



## Metal extraction and indirect mineral carbonation of waste cement material using ammonium salt solutions



Hwanju Jo<sup>a</sup>, So-Hee Park<sup>b</sup>, Young-Nam Jang<sup>a</sup>, Soo-Chun Chae<sup>a</sup>, Pyeong-Koo Lee<sup>a</sup>, Ho Young Jo<sup>b,\*</sup>

<sup>a</sup> CO<sub>2</sub> Sequestration Department, Korea Institute of Geoscience and Mineral Resources, 30 Kajung-dong, Gwahang-no 124, Yusung-gu, Daejeon 305-350, Republic of Korea  
<sup>b</sup> Department of Earth and Environmental Sciences, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-713, Republic of Korea

### HIGHLIGHTS

- The type of ammonium salt solution affects the Ca extraction from waste cement.
- A direct relationship between Ca extraction and carbonation is observed.
- NH<sub>4</sub>NO<sub>3</sub> solution is an efficient solvent for mineral carbonation of waste cement.
- High purity vaterite is obtained, regardless of the type of ammonium salt.

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### ABSTRACT

The effects of different ammonium salts on the cation extraction and mineral carbonation of waste cement were evaluated using four different ammonium salt solutions: CH<sub>3</sub>COONH<sub>4</sub>, NH<sub>4</sub>Cl, NH<sub>4</sub>NO<sub>3</sub>, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Extraction and carbonation tests were conducted using waste cement powder as the raw material under ambient temperature and pressure conditions at a solid to liquid ratio of 50 g/L with two different concentrations of ammonium salt solution (0.5 M and 1.0 M). At higher concentration (1 M), the Ca extraction efficiency (~70%) was higher in the CH<sub>3</sub>COONH<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub> solutions, but lower in the NH<sub>4</sub>Cl (32%) and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solutions (5%). The Ca selectivity (~98%) was higher in the CH<sub>3</sub>COONH<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub>, and NH<sub>4</sub>Cl solutions, but lower in the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution (90%). The carbonation efficiency was comparable to the extraction efficiency. The carbonation efficiency with the CH<sub>3</sub>COONH<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub> solutions was higher. Regardless of the type of ammonium salt, high purity vaterite was precipitated after CO<sub>2</sub> injection.

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### 1. Introduction

Carbon capture and storage (CCS) is a promising geoeengineering technique to reduce atmospheric CO<sub>2</sub> concentration. Among the CCS options, CO<sub>2</sub> mineral carbonation can permanently sequester CO<sub>2</sub> as a form of carbonate minerals without long-term monitoring. CO<sub>2</sub> mineral carbonation is a process in which alkaline earth metals (primarily Ca and Mg) are combined with CO<sub>2</sub> to form carbonate minerals with or without aqueous phase [1].

The carbonate minerals formed during the CO<sub>2</sub> mineral carbonation process have industrial uses provided that their purity and morphology are controlled. For example, calcium carbonate (CaCO<sub>3</sub>) is used as a filler and coating pigment in papers, plastics, paints, and rubbers [2]. Industrial CaCO<sub>3</sub> is currently produced by

the following three methods: (1) mixing CO<sub>2</sub> with calcium hydroxide slurry; (2) reacting lime and sodium carbonate in aqueous solutions; and (3) mixing calcium chloride and soda ash solutions. However, these methods require lime (CaO) obtained from limestone calcination, which is energy intensive and emits CO<sub>2</sub> [3]. Thus, several studies have proposed the CaCO<sub>3</sub> precipitation method without energy consumption or CO<sub>2</sub> emission by using recyclable solvents to extract Ca selectively from raw materials for the industrial use of precipitated CaCO<sub>3</sub> [3,4–10]. For example, Eloneva et al. [5] showed that ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), ammonium chloride (NH<sub>4</sub>Cl), and ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>) can be used as recyclable extraction solvents to extract Ca from steel slag. Wang and Maroto-Valer [6] proposed a pH-swing CO<sub>2</sub> mineral carbonation process by using recyclable ammonium salts at elevated temperature (80 °C). Aqueous NH<sub>4</sub>HSO<sub>4</sub> was used to extract Mg from serpentine and the Mg-rich solution was then reacted with NH<sub>4</sub>HCO<sub>3</sub> and NH<sub>3</sub> solutions to

\* Corresponding author. Tel.: +82 2 3290 3179; fax: +82 2 3290 3189.

E-mail address: [hyjo@korea.ac.kr](mailto:hyjo@korea.ac.kr) (H.Y. Jo).

precipitate magnesium carbonates, with a carbonation efficiency of 95.9%. Said et al. [3] also reported that  $\text{NH}_4\text{NO}_3$ ,  $\text{CH}_3\text{COONH}_4$ , and  $\text{NH}_4\text{Cl}$  can be used as solvents for extracting Ca from steelmaking slag, with a maximum Ca extraction efficiency of 73% under certain conditions. The Ca extraction efficiency of steelmaking slag was strongly affected by the test conditions such as the grain size of the steelmaking slag and the solid to liquid ratio.

Alkaline industrial wastes containing a large amount of Ca or Mg (e.g., steel slag, waste concrete, fly ash, red mud, and paper mill waste) have been extensively evaluated as raw materials for  $\text{CO}_2$  mineral carbonation [7,11–26]. Among the alkaline industrial wastes, waste cement, which is a by-product of a waste concrete recycling process to obtain aggregates, has been proposed as a raw material for mineral carbonation due to its high volume production, high Ca content, and small grain size [12,25,27–31]. For example, Huntzinger et al. [30] reported that the  $\text{CO}_2$  sequestration capacity of cement kiln dust (CKD), which is a by-product of a cement manufacturing process, was 0.24 g  $\text{CO}_2/\text{g}$  CKD with 48.0 wt.% of CaO. Recently, Jo et al. [25] showed that the carbonation efficiency of waste cement material was strongly affected by both Ca extraction efficiency and the chemical characteristics of the extraction solvents.

Despite these investigations into the effects of ammonium salts on Ca or Mg extraction from steel slag or serpentine and their carbonation, the influence of ammonium salts on the Ca extraction and carbonation efficiency when waste cement is used as a raw material has rarely been evaluated. The Ca extraction and carbonation efficiency may vary depending on the type of extraction solvent and raw material because raw materials contain various types of Ca-bearing mineral, which have different solubilities in different solvents [7,32]. Thus, the objective of this study was to investigate the effect of four different ammonium salts ( $\text{CH}_3\text{COONH}_4$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ , and  $(\text{NH}_4)_2\text{SO}_4$ ) on the metal extraction and  $\text{CO}_2$  mineral carbonation characteristics when using waste cement as the raw material. Ca extraction and carbonation tests were conducted at different test conditions (ammonium salt concentration and  $\text{CO}_2$  flow rate) to evaluate the feasibility for industrial consumption of the precipitated calcium carbonates formed as a result of  $\text{CO}_2$  mineral carbonation.

## 2. Materials and methods

### 2.1. Materials

Type I ordinary Portland cement was mixed with tap water to form ball shaped mixtures that were cured at room temperature and stored at atmospheric condition for 3 years to simulate waste cement. The matured samples were pulverized using a ball milling machine and then passed through US standard #100 sieve (0.15 mm). In Korea, the waste concrete produced from construction industries is pulverized and then sorted by size. The large aggregates are recycled to make concrete as an additive. Water and flocculent are added to the remaining powder to prevent dust loss into the atmosphere. The solidified powder is then disposed in landfills. Thus, only the waste cement powder that had been passed through #100 sieve was used in this study to evaluate the feasibility of using the waste cement powder as a raw material for  $\text{CO}_2$  mineral carbonation.

Analytical grade  $\text{CH}_3\text{COONH}_4$ ,  $\text{NH}_4\text{NO}_3$  (both Junsei Chemical Co. Ltd),  $\text{NH}_4\text{Cl}$ , and  $(\text{NH}_4)_2\text{SO}_4$  (both Sigma–Aldrich Co.) were used to evaluate the effect of the type of ammonium salt solution on metal extraction and  $\text{CO}_2$  mineral carbonation. Two different concentrations (i.e., 0.5 M and 1.0 M) were used to evaluate the effect of ammonium salt concentration on the metal extraction and mineral carbonation for a given amount of waste cement. The

ammonium salt solutions were prepared by dissolving the analytical grade ammonium salts in deionized (DI) water.

### 2.2. Extraction and carbonation tests

The extraction test was conducted on the waste cement powder in a 500 ml Erlenmeyer flask using an ammonium salt solution as a solvent. For the extraction test, the slurry was prepared by pouring 25 g of air-dried waste cement powder into the 500 ml Erlenmeyer flask with 0.5 M or 1.0 M 500 ml-ammonium salt solution to give a solid to liquid ratio of 50 g/l. The Erlenmeyer flask was sealed with parafilm. The slurry was shaken in a sealed water bath shaker at 130 rpm for 4 h at 20 °C. After shaking, the pH of the slurry was immediately measured using a pH electrode (Thermo Scientific) and the slurry was then filtered through a 0.2  $\mu\text{m}$  membrane filter (ADVANTEC®). 300 ml of filtrate was placed in the 500 ml Erlenmeyer flask for the carbonation test. Approximately 30 ml of filtrate was stored in a 50 ml polyethylene bottle, and acidified by adding  $\text{HNO}_3$  solution for chemical analysis. The filter cake on the membrane filter was oven dried for 3 days at 80 °C and stored in a vacuum desiccator for material characterizations.

The carbonation test was conducted on the 300 ml filtered solution placed in the 500 ml Erlenmeyer flask at a stirring rate of approximately 300 rpm, which was obtained from the extraction test, by injecting a  $\text{CO}_2$  gas mixture of 15 vol.%  $\text{CO}_2$  and 85 vol.%  $\text{N}_2$ , chosen because the flue gas from fire power plants in Korea generally contains 15 vol.%  $\text{CO}_2$ . The pH electrode and  $\text{CO}_2$  injection Teflon tube with inner diameter of 4 mm were placed in the 500 ml Erlenmeyer flask containing the 300 ml filtered solution. The gas mixture was injected directly from the Teflon tube into the bottom of the Erlenmeyer flask at a flow rate of 40 or 200 ml/min, as controlled by a mass flow controller (Alicat 500SCCM). During the  $\text{CO}_2$  injection, the solution was stirred using a magnetic stirrer for homogeneous mixing. The pH was recorded automatically using a personal computer with hyper-terminal program to monitor temporal changes in the chemical characteristics of the solution during  $\text{CO}_2$  injection. The carbonation test was terminated when a pH of around 8.0 was attained to prevent dissolution of the precipitated  $\text{CaCO}_3$ , which remains dissolved at  $\text{pH} < 8.3$  [33]. After  $\text{CO}_2$  injection, the mixture was filtered through a 0.2  $\mu\text{m}$  membrane filter (ADVANTEC®). Approximately 30 ml of filtrate was stored in a 50 ml polyethylene bottle, and acidified by adding  $\text{HNO}_3$  solution for chemical analysis. The filter cakes on the membrane filter was oven dried for 3 days at 80 °C and stored in a vacuum desiccator for material characterizations.

### 2.3. Chemical analysis and material characterization

The leachates obtained from the extraction and carbonation tests were analyzed by using an inductivity coupled plasma-atomic emission spectroscopy (ICP-AES, OPTIMA 3000XL, PerkinElmer) in Korea Basic Science Institute (KBSI). The leachate samples were analyzed three times and averaged. The chemical composition of the unreacted material was analyzed by using X-ray fluorescence (XRF: ZSX Primuss II, Rigaku). The mineral component of the unreacted and reacted materials was analyzed by using X-ray diffractometer (XRD: Analytical X-ray BV X'pert-MPD, philips). The morphology and chemical composition of the unreacted and reacted materials were analyzed by using a field emission scanning electron microscope (FE-SEM: Hitachi S-4300) equipped with energy dispersive X-ray spectroscopy (EDX: Horiba EX-20). The calcium carbonate ( $\text{CaCO}_3$ ) content of the reacted materials obtained from the extraction and carbonation tests was analyzed by using differential thermal and thermogravimetric analysis (DT-TGA: Shimadzu DTG-60H). The  $\text{CaCO}_3$  content based on the results of DT-TGA can be determined using the following equation:

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