

사문암(Serpentinite)을 이용한 광물탄산화: Mg 추출과 pH swing 및 탄산화

Mineral Carbonation of Serpentinite: Extraction, pH swing, and Carbonation

이승우(Seung-Woo LEE)¹ · 원혜인(Hyein Won)¹ · 최병영(Byoung-Young Choi)² ·
채수천(Soochun Chae)¹ · 방준환(Jun-Hwan Bang)¹ · 박권규(Kwon Gyu Park)^{2,*}

¹탄소광물화사업단 한국지질자원연구원

(Center for carbon mineralization, Korea Institute of Geosciences and Mineral Resources)

²지중저장연구단 한국지질자원연구원

(Center for CO₂ geological storage, Korea Institute of Geosciences and Mineral Resources)

요약 : 간접 탄산화(indirect method) 및 양이온 공급원으로 사문암(serpentinite)을 이용하여 광물탄산화 연구를 수행하였다. 이산화탄소와 사문암 내 알칼리 토금속(칼슘과 마그네슘)의 탄산화 반응을 통해 고 순도의 탄산칼슘과 탄산마그네슘을 합성할 수 있었다. 마그네슘 추출을 위해 황산암모늄을 사용하였고 Mg 추출률 향상을 위해 황산암모늄 농도, 반응온도 및 사문암과 추출 용매의 비(고액비) 등 여러 반응 변수를 검토하였다. 본 연구로부터 2 M 황산암모늄을 사용하여 300°C 반응온도에서 고액비(5 g/66 mL) 실험을 진행한 경우 약 80 wt% 이상의 Mg를 얻을 수 있었다. Mg 추출률은 추출 용매 농도 및 반응온도와 비례하여 증가하였다. 사문암의 Mg 추출 과정에서 얻어진 암모니아(NH₃)는 회수하여 탄산화 과정에서 필요한 pH 복원제(pH swing agent)로 활용하였다. 본 연구를 통해 약 1.78 M 암모니아를 회수할 수 있었고 지구화학 모델링을 통해 사문암의 Mg 추출 과정의 핵심 단계를 해석하고자 하였다.

주요어 : 이산화탄소, 광물탄산화, 사문암, 마그네슘 추출, pH 전환

ABSTRACT : Mineral carbonation by indirect method has been studied by serpentinite as cation source. Through the carbonation of CO₂ and alkaline earth ions (calcium and magnesium) from serpentinite, the pure carbonates including MgCO₃ and CaCO₃ were synthesized. The extraction solvent used to extract magnesium (Mg) was ammonium sulfate ((NH₄)₂SO₄), and the investigated experimental factors were the concentration of (NH₄)₂SO₄, reaction temperature, and ratio of serpentinite to the extraction solvent. From this study, the Mg extraction efficiency of approximately 80 wt% was obtained under the conditions of 2 M (NH₄)₂SO₄, 300°C, and a ratio of 5 g of serpentinite/75 mL of extraction solvent. The Mg extraction efficiency was proportional to the concentration and reaction temperature. NH₃ produced from the Mg extraction of serpentinite was used as a pH swing agent for carbonation to increase the pH value. About 1.78 M of NH₃ as the form of NH₄⁺ was recovered after Mg extraction from serpentinite. And, the main step in Mg extraction process of serpentinite was estimated by geochemical modeling.

Key words : Carbon dioxide, Mineral Carbonation, Serpentinite, Mg extraction, pH swing

*Corresponding author: +82-42-868-3250, E-mail: kgpark@kigam.re.kr

Introduction

Serpentinites are rocks consisting mostly of serpentine group minerals. Minerals in this group are formed by serpentinization, a hydration and metamorphic transformation by Earth surface conditions and hydrothermal temperatures (Evans *et al.*, 2013). Serpentine group minerals have the approximate formula, $(R_6^{2+}) Si_4O_{10}$ (R: Mg^{2+} , Fe^{2+} , Mn^{2+} , or Ni^{2+}), and mainly consists of antigorite, lizardite, and chrysotile (Bailey, 1988).

During the last two decades the interest in how to keep the captured CO_2 permanently away from the atmosphere has increased, especially at the point of CCS (Carbon Capture & Storage) and mineral carbonation (Carneiro *et al.*, 2011; Zhang and Bachu, 2011; Wolterbeek *et al.*, 2013). Mineral carbonation is a technology to reduce CO_2 on the basis of alkaline metals in natural minerals or industrial wastes. It can proceed through direct method (carbonation) and indirect method (extraction and carbonation) (Azdarpour, 2015).

Research investigating CCS has been demonstrated in the USA, England, and Australia, countries which have a commercialized gas or oil field. On the other hand, research investigating mineral carbonation could be profitable for the countries that do not have enough sites for CO_2 storage but produce Ca- or Mg-rich rock through mining. The advantages of CCS are the availability of a large amount of CO_2 storage and a relatively lower processing cost compared to mineral carbonation. The merit of mineral carbonation is CO_2 storage ability in a thermodynamically stable form, carbonate minerals, and the minimization of future costs associated with the monitoring of the risk of CO_2 leakage. Of course, there are disadvantages of mineral carbonation. Especially, the weakest point of mineral carbonation (indirect method) is that the supply cost of extraction solvent is high at the viewpoint of economic feasibility (Azarpour *et al.*, 2015; Lee *et al.*, 2016). Thus, the development of technology that can reduce the processing cost is so important.

At the point of mineral carbonation, Mg-silicate rock including serpentinite has the potential to be used as materials for carbonation because of its

higher Mg content and relatively lower reaction temperature compared to other minerals (Béarat *et al.*, 2002; Lin *et al.*, 2008; Wang and Maroto-Valer, 2011). However, natural minerals including serpentinite need to be mined and pulverized. Thus, the total cost of mineral carbonation using natural minerals or rocks would be increased due to material pretreatment. To create a cost-effective process for mineral carbonation, there are several prerequisites. First, the maximum extraction efficiency for alkaline earth metals is an essential. For example, the extraction of magnesium from Mg-silicate rocks during mineral carbonation can determine the amount of stored CO_2 as carbonate minerals. The second requirement is the recovery and reuse of the extraction solvent for a cost-effective mineral carbonation process. Finally, there is the development of high value-added product. Researchers investigating mineral carbonation have to consider how to apply the carbonate materials such as $MgCO_3$ and $CaCO_3$ after CO_2 fixation to relevant industrial fields such as paper, paint, building structures, fire proofing, fire extinguishing compositions, and so on. There are many studies on mineral carbonation using various methods worldwide. However, the most important studies are those that propose a cost-effective process for mineral carbonation. The process will unify the entire CO_2 market related to mineral carbonation.

In the study, we have tried to propose a model of a cost-effective process using serpentinite and $(NH_4)_2SO_4$. The optimum experimental factors including the concentration of ammonium sulfate, ratio of serpentinite to extraction solvent, and reaction temperature were identified for the maximum Mg extraction efficiency at $300^\circ C$ of reaction temperature, the recovery and the reuse of NH_3 as a pH swing agent for carbonation.

Materials and Method

Materials

The serpentinite used in the experiment was obtained from Andong serpentinite mine (South Korea), and was pulverized. The serpentinite

pulverized below 75 μm was used for the Mg extraction. The elemental analysis of serpentinite was carried out by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 5300 DV, Perkin Elmer).

Quantitative Analysis using X-ray diffraction pattern

Rietveld analysis was employed in the quantitative phase analysis of the serpentinite. All calculations were performed with Diffrac. TOPAS (ver. 4.2.0.2, Bruker AXS GmbH). The XRD pattern of the serpentinite was acquired by a high resolution X-ray diffractometer (D8 Discover, Bruker AXS GmbH). Diffraction patterns of sufficient resolution for Rietveld analysis were obtained under the following conditions: step interval, 0.05° between 5 and 120° (2θ); and wavelength of 1.893 \AA . The refinement was carried out until the agreement factor (good of fitness (GOF)) was below 1.5.

Magnesium extraction

To increase the Mg extraction efficiency, several experimental factors were investigated including the concentration of the extraction solvent $(\text{NH}_4)_2\text{SO}_4$, reaction temperature, and ratio of serpentinite (g) to extraction solvent (mL). $(\text{NH}_4)_2\text{SO}_4$ was used as the extraction solvent to extract magnesium from serpentinite. The concentration range of $(\text{NH}_4)_2\text{SO}_4$ was from 0.5 M to 2 M. And the range of reaction temperature was from 200°C to 300°C . The interval of the reaction temperatures was set at 50°C . The ratios of serpentinite (g) to extraction solvent (ml) investigated were 5 g/100 mL, 5 g/75 mL, and 5 g/50 mL, and N_2 gas was injected into the reactor until a pressure of 5 bar to check the sealing of the reactor. The degree of Mg extraction was calculated by equation (1).

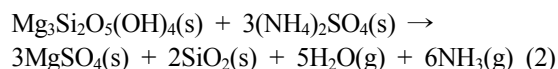
$$\eta_{\text{Mg}}(\%) = \frac{C_{\text{Mg}}(\text{g/mol}) \times V(l)}{M_{\text{serpentinite}}(\text{g}) \times X_{\text{Mg}}(\text{g})} \times 100 \quad (1)$$

C_{Mg} is the Mg concentration in solution after the extraction, and it was analyzed by ICP-OES. $M_{\text{serpentinite}}$ is the mass (g) of serpentinite used in the experiment, and X_{Mg} is the Mg concentration of serpentinite before extraction. V indicates the volume of solution including $(\text{NH}_4)_2\text{SO}_4$ and distilled water.

To extract Mg from serpentinite, the autoclave (C-276) made by Hastelloy, containing a nickel-molybdenum-chromium alloy was used (III in Fig. 1C). The holding time at each reaction temperature is 10 seconds, and the power of the reactor was cut off after 10 seconds. After the reactor was stopped and cooled down, the produced gas including N_2 and NH_3 was introduced into 75 mL of distilled water for the recovery and reuse of NH_3 . The solid and liquid in the extraction solvent after the experiment were separated by filtration.

Recovery of NH_3 for reuse as a pH swing agent

The reuse of the extraction solvent is an important technique to obtain a cost-effective process for mineral carbonation. The $(\text{NH}_4)_2\text{SO}_4$ used as the extraction solvent could be decomposed at approximately 300°C . As shown in reaction (2), the serpentinite reacted with ammonium sulfate reacted, and then 6 M NH_3 can be produced from 3 M $(\text{NH}_4)_2\text{SO}_4$ above 250°C .



After Mg extraction from serpentinite, the solid (serpentinite residue) and liquid (solution) were separated by filtration. The pH value of the extraction solvent $(\text{NH}_4)_2\text{SO}_4$ before and after Mg extraction was analyzed by a pH meter (Orion 3 Star, Thermo Scientific). The concentration of ammonium ion existing in the extraction solvent after Mg extraction was analyzed by ion chromatography (883 Basic IC Plus, Metrohm). The NH_4^+ rich solution was used as a pH swing

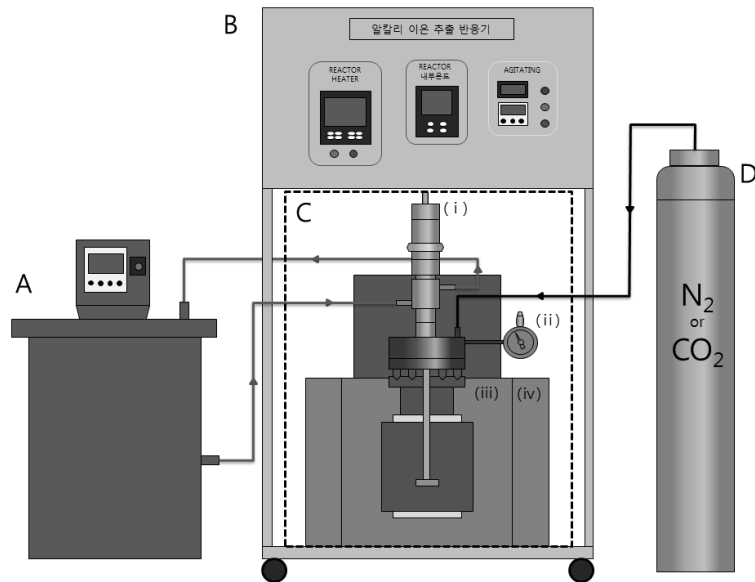


Fig. 1. Schematic illustration of the extraction system for magnesium from serpentinite (A: water bath, B: controller, C: reactor including stirrer, and D: gas (N₂ or CO₂). The dotted line indicates the main part of the extraction system. That part consists of a stirrer (i) cooled by a water bath, a pressure gauge (ii), a reactor (iii), and a furnace (iv). N₂ gas was inserted into the reactor for extraction, and CO₂ gas was inserted into the reactor for carbonation.

agent for the carbonation between CO₂ and the Mg-rich solution.

Characterization after Mg extraction and carbonation

After Mg extraction using (NH₄)₂SO₄, the content of magnesium in the extraction solvent was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 5300 DV, Perkin Elmer). The morphologies of the synthesized carbonation minerals (MgCO₃ and CaCO₃) were analyzed by a field emission scanning electron microscope (FE-SEM, MERIN, Carl Zeiss), and the surface elements of the carbonate minerals were analyzed by an energy dispersive spectrometer (EDS, Xflash 6, Bruker).

Geochemical reaction path model

To trace the geochemical reactions during the experiments, reaction path modeling was per-

formed using PHREEQC v. 3 (Parkhurst and Appelo, 2017) for the case showing the highest extraction efficiency of Mg: 2M (NH₄)₂SO₄, 5 g/75 mL. Thermodynamic database used for the water-rock interactions were THERMODDEM.DAT (Blanc *et al.*, 2012) because it has the thermodynamic data for all minerals identified in this study. Instead, ammonia redox state was decoupled from nitrogen gas to inhibit the complete oxidation of ammonium into nitrogen gas. In this study, the dissolution/precipitation of all minerals was simulated considering the dissolution kinetics of minerals and the gradual increase of temperature up to 300°C. The dissolution kinetics was based on the transition state theory (Lasaga, 1998) as the following equation:

$$r_n = \pm k_n A_n \left[1 - \left(\frac{Q_n}{K_n} \right)^{\theta/n} \right] \quad (3)$$

where n is mineral index, r is the kinetic rate for dissolution (positive values) and precipitation

Table 1. Kinetic parameters of minerals used in this model

Minerals	Kinetic parameters ^a							
	Neutral mechanism		Acid mechanism			Base mechanism		
	logK ₂₅ (mol/m ² /s)	E _a (kJ/mol)	logK ₂₅ (mol/m ² /s)	E _a (kJ/mol)	n (H ⁺)	logK ₂₅ (mol/m ² /s)	E _a (kJ/mol)	n (H ⁺)
Antigorite	-12.04 ^b	56.6	-9.01 ^b	75.5	0.8	-	-	-
Calcite	-5.80	24.0	-0.30	14.0	1	-	-	-
Chlorite	-12.52	88.0	-11.11	88.0	0.5	-	-	-
Clinochlore	-12.52	88.0	-11.11	88.0	0.5	-	-	-
Enstatite	-12.72	80.0	-9.02	80.0	0.6	-	-	-
Lizardite	-12.04 ^b	56.6	-9.01 ^b	75.5	0.8	-	-	-
Magnetite	-10.78	18.6	-8.59	18.6	0.279	-	-	-
Wollastonite	-8.88	54.7	-5.37	54.7	0.4	-	-	-

^a: from reference (Parkhurst and Appelo, 2017), ^b: from reference (Critelli *et al.*, 2015).

Table 2. Elemental analysis of serpentinite before extraction (units: wt%). All elements except sulfur are presented as oxide forms

Composition	SiO ₂	Fe ₂ O ₃	FeO	CaO	MgO	S	I _{gloss}
	34.0	11.4	0.43	2.91	37.2	0.21	11.9

(negative values), k is the rate constant (moles per unit mineral surface area and unit time), A is the specific reactive surface area per gram of mineral, Q is the reaction quotient, and K is the equilibrium constant. The parameters Θ and η are commonly taken equal to unity. The kinetics of minerals is pH-dependent and is catalyzed by H⁺, H₂O, and OH⁻. The overall reaction rate is the sum of the rates of the individual reaction mechanism and is calculated as follows (Palandri and Kharaka, 2004):

$$k = k_{25}^{nu} \exp \left[\frac{-E_a^{nu}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] + k_{25}^H \exp \left[\frac{-E_a^H}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_H^{n_H} + k_{25}^{OH} \exp \left[\frac{-E_a^{OH}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_{OH}^{n_{OH}} \quad (4)$$

where nu, H, and OH represent the neutral, acid and base mechanisms, respectively. E is activation energy, K_{25} is rate constant at 25°C, R

is the gas constant, T is the absolute temperature, a is activity of the species, and n is the power constant. Most kinetic parameters were taken from Palandri and Kharaka (2004) and the rate constants of serpentinite minerals were from Critelli *et al.* (2015) (Table 1).

Results and Discussion

Characterization of serpentinite

As shown in ICP-OES (Table 2), the serpentinite used in the experiment has a higher content of magnesium (MgO : 37.2 wt%) than calcium (CaO : 2.91 wt%). The serpentinite contains 34 wt% of SiO₂ and approximately 11 wt% of iron including Fe₂O₃ and FeO. The first objective in the study was to extract Mg from the serpentinite as effectively as possible.

From the Rietveld refinement (Table 3), the crystal phases of the serpentinite showed that antigorite (41.49%) and lizardite (18.91%) occupied

Table 3. Crystalline composition of serpentinite obtained from Rietveld refinement

Crystal phase	Value (%)
Wollastonite-1A	3.18
Calcite	2.77
Chlorite	15.18
Magnetite	3.02
Lizardite	18.91
Antigorite	41.49
MgSiO ₃	3.15
Clinochlore	12.27

approximately 60% of total crystalline minerals, and approximately 2.77% of the total crystalline minerals was identified as calcite. The CaCO₃ is inferred from the result of the weathering of serpentinite.

Mg extraction

To obtain the highest Mg extraction efficiency from the serpentinite, the concentration of ext-

Table 4. Extraction efficiency of magnesium from serpentinite. (NH₄)₂SO₄ was used as the extraction solution for Mg extraction. Experimental parameters were as follows: concentration of the extraction solution, ratio of serpentinite to the extraction solution, and reaction temperature

Conc. of solution (mol)	Ratio (serpentinite/solution) (g/mL)	Reaction Temperature (°C)	Extraction of Mg (%)
0.5 M	5 g/100 mL	200°C	8.35
		250°C	11.77
		300°C	16.30
	5 g/75 mL	200°C	6.42
		250°C	11.29
		300°C	17.33
	5 g/50 mL	200°C	6.76
		250°C	14.67
		300°C	15.68
1 M	5 g/100 mL	200°C	15.52
		250°C	26.97
		300°C	47.98
	5 g/75 mL	200°C	11.88
		250°C	18.01
		300°C	61.62
	5 g/50 mL	200°C	11.31
		250°C	20.16
		300°C	30.91
2 M	5 g/100 mL	200°C	20.22
		250°C	29.79
		300°C	77.32
	5 g/75 mL	200°C	17.47
		250°C	26.07
		300°C	84.11
	5 g/50 mL	200°C	14.11
		250°C	23.74
		300°C	31.36

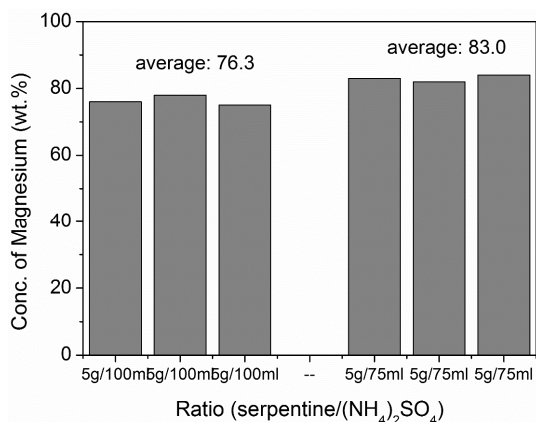


Fig. 2. Extraction yield of magnesium (experimental conditions: 2 M ammonium sulfate, 200 RPM, 30 °C). The ratio of serpentine (g) to extraction solution (L) (NH₄)₂SO₄ was fixed to 5/100 and 5/75, and the values (76.3 ± 1.53 and 83.0 ± 1.02) are the averages the second deviation of three experiments.

reaction solvent, (NH₄)₂SO₄, ratio of serpentine to extraction solvent, and reaction temperature were investigated (Table 4). As shown in Table 4, the higher the concentration of (NH₄)₂SO₄ and reaction temperature, the greater the Mg extraction efficiency. However, the ratio of serpentine to extraction solvent was not directly proportional to the Mg extraction efficiency. In the case of 2 M (NH₄)₂SO₄ as the extraction solvent, the Mg extraction efficiency at the ratio 5 g/75 mL was higher than that at the ratio 5 g/100 mL (Fig. 2). The best Mg extraction efficiency in the study was 83.0 wt% on average, and the experiment was carried out three times for the identification of reproducibility. The prime experimental factor determining the Mg extraction efficiency was the reaction temperature, which is related to the decomposition of the extraction solvent, (NH₄)₂SO₄. The melting point range of (NH₄)₂SO₄ is 235-280 °C. At that point, (NH₄)₂SO₄ can be thermally decomposed and reacted with serpentine. Thus, a reaction temperature above 300 °C was an important factor to extract higher amounts of Mg from serpentine compared to temperatures of 200 °C and 250 °C. From the

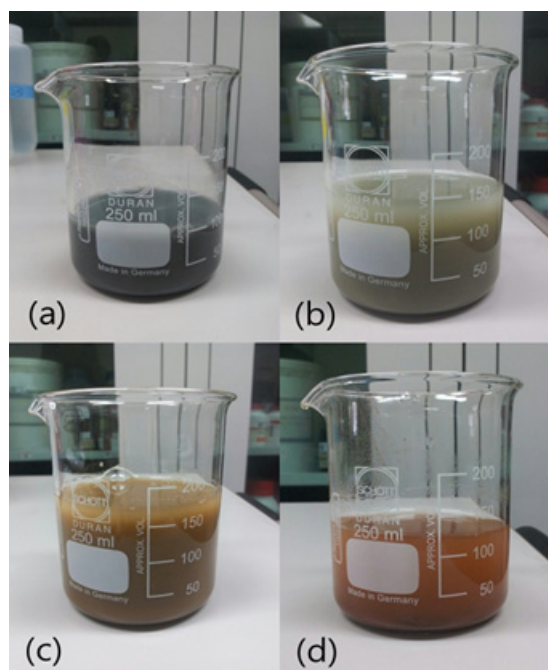


Fig. S1. Photos before and after extraction: (a) slurry solution including serpentine and (NH₄)₂SO₄ before extraction, (b) slurry solution after extraction at 200 °C, (c) slurry solution after extraction at 250 °C, and (d) slurry solution after extraction at 300 °C.

measurement of the color of the slurry including serpentine and (NH₄)₂SO₄ (supplementary information, Fig. S1), a difference in the color was identified before and after Mg extraction. The color of the slurry before extraction was blue celeste. On the other hand, the color of the slurry after the experiment was red corresponding with the increase in the reaction temperature. This effect could be inferred to be due to the dissolution of iron (Fe₂O₃, 11.4%) in serpentine (Table 2). As the reaction temperature was increased, the color of the slurry was changed to reddish.

The pH value of the Mg-rich extraction solvent after extraction was measured. The range of the pH values according to the reaction temperature was 10.69-11.04, and the average of pH was 10.88 (supplementary information, Fig. S2). The high pH value resulted from the production of

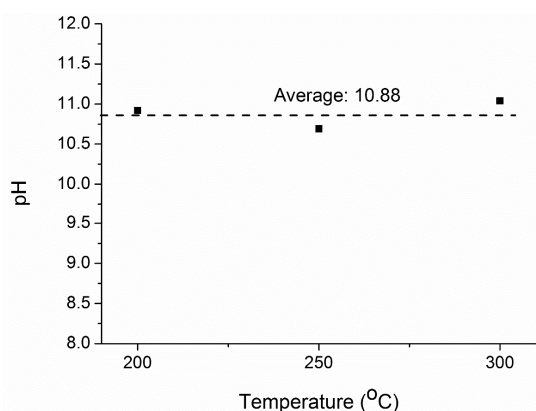


Fig. S2. pH value of the solution after extraction. Depending on the reaction temperature, the pH value shows a range of 10.88 ± 0.18 .

NH_3 due to the decomposition of $(\text{NH}_4)_2\text{SO}_4$.

At the point of CO_2 sequestration, the process related to mineral carbonation needs a high extraction efficiency of calcium and/or magnesium because the amount of earth metal ions determines the mass of CO_2 to be stored. Thus, the development of a high extraction method for Mg and/or Ca would be one of prerequisites for the proposal of a cost-effective CO_2 utilization process. In this study, we analyzed experimental factors including the concentration of the extraction solvent $(\text{NH}_4)_2\text{SO}_4$, ratio of serpentinite

to extraction solvent, and reaction temperature to obtain the highest Mg extraction efficiency from the serpentinite. We found the best experimental conditions to be 2 M $(\text{NH}_4)_2\text{SO}_4$, a ratio of 5 g/75 mL, and 300°C. Using these experimental conditions, around an 83 wt% Mg extraction efficiency was obtained.

Reuse of the extraction solvent as a pH swing agent

Through the dissolution of NH_3 (gas phase) into distilled water during Mg extraction at 300°C (reaction temperature), a NH_4^+ rich solution can be prepared (Dissolution part in Fig. 2). From the analysis of ion chromatography (IC) after Mg extraction, the quantity of NH_4^+ was measured to approximately 30,000 ppm (Table 5). Based on the reaction (equation 2) of serpentine group ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) and $3(\text{NH}_4)_2\text{SO}_4$ (extraction solvent) equation, the measured quantity of NH_4^+ , 30,000 ppm, was calculated from the amount of NH_3 produced from the reaction of serpentinite and $(\text{NH}_4)_2\text{SO}_4$.

The amount of NH_3 was 1.78 mol, meaning 44% of ammonia was able to be produced through equation (2). Considering the solubility (33% w/w) of NH_3 at 25°C (Oxtoby *et al.*, 2012),

Table 5. Concentration of ammonium ions after Mg extraction from serpentinite. $(\text{NH}_4)_2\text{SO}_4$ was used as the solution for extraction. The concentration (*) of ammonium ions was analyzed in the extraction solution after Mg extraction. The NH_4^+ was analyzed by ion chromatography (IC)

Conc. of solution (mol)	Ratio (serpentinite/solution) (g/mL)	Reaction Temperature (°C)	Conc. (NH_4^+)* (ppm)	Average of NH_4^+ (ppm)
2 M $(\text{NH}_4)_2\text{SO}_4$	5 g/100 mL	200°C	37,285	36,717
		250°C	36,603	
		300°C	36,263	
	5 g/75 mL	200°C	32,333	31,738
		250°C	30,632	
		300°C	32,249	
	5 g/50 mL	200°C	27,465	25,407
		250°C	24,304	
		300°C	24,452	

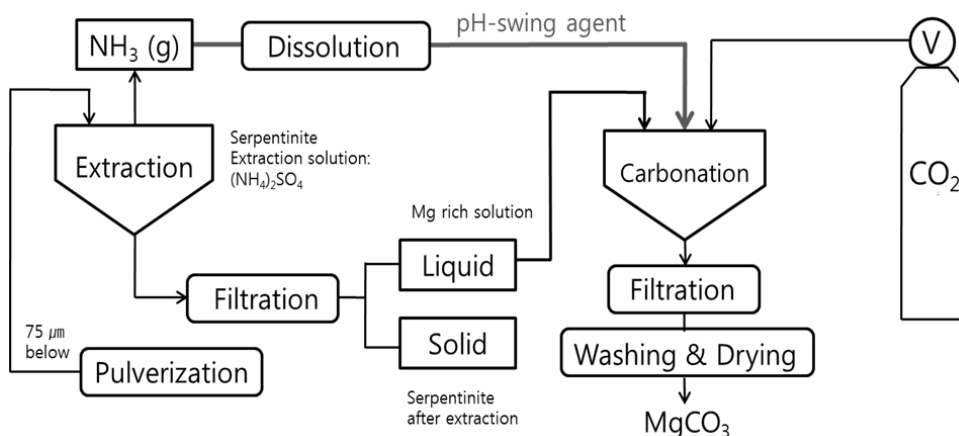


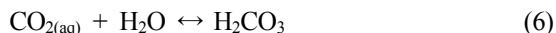
Fig. 3. The pH swing process on serpentine (Mg-silicates) and blast furnace slag (Ca-silicates). The concept of this process is the reuse of a NH_4^+ -rich solution for carbonation. The NH_4^+ -rich solution was obtained from the Mg extraction of serpentine. To synthesize CaCO_3 precipitate, a high pH value above 10 is needed, and the NH_4^+ -rich solution was used as the pH swing agent for the carbonation processes of both serpentine and BF slag after Mg and Ca extraction. The V means valve of CO_2 gas.

a large amount of NH_3 would be dissolved in the $(\text{NH}_4)_2\text{SO}_4$ solvent after Mg extraction. Previous researchers reported the potential of ammonium salt for mineral carbonation (Park and Fan, 2004; Mirjafari *et al.*, 2007; Lee *et al.*, 2010; Wang and Martoto-Valer, 2011; Sanna *et al.*, 2013). The pH value of solution including dissolved NH_3 and extraction solvent was approximately 11 because of the presence of NH_4^+ in solution.

To develop a cost-effective process for mineral carbonation, we propose a new process focused on the recovery and the reuse of the NH_3 after Mg extraction at 300°C as a pH swing agent (blue line in Fig. 3). The NH_3 after Mg extraction was dissolved in distilled water and supplied to carbonation reactor to increase pH value. The important factor of the carbonation process is the pH value. The conversion of gaseous carbon dioxide (CO_2) into a carbonate ion (CO_3^{2-}) has to proceed through several steps, as shown in reaction (5-9) (Cartwright *et al.*, 2012). First, gaseous carbon dioxide has to be dissolved.



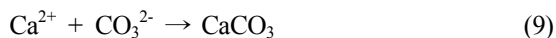
Then, aqueous CO_2 reacts with water to form carbonic acid



In the next step, carbonic acid dissociates to bicarbonate and carbonate ions.



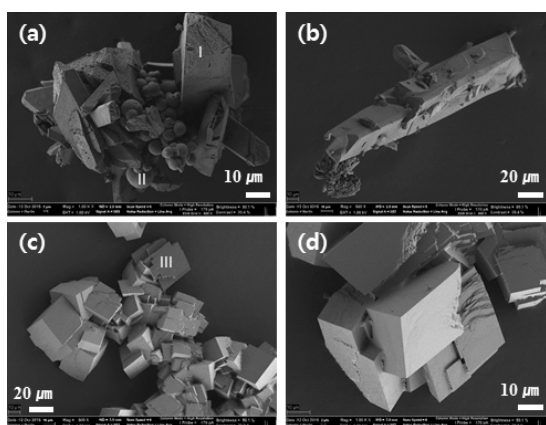
Finally, in the presence of calcium cations, calcium carbonate forms and precipitates.



Under acidic conditions, carbonation cannot occur because bicarbonate ions (HCO_3^-) could not be converted into carbonate ions (CO_3^{2-}) but would be converted to carbonic acid (H_2CO_3) instead. Consequently, CaCO_3 cannot be precipitated in the above acidic condition. The advantage of basic conditions for carbonation is that it is easy to control the conversion and purity of CaCO_3 .

Table 6. EDS analysis of particles after the carbonation of serpentinite and BF slag (unit: atomic ratio)

Sample	Calcium	Magnesium	Carbon	Oxygen
(I) Particle in Fig. 7a	0.03	1.28	1.88	2.61
(II) Sphere in Fig. 7a	0.42	0.06	2.16	3.21
(III) Particle in Fig. 7b	1.53	-	1.03	2.08

**Fig. 4.** FE-SEM images after carbonation of a Mg-rich solution (serpentinite) (a and b) and a Ca-rich solution (BF slag) (c and d). The scale bar indicates 10 μm (a and d) and 20 μm (b and c), respectively. The characters I, II, and III are the points analyzed by EDS.

Carbonation

The effect of the pH swing agent, a NH_4^+ -rich solution, on carbonation was identified. The first acid ionization constant of CO_2 , K_{a1} , is 4.3×10^{-7} at 25°C , and the concentration of hydrogen ion (H^+) is 2.1×10^{-4} (Mirjafari *et al.*, 2007). Based on 2 M $(\text{NH}_4)_2\text{SO}_4$ (100 mL) and 5 g of serpentinite, the average Mg extraction is 6,600 ppm at a reaction temperature of 300°C . On the other hand, the average Ca extraction is approximately 1,000 ppm.

From the electron microscope analysis of the precipitates after carbonation, distinct shaped particles obtained from carbonation were identified (Fig. 4). The carbonation of the Mg-rich solution obtained from serpentinite and CO_2 showed synthesized particles with a rhombohedral form (I in Fig. 4a) and sphere-shaped form (II in

Fig. 4a). Additionally, cubic-like particles (III in Fig. 3c) were identified through the carbonation. From the EDS analysis (Table 6), we found that the particles with angled forms (I in Fig. 4a) contain relatively higher Mg contents compared to the other shaped particles, whereas the sphere-shaped particles (I in Fig. 4a) have relatively higher Ca contents. The existence of calcium in the sphere-shaped particles resulted from the extraction of Ca contained in serpentinite. On the other hand, the cubic-like particles (III in Fig. 4c) showed the typical atomic ratio of CaCO_3 (Table 6).

There are three anhydrous crystalline polymorphs of CaCO_3 , which are ordered by their decreasing thermodynamic stabilities under atmospheric conditions: calcite, aragonite, and vaterite (Cartwright *et al.*, 2012). Among them, calcite is the most thermodynamically stable and is the crystal structure (trigonal) typically found in nature. On the contrary, vaterite has a higher free energy than calcite, and calcite is usually formed from the transformation of vaterite or amorphous calcium carbonate (Rodriguez-Blanco *et al.*, 2011). However, the kinetics and mechanisms still need to be studied. From previous studies (Song *et al.*, 2014; Luo *et al.*, 2015), the shape of calcite has been reported to be cubic and that of vaterite has been reported to be spherical. Thus, the synthesized sphere-shaped particles and cubic particles can be considered to be vaterite and calcite, respectively. Based on the atomic ratio from EDS (Table 6), the particles with a rhombohedral form (I in Fig. 4) were determined to be MgCO_3 . As the results were obtained from this study, the carbonation at atmospheric condition preferred CaCO_3 . The preference of CaCO_3 for carbonation as compared with MgCO_3 could

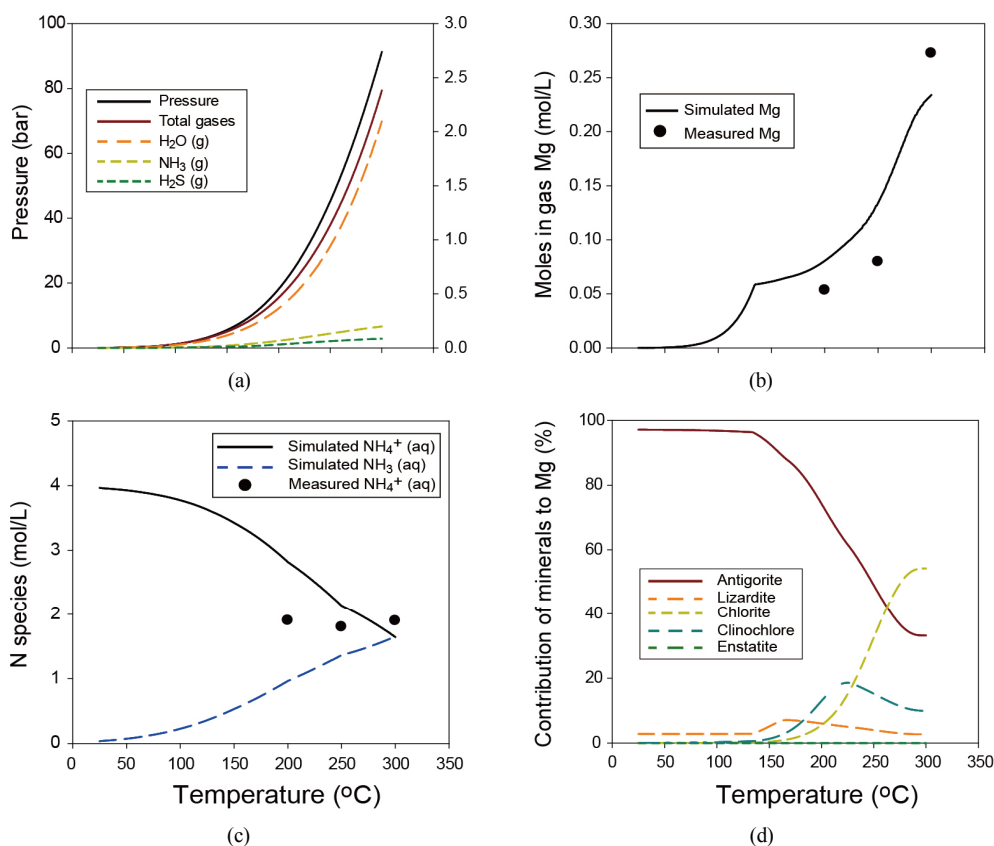


Fig. 5. The results of geochemical modeling; The change in (a) pressure, (b) Mg concentration, (c) N species (NH₄⁺ and NH₃) concentrations, and (d) contribution of each mineral to Mg concentration, respectively. The solid and dotted line indicate the modeling result. The solid circle indicates the measured data.

be understood by solubility product constant. The solubility product constant (K_{sp}) of CaCO₃ (3.36×10^{-9}) at 25°C is lower than that of MgCO₃ (6.82×10^{-6}) (Lide and Frederikse, 1998). The characteristics of carbonates including the solubility product constant have a significant effect on the rate of precipitation of CaCO₃ and MgCO₃, respectively.

The control of the morphology CaCO₃ and MgCO₃ is one of the important factors for the industrial application of synthesized carbonation minerals from mineral carbonation, and the transformation has significant effects on the morphological changes of carbonate minerals. Thus, future research should include a study to investigate the morphological changes via

transformation as well as the optimization of the proposed process.

Geochemical reaction path model

The simulation results are presented in Fig. 5. In the experiment, total pressure in reaction vessels approaches up to 100 bars at 300°C. The simulated pressure also increases up to near 100 bars at 300°C (Fig. 5a). The modeling result also shows that total pressure is mostly composed of vapor pressure. The contribution of NH₃ (g) to total pressure is small but slightly increases with the increase in temperature. The simulated Mg concentrations are presented with the measured values (Fig. 5b). As shown the figure, the

modeling results coincide with the proximity to the experiment results. Similarly, the simulated NH_4^+ concentrations approach to the measured values (Fig. 5c). According to the modeling result, the concentration of NH_4^+ decreases whereas that of NH_3 increases with the increase in temperature. This indicates that NH_4^+ decomposes to NH_3 , finally NH_3 (g). To identify the contributions of the minerals to Mg extraction, we calculate the percentage of Mg leached from each mineral to the total leached Mg (Fig. 5d). This result shows that most Mg is released from the dissolution of antigorite. However, modeling result also shows that the contribution of chlorite increases with the increase in temperature above 150°C. Thus, our modeling results shows that NH_4^+ decomposes into NH_3 (g) with the increase in temperature and most Mg is leached from antigorite and chlorite.

Conclusion

To develop a cost-effective process for mineral carbonation, magnesium extraction from serpentinite has been studied by evaluating the experimental factors, including the concentration of $(\text{NH}_4)_2\text{SO}_4$, reaction temperature, and ratio of serpentinite/extraction solvent. From this study, the following conclusions were made:

Maximum Mg extraction from serpentinite is approximately 80 wt%, and the best experimental conditions are 2 M $(\text{NH}_4)_2\text{SO}_4$ as the concentration of the extraction solvent, 5 g/100 mL as the ratio, and 300°C as the reaction temperature.

The amount of recovered NH_4^+ through the decomposition of $(\text{NH}_4)_2\text{SO}_4$ is approximately 1.78 M, which is used as a pH swing agent for carbonation to induce the precipitation of carbonation materials, such as MgCO_3 and CaCO_3 .

After carbonation, MgCO_3 and CaCO_3 (vaterite) from the extraction solvent of serpentinite are synthesized by reaction with CO_2 , and CaCO_3 (calcite) from the extraction solvent of slag is formed by carbonation. From the results of carbonation, we can identify that the use of a pH

swing agent is effective for the carbonation step.

There are several conditions that still need to be improved for the development of a cost-effective process for mineral carbonation. First, Mg-rich industrial wastes, such as ferro-Ni slag, have to be used as the raw material for mineral carbonation instead of natural minerals. Second, various ammonium solvents need to be tested to obtain the best Mg extraction efficiency. Finally, the high value-added conversion of synthesized MgCO_3 and CaCO_3 can be applied to various industries, which will aid the goal of developing a cost-effective process for mineral carbonation.

Acknowledgements

This research was supported by the Basic Research Project of the Korea Institute of Geoscience and Mineral resources (KIGAM) funded by the Ministry of Science, ICT and Future Planning of Korea.

REFERENCES

- Azdarpour, A., Asadullah, M., Mohammadian, E., Hamidi, H., Junin, R., and Karaei, M.A. (2015) A review on carbon dioxide mineral carbonation through pH-swing process. *Chemical Engineering Journal*, 279, 615-630.
- Bailey, S.W. (1988) Polytypism of 1:1 layer silicates. In: Bailey S.W. (Eds.) *Hydrous phyllosilicates (exclusive of mica)* (1st ed.), Vol. 19, MSA Reviews in Mineralogy, 9-37.
- Béarat, H., Mckelvy, M.J., Chizmeshya, A.V.G., Sharma, R., and Carpenter, R.W. (2002) Magnesium hydroxide dihydroxylation/ carbonation reaction processes: Implication for carbon dioxide mineral sequestration. *Journal of the American Ceramic Society*, 4, 742-748.
- Blanc, P., Lassin, A., Piantone, P., Azaroual, M., Jacquemet, N., Fabbri, A., and Gaucher, E.C. (2012) THERMODDEM: A geochemical database focused on low temperature water/rock interactions and waste materials. *Applied Geochemistry*, 27, 2107-2116.
- Carneiro, J.F., Boavida, D., and Silva, R. (2011) First assessment of sources and sinks for carbon capture and geological storage in Portugal. *International Journal of Greenhouse Gas Control*, 5, 538-548.

- Cartwright, J.H.E., Checa, A.G., Gale, J.D., Gebauer, D., and Sainz-Diaz, C.I. (2012) Calcium carbonate polymorphism and its role in biomineralization: how many amorphous calcium carbonates are there?. *Angewandte Chemie International Edition*, 51, 11960-11970.
- Critelli, T., Marini, L., Schott, J., Mavromatis, V., Apollaro, C., Rinder, T., De Rosa, R., and Oelkers, E.H. (2015) Dissolution rate of antigorite from a whole-rock experimental study of serpentinite dissolution from $2 < \text{pH} < 9$ at 25°C : Implications for carbon mitigation via enhanced serpentinite weathering. *Applied Geochemistry*, 61, 259-271.
- Evans, B.W., Hattori, K., and Baronnet, A. (2013) Serpentinite: What, Why, Where?. *Elements*, 9, 99-106.
- Lasaga, A.C. (1998) *Kinetic theory in the earth science* (1st ed.), Princeton University Press, New York, 152p.
- Lee, S., Kim, J., Chae, S., Bang, J.H., and Lee, S.W. (2016) CO₂ sequestration technology through mineral carbonation: An extraction and carbonation of blast slag. *Journal of CO₂ Utilization*, 16, 336-345.
- Lee, S.W., Park, S.B., Jeong, S.W., Lim, K.S., Lee, S.H., and Trachtenberg, M.C. (2010) On carbon dioxide storage based on biomineralization strategies. *Micron*, 41, 273-282.
- Lide, D.R. and Frederikse, H.P.R. (1998) *CRC handbook of chemistry and physics* (78th ed.), CRC Press, New York, 8p.
- Lin, P.C., Huang, C.W., Hsiao, C.T., and Teng, H. (2008) Magnesium hydroxide extracted from a magnesium-rich mineral for CO₂ sequestration in a gas-solid system. *Environmental Science & Technology*, 42, 2748-2752.
- Luo, J., Kong, F., and Ma, X. (2015) Role of aspartic acid on the synthesis of spherical vaterite by the Ca(OH)-CO reaction. *Crystal Growth & Design*, 16, 728-736.
- Mirjafari, P., Asghari, K., and Mahinpey, N. (2007) Investigation the application of enzyme carbonic anhydrase for CO₂ sequestration purposes. *Industrial & Engineering Chemistry Research*, 46, 921-926.
- Oxtoby, D.W., Gillis, H.P., and Campion, A. (2012) *Principle modern chemistry* (7th ed.), Brooks Cole, London, 735p.
- Palandri, J.L. and Kharaka, Y.K. (2004) A compilation of rate parameter of water-mineral interaction kinetics for application to geochemical modeling (1st ed.) (U.S. Geological Survey Open File Report), 1-64p.
- Park, A.H.A. and Fan, L.S. (2004) CO₂ mineral sequestration: physically activated dissolution of serpentinite and pH swing process. *Chemical Engineering Science*, 59, 5241-5247.
- Parkhurst, D.L. and Appelo, C.A.J. (2017) Description of input and examples for PHREEQC (ver. 3) -A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. geological survey techniques and methods, book 6, chap. A43, 497 p., available only at <http://pubs.usgs.gov/tm/06/a43> (accessed on 25 April 2017).
- Rodriguez-Blanco, J.D., Shaw, S., and Benning, L.G. (2011) The kinetics and mechanisms of amorphous calcium carbonate (ACC) crystallization to calcite, *via* vaterite. *Nanoscale*, 3, 265-271.
- Sanna, A., Dri, M., and Maroto-Valer, M.M. (2013) Carbon dioxide capture and storage with mineralization using recyclable ammonium salts. *Energy*, 51, 431-161.
- Song, K., Jang, Y.N., Kim, W., Lee, M.G., Shin, D., Bang, J.W., Jeon, C.W., and Chae, S.C. (2014) Factors affecting the precipitation of pure calcium carbonate during the direct aqueous carbonation of flue gas desulfurization gypsum. *Energy*, 65, 527-532.
- Wang, X. and Maroto-Valer, M.M. (2011) Dissolution of serpentinite using recyclable ammonium salts for CO₂ mineral carbonation. *Fuel*, 90, 1229-1237.
- Wang, X. and Maroto-Valer, M.M. (2011) Integration of CO₂ capture and mineral carbonation by using recyclable ammonium salts. *ChemSusChem*, 4, 1291-1300.
- Wolterbeek, T.K.T., Peach, C.J., and Spiers, C.J. (2013) Reaction and transport in wellbore interfaces under CO₂ storage conditions: Experiments simulating debonded cement-casing interfaces. *International Journal of Greenhouse Gas Control*, 19, 519-529.
- Zhang, M. and Bachu, S. (2011) Review of integrity of existing wells in relation to CO₂ geological storage: What do we know?. *International Journal of Greenhouse Gas Control*, 5, 826-840.

Received November 16, 2017, Revised December 28, 2017, Accepted December 28, 2017, Associate Editor: Jeong Hun Seo