for 2 days, and examined by X-ray diffraction (Analytical X-ray B.V. X'pert-MPD, Philips). The quantitative analysis of the phases of the particles was conducted using the software attached to the XRD (Siroquant 3.0, Sietronics Pty Limited, Australia).

2.4. Control experiments

Several control experiments have been made to evaluate the efficiency of carbonate mineralization by MBG in comparison to that of an air diffuser in CO_2 injection methods. An air diffuser (shown in Fig. 1 (B)) was a conventionally used one for air supply which is ball-like shaped having a diameter around 3 cm. Since the mixing of the suspension by an air diffuser was not powerful as MBG, a 400 rpm magnetic stirring was allowed for vigorous mixing. The concentration of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and the CO_2 flow rate were 0.3 M, and 0.4, 0.8 and 1.0 L/min, respectively. The volumes of 6 M NaOH solution added into the suspension were 25, 50, 75, and 100 mL.

3. Results and discussion

3.1. Determination of the CO_2 conversion efficiencies by quantitative analysis of X-ray diffraction

The qualitative and quantitative study on the phases of solid particles after the reaction can provide important information on

Download English Version:

<https://daneshyari.com/en/article/147764>

Download Persian Version:

<https://daneshyari.com/article/147764>

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