

Article

Direct Aqueous Mineral Carbonation of Waste Slate Using Ammonium Salt Solutions

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Academic Editors: Suresh Bhargava, Mark Pownceby and Rahul Ram

Received: 18 October 2015 / Accepted: 15 December 2015 / Published: 18 December 2015

Abstract: The carbonation of asbestos-containing waste slate using a direct aqueous mineral carbonation method was evaluated. Leaching and carbonation tests were conducted on asbestos-containing waste slate using ammonium salt ($\text{CH}_3\text{COONH}_4$, NH_4NO_3 , and NH_4HSO_4) solutions at various concentrations. The $\text{CH}_3\text{COONH}_4$ solution had the highest Ca-leaching efficiency (17%–35%) and the NH_4HSO_4 solution had the highest Mg-leaching efficiency (7%–24%) at various solid dosages and solvent concentrations. The CaCO_3 content of the reacted materials based on thermogravimetric analysis (TGA) was approximately 10%–17% higher than that of the as-received material for the 1 M $\text{CH}_3\text{COONH}_4$ and the 1 M NH_4HSO_4 solutions. The carbonates were precipitated on the surface of chrysotile, which was contained in the waste slate reacted with CO_2 . These results imply that CO_2 can be sequestered by a direct aqueous mineral carbonation using waste slate.

Keywords: CO_2 sequestration; mineral carbonation; waste slate; ammonium salts; asbestos

1. Introduction

CO₂ mineral carbonation is a method to permanently sequester CO₂ as a form of carbonate minerals with or without aqueous phase. For the CO₂ mineral carbonation process with aqueous phase, CO₂ is reacted with raw materials containing alkaline earth metals (mostly Ca and Mg) in aqueous solutions (*i.e.*, direct aqueous mineral carbonation) or is reacted with alkaline earth metals leached from raw materials in aqueous solutions (*i.e.*, indirect aqueous mineral carbonation) to form carbonate minerals [1,2].

The mineral carbonation to sequester CO₂ has been extensively studied due to its following advantages: (1) non-requirement for any underground geological storage sites; (2) permanent CO₂ sequestration without long-term monitoring; (3) potential immobilization of toxic elements contained in raw materials; and (4) beneficial use of produced carbonates. However, the major challenge of the mineral carbonation method is to enhance the leaching capacity of alkaline earth metals from raw materials, which is a main factor affecting rate and degree of mineral carbonation [3,4]. The leaching processes of alkaline earth metals from raw materials are generally expensive due to the need for increasing temperature and pressure, acid or base solutions, and grinding raw materials.

Previous researches regarding aqueous mineral carbonation have mainly focused on enhancing the leaching efficiency of alkaline earth metals by pre-treating raw materials before carbonation processes [4,5–8]. Natural alkaline materials and alkaline industrial wastes have been extensively evaluated for the mineral carbonation, *e.g.*, [8,9–19]. Natural alkaline materials are relatively abundant compared with alkaline industrial wastes but their use requires pretreatment to enhance the leaching of the alkaline earth metal due to their strong chemical stability. Even if industrial wastes have more limited availability, the alkaline earth metals can be relatively easily leached from the alkaline industrial byproducts because of their chemical instability [20].

Asbestos-containing waste slate is one of the potential alkaline industrial wastes to sequester CO₂ due to its high content of Ca and Mg. Asbestos-containing waste slate is mostly comprised of cement, which is a Ca source, and chrysotile, which is an Mg source. Chrysotile, which is considered as a carcinogenic material, is the fibrous magnesium silicate mineral (Mg₃(Si₂O₅)(OH)₄) in the serpentine group. Asbestos-containing slate was used as a roofing material in South Korea during 1960 and 1970s due to its high insulating capacity, but subsequently has not been legally allowed for use due to the toxicity of chrysotile, which is a form of asbestos. Currently, the asbestos containing waste slate is mostly disposed of in government certified landfills without reuse in South Korea.

Due to the health risks such as asbestosis, lung cancer, and mesothelioma, a number of studies suggested safe disposal schemes of asbestos containing materials. Most treatment methods of asbestos-containing materials focused on morphological alteration of asbestos using chemical and thermal treatment. Chemical treatment methods of asbestos-containing material using oxalic acid [21], Na-oxalate and Na-acetate [22], sulfuric acid [23], and hydrogen peroxide [24] could alter significantly asbestos material. Thermal treatment methods of asbestos using microwave [25–27] and microwave air plasma [28] could also alter effectively asbestos to non-hazardous form. However, thermal treatment requires vast amount of energy. Gualtieri and Tartaglia [29] reported that temperature higher than 1000 °C is required to entire transformation of asbestos to non-hazardous silicate glass phase.

Yoshikawa *et al.* [27] also showed that asbestos was completely transformed to non-hazardous form at the temperature $>1000\text{ }^{\circ}\text{C}$ with microwave treatment.

The main objective of this study was to evaluate the feasibility of CO_2 sequestration using waste slate by a direct aqueous mineral carbonation. Ammonium salt ($\text{CH}_3\text{COONH}_4$, NH_4Cl , NH_4NO_3 , and NH_4HSO_4) solutions were used as solvents for a direct aqueous mineral carbonation of asbestos-containing waste slate. The leaching and carbonation behaviors of asbestos-containing waste slate were investigated at room temperature and atmospheric pressure conditions. For the carbonation tests, CO_2 was injected into the mixture of waste slate and ammonium salt solution. Morphological alteration of asbestos-containing waste slate after carbonation was also evaluated.

2. Experimental Section

2.1. Materials

Waste roofing slate panels were collected from an abandoned house in South Korea. The waste slate was broken using a hand hammer to get particle size less than 0.425 mm. The slate particles were used in the leaching and carbonation tests. $\text{CH}_3\text{COONH}_4$, NH_4NO_3 , and NH_4HSO_4 (Sigma-Aldrich Co., St. Louis, Mo, USA) solutions were used as solvents. Deionized (DI) water was used to prepare the ammonium salt solutions.

2.2. Leaching Tests

The leaching test was performed with various slate solid dosages ranging between 20 and 150 g/L in a 50 mL polypropylene copolymer centrifuge tube using an ammonium salt solution for four hours. 1–10 g of oven-dried slate was added into a 50 mL polypropylene copolymer centrifuge tube with 1, 2, and 4 M solutions. The mixture was shaken at room temperature and atmospheric pressure using a water bath shaker and the pH and electrical conductivity (EC) were then measured. The mixture was centrifuged at 5000 rpm for 30 min (VS-550i, Vision Scientific CO., Daejeon, Korea) and was then filtered using a 0.2 μm filter (ADVANTEC®, Advantec MFS, Inc. Tokyo, Japan). All of the leaching tests were conducted a single time.

2.3. Carbonation Tests

For the carbonation test, the waste slate and 1 M $\text{CH}_3\text{COONH}_4$ solution or 1 M NH_4HSO_4 solution at various solid dosages ranged from 20 to 150 g/L were mixed thoroughly for four hours in a 500 mL Erlenmeyer flask (Dongsung Scientific, Busan, Korea). The initial pH of the mixtures of the waste slate and 1 M $\text{CH}_3\text{COONH}_4$ solution or 1 M NH_4HSO_4 solution were about 9.4 and 9.2, respectively. A 15 vol. % CO_2 gas mixture with 85 vol. % N_2 was then injected at a flow rate of 200 mL/min into the slurry of waste slate and 1 M $\text{CH}_3\text{COONH}_4$ solution or 1 M NH_4HSO_4 solution at various solid dosages in the 500 mL Erlenmeyer flask. The 15 vol. % CO_2 gas mixture was chosen because the flue gas from coal fired power plants in South Korea generally contains 15 vol. % CO_2 . During the carbonation tests, the slurry was mixed using a magnetic stirrer at a stirring rate of approximately 300 rpm. The procedure of the carbonation test used in this study is similar to that used in Jo *et al.* [8]. The carbonation test was performed at a room temperature and atmospheric pressure. The CO_2

injection was stopped at a pH of around 7.5 for preventing CaCO_3 dissolution [30]. All of the carbonation tests were conducted a single time.

2.4. Chemical Analysis and Material Characterization

The cation concentrations of filtrates from the leaching and carbonation tests were analyzed by inductivity coupled plasma-atomic emission spectroscopy (ICP-AES, OPTIMA 3000XL, Perkin Elmer, Wellesley, MA, USA). The elemental composition of the as-received material was determined by using microwave digestion. 0.5 g of the waste slate raw material with 10 mL of HNO_3 was digested using microwave digestion for 10 min at 175 °C and the leachate was then analyzed by ICP-AES (Perkin Elmer, Wellesley, MA, USA).

An X-ray diffractometer (Xpert MPD, Phillips, Almelo, The Netherlands) and a field emission scanning electron microscope (FE-SEM: S-4300, Hitachi, Tokyo, Japan) equipped with energy dispersive X-ray spectroscopy (EDX: Ex-20, Horiba, Kyoto, Japan) were used to characterize the as-received and reacted materials. The thermogravimetric analysis (TGA) (SDTG-60H, Shimadzu Corp., Kyoto, Japan) was performed on the reactant and products to determine the calcium carbonate (CaCO_3) content.

3. Results and Discussion

3.1. Raw Material

The as-received waste slate contained mainly Ca (25.2%). (Table 1). Table 1 shows selected elemental composition determined by using microwave digestion. The as-received waste slate mainly consists of calcite, chrysotile, and Ca-Mg-Al silicates (Figure 1). The CaCO_3 content of the waste slate determined using the results of TGA [8], as shown in Figure 2 was approximately 29.8%. The CaCO_3 may have been formed by natural carbonation because the slate had been exposed to atmosphere for a very long period of more than 20 years. It is well known that cement based materials exposed to atmosphere can absorb CO_2 during the service life [31].

Table 1. Chemical and mineralogical characteristics of as-received waste slate sample.

Materials	Composition (wt. %)					Minerals (XRD)
	Ca	Mg	Al	Fe	Si	
Waste slate	25.2	2.2	1.4	1.3	1.4	Calcite, Chrysotile, and Ca-Mg-Al-Si-oxide minerals

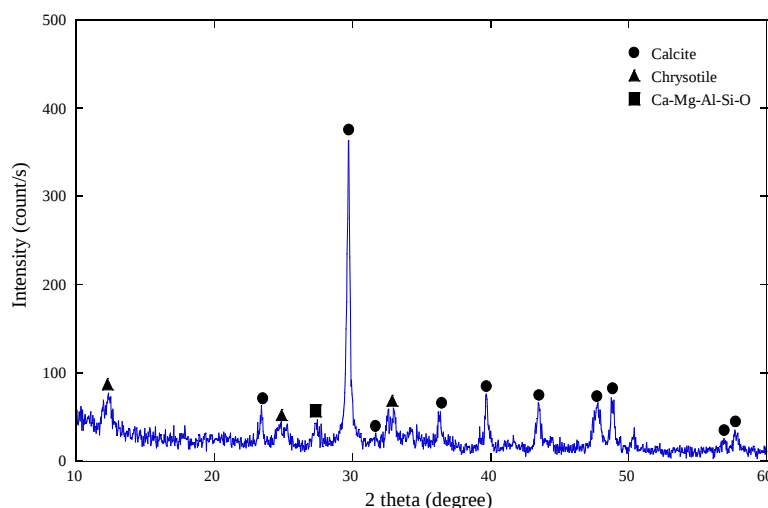


Figure 1. X-ray diffraction (XRD) patterns of as-received waste slate.

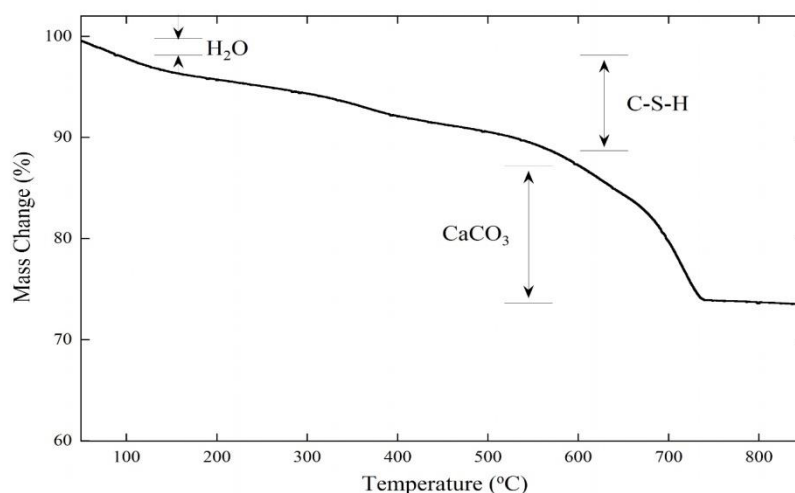


Figure 2. Thermogravimetric analysis (TGA) results of as-received waste slate. “H₂O”, “C–S–H”, and “CaCO₃” indicate the mass change occurred by the decomposition of H₂O, C–S–H, and CaCO₃, respectively.

3.2. Leaching Behaviors

The Ca- and Mg-leaching efficiencies after leaching tests as a function of solid dosage (20, 50, 100, 150, and 200 g/L) and solvent concentration (1, 2, and 4 M) are shown in Figures 3 and 4. The leaching efficiency was determined by following equation:

$$\text{Metal leaching efficiency (\%)} = \frac{M_{\text{Me-leached}}(\text{g})}{M_t(\text{g}) \times C_{\text{MeO}}(\%)} \times 100 \quad (1)$$

where $M_{\text{Me-leached}}$ is the mass (g) of the metal in the leachate obtained after the leaching test, M_t is the total mass (g) of the material used in the leaching test, C_{MeO} is the metal content of the material determined by the total elemental analysis.

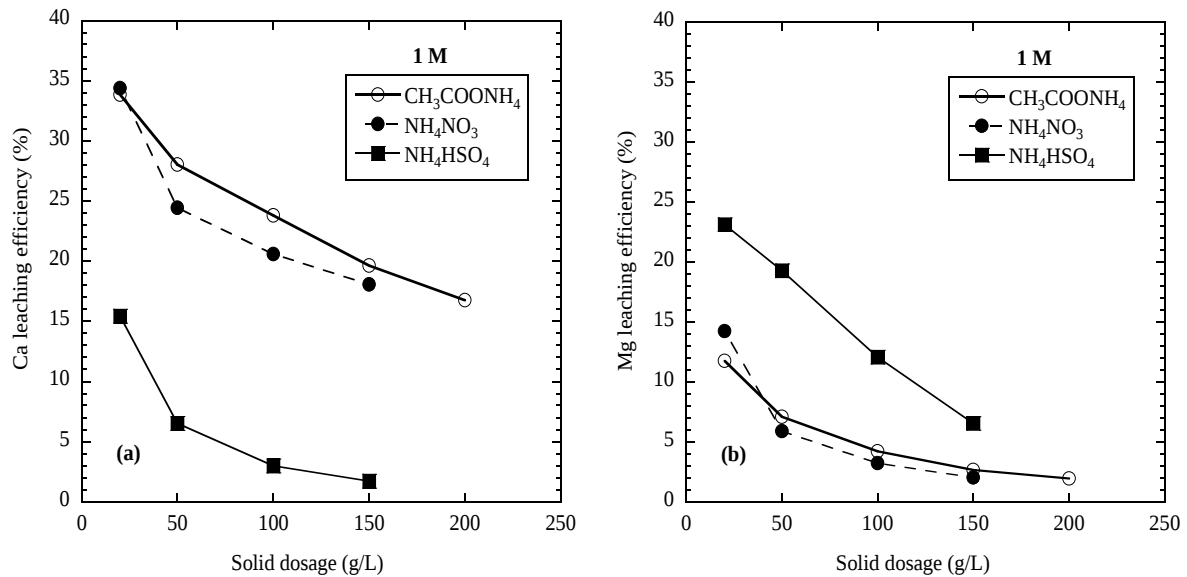


Figure 3. Ca and Mg-leaching efficiencies as a function of the solid dosage with the 1.0 M ammonium solution for waste slate samples.

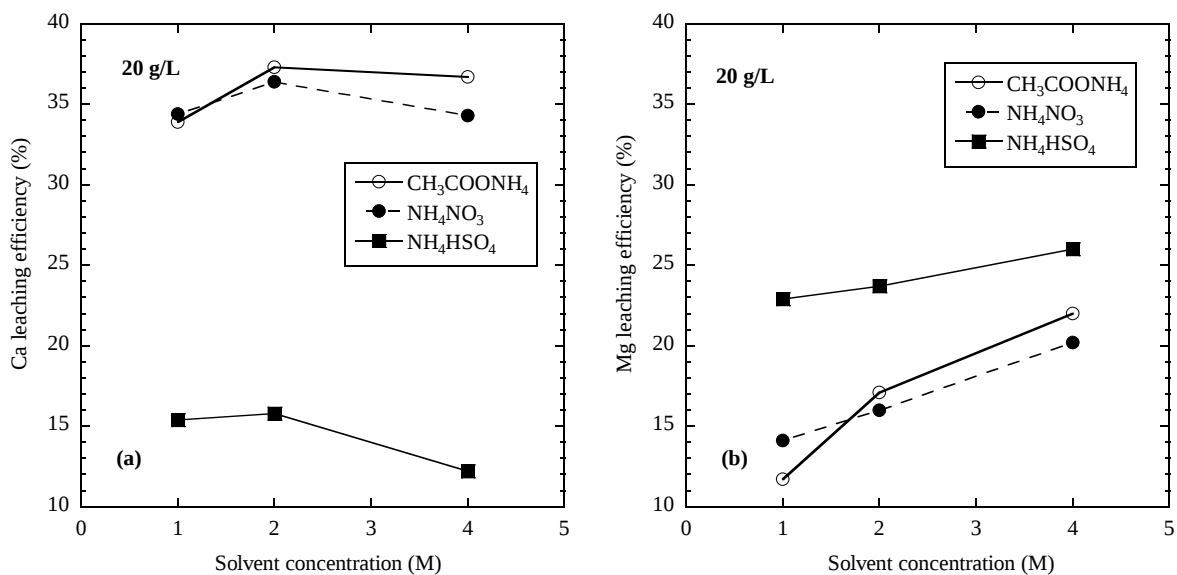


Figure 4. Ca and Mg-leaching efficiencies as a function of solvent concentration at the solid dosage of 20 g/L for waste slate samples.

For all solvent conditions, the metal leaching efficiencies were decreased when the solid dosage increased from 20 to 200 g/L (Figures 3 and 4). Among the 1 M ammonium salts solutions, the $\text{CH}_3\text{COONH}_4$ and NH_4NO_3 solutions had higher Ca-leaching efficiencies than did the NH_4HSO_4 solution, regardless of solid dosage. Jo *et al.* [8] reported that 1 M NH_4NO_3 and $\text{CH}_3\text{COONH}_4$ solutions could effectively dissolve Ca ions from waste cement. The NH_4HSO_4 solution may have had a lower Ca-leaching efficiency than the NH_4NO_3 and $\text{CH}_3\text{COONH}_4$ solutions due to the lower Ca selectivity or the precipitation of gypsum (CaSO_4) during the leaching step (Figure 5). In contrast, the NH_4HSO_4 solution had the highest Mg-leaching efficiency among all the solvents. Wang and

Maroto-Valer [6] reported that 1.4 M NH_4HSO_4 solution leached 100% of Mg and 98% of Fe, but only 13.6% of Si, from serpentine at 100 °C. However, the lower Mg-leaching efficiency (<24%) obtained in this study was probably due to the lower temperature and solvent concentration. Nevertheless, Mg ions were leached dominantly from waste slate in the NH_4HSO_4 solution.

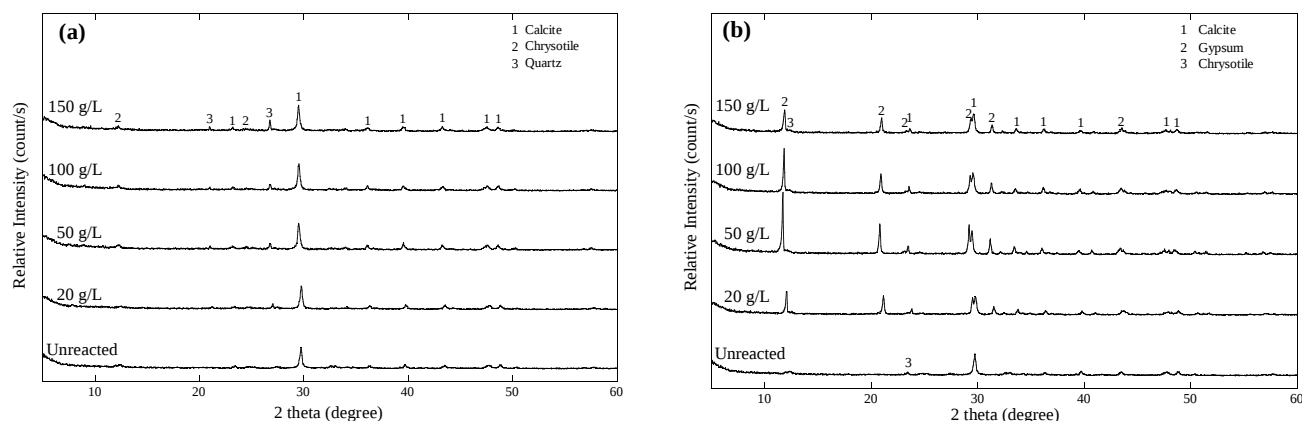


Figure 5. X-ray diffraction (XRD) patterns of as-received waste slate (Unreacted) and reacted waste slate samples obtained from leaching tests using the (a) 1 M $\text{CH}_3\text{COONH}_4$ and (b) 1 M NH_4HSO_4 solutions at various solid dosages (20, 50, 100, and 150 g/L).

For the 20 g/L of the solid dosage, the $\text{CH}_3\text{COONH}_4$ and NH_4NO_3 solutions had relatively high Ca-leaching efficiencies (~37%) at high solvent concentrations (>2 M) (Figure 4). However, the $\text{CH}_3\text{COONH}_4$ and NH_4NO_3 solutions had a slightly lower Ca-leaching efficiency (34%) at low solvent concentration (1 M). The NH_4HSO_4 solution had the lowest Ca-leaching efficiency at all solvent concentrations. On the contrary, the NH_4HSO_4 solution had the highest Mg-leaching efficiency (18%–20%) at all solvent concentrations. The Mg-leaching efficiencies of both $\text{CH}_3\text{COONH}_4$ and NH_4NO_3 solutions were lower than that of the NH_4HSO_4 solution but increased with increasing the solvent concentration. The Mg-leaching efficiency of NH_4HSO_4 was slightly affected by the solvent concentration, suggesting that the $\text{CH}_3\text{COONH}_4$ and NH_4HSO_4 solutions were the most efficient solvents for Ca and Mg leaching from waste slate, respectively.

The XRD patterns on the unreacted and reacted waste samples are shown in Figure 5. For the 1 M $\text{CH}_3\text{COONH}_4$ solution, the chrysotile peak intensity was slightly decreased, regardless of the solid dosage (Figure 5). Even though Ca ions were dissolved into the leachate, the calcite peak intensity barely changed after the leaching tests, possibly indicating that Ca-silicates in the waste slate was a main Ca source in the slurry. The quartz peak identified after the leaching tests was further possible evidence for the dissolution of Ca-silicates.

For the 1 M NH_4HSO_4 solution, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was identified at all solid dosages, suggesting that gypsum was precipitated during the leaching process. The gypsum peak intensity was higher at the solid dosage of 50 g/L and decreased with increasing the solid dosage. The calcite peak intensity also barely changed after the leaching test using the 1 M NH_4HSO_4 solution. In addition, the chrysotile peak was still observed after the leaching tests. The Mg-leaching efficiency (~20%) also confirmed that chrysotile, which was an Mg source, was not fully decomposed after the leaching tests using the $\text{CH}_3\text{COONH}_4$, NH_4NO_3 , and NH_4HSO_4 solutions.

3.3. Carbonation Behaviors

The carbonation tests were carried out on suspensions from the leaching test using 1 M $\text{CH}_3\text{COONH}_4$ and 1 M NH_4HSO_4 solutions. The 1 M $\text{CH}_3\text{COONH}_4$ and NH_4HSO_4 solutions were selected due to their high metal leaching efficiency and selectivity in the leaching test. The 1 M $\text{CH}_3\text{COONH}_4$ solution had a high Ca-leaching efficiency and Ca selectivity and the 1 M solution NH_4HSO_4 showed high Mg-leaching efficiency and Mg selectivity (Figures 3 and 4).

The cation concentrations of filtrates obtained from the leaching and carbonation tests are shown in Table 2. After the leaching tests, the pH of mixtures using 1 M $\text{CH}_3\text{COONH}_4$ and 1 M NH_4HSO_4 solutions ranged between 9.0 and 9.8, which was suitable for mineral carbonation. For the $\text{CH}_3\text{COONH}_4$ solution, the Ca concentration decreased significantly after carbonation test due to the precipitation of CaCO_3 . For the NH_4HSO_4 solution, however, the Ca concentration was not greatly changed after the carbonation test. In contrast, the Mg concentration increased after the carbonation test for both $\text{CH}_3\text{COONH}_4$ and NH_4HSO_4 solutions, probably because Mg ions were released from the solid phase during the CO_2 injection. Dissolution of Mg ion is favorable at $\text{pH} < 8.0$ [32]. The Mg ion might dissolve further during carbonation because CO_2 injection was stopped when pH of the suspension reached about 7.5. The Si concentration decreased after the carbonation for both $\text{CH}_3\text{COONH}_4$ and NH_4HSO_4 solution, probably due to the precipitation of SiO_2 from dissolved Ca-Mg-Al-Si-O complex during the CO_2 injection.

Table 2. Results of chemical analysis for filtrates obtained from leaching and carbonation tests.

		pH	Cation Concentration (mg/L)							
			Ca		Mg		Fe		Si	
Solvent	Solid dosage (g/L)	Leaching	Leaching	Carbonation	Leaching	Carbonation	Leaching	Carbonation	Leaching	Carbonation
1 M CH ₃ COONH ₄	20	9.0	1707.2	375.2	51.3	136.8	0.1	0.9	44.3	21.6
	50	9.4	3533.2	652.3	77.5	345.9	0.2	0.6	41.3	32.1
	100	9.7	6002.2	1955.0	91.9	784.1	0.2	0.5	39.9	24.7
	150	9.8	7429.2	2597.0	87.4	1200	0.7	0.4	37.0	30.2
1 M NH ₄ HSO ₄	20	9.0	778.1	709.9	100.9	154.4	1.0	0.6	40.5	16.4
	50	9.2	822.9	797.5	210.3	342.7	0.1	0.4	50.3	24.0
	100	9.7	755.9	751.9	263.3	824.1	0.4	1.2	52.5	16.1
	150	9.8	655.1	852.7	214.3	1234	0.3	0.5	48.9	26.3

The carbonation efficiency was determined using the Ca concentration of the filtrates obtained from the leaching and carbonation tests using the following equation:

$$\text{Ca carbonation efficiency (\%)} = \frac{M_{\text{Ca-leached}}(\text{g}) - M_{\text{Ca-carbonation}}(\text{g})}{M_t(\text{g}) \times \frac{C_{\text{Ca}}(\%)}{100}} \times 100(\%) \quad (2)$$

where $M_{\text{Ca-leached}}$ is the mass (g) of Ca in the filtrate obtained from the leaching test, $M_{\text{carbonation}}$ is the mass (g) of Ca in the filtrate obtained from the carbonation test, M_t is the total mass (g) of the waste

slate used in the tests, and C_{Ca} is the calcium content (%) of the waste slate determined by total elemental analysis (Table 1).

The carbonation efficiency is shown in Figure 6. The 1 M $\text{CH}_3\text{COONH}_4$ solution had a higher Ca carbonation efficiency than the 1 M NH_4HSO_4 solution, regardless of the solid dosage. The Ca carbonation efficiencies for both 1 M $\text{CH}_3\text{COONH}_4$ and 1 M NH_4HSO_4 solutions decreased as the solid dosage increased, which was comparable to the Ca-leaching efficiency.

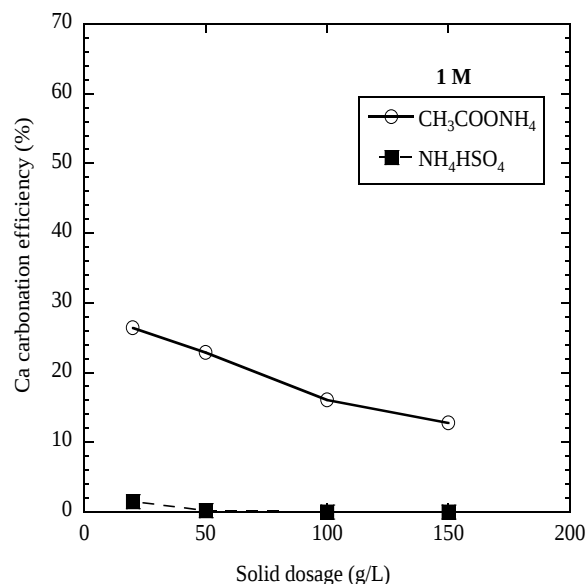


Figure 6. Ca carbonation efficiencies as a function of the solid dosage with the 1.0 M $\text{CH}_3\text{COONH}_4$ and 1.0 M NH_4HSO_4 solutions for waste slate samples.

3.4. Characteristics of Reacted Asbestos-Containing Waste Slate

The CaCO_3 content of the reacted materials determined using results of TGA is shown in Figure 7. The CaCO_3 content of the reacted material was approximately 10%–17% higher than that of the as-received material, except for the 1 M NH_4HSO_4 solution, at a solid dosage of 100 g/L. These results suggest that a maximum CO_2 sequestration capacity of ~ 0.048 kg CO_2 /kg waste slate was obtained at a solid dosage of 20 g/L using the 1 M $\text{CH}_3\text{COONH}_4$ solution. The CaCO_3 content of the reacted material was slightly decreased with increasing the solid dosage from 20 to 150 g/L, except the solid dosage of 100 g/L, with the 1 M NH_4HSO_4 solution. The CaCO_3 content in the 1 M $\text{CH}_3\text{COONH}_4$ solution was approximately 10% higher than that in the 1 M NH_4HSO_4 solution. On the other hand, the carbonation efficiency in the 1 M $\text{CH}_3\text{COONH}_4$ solution based on Ca concentrations in the filtrate was approximately 20% higher than that in the 1 M NH_4HSO_4 solution. These results suggest that Ca ions obtained during the leaching process and Ca ions obtained by dissolving further from waste slate might be precipitated during the CO_2 injection.

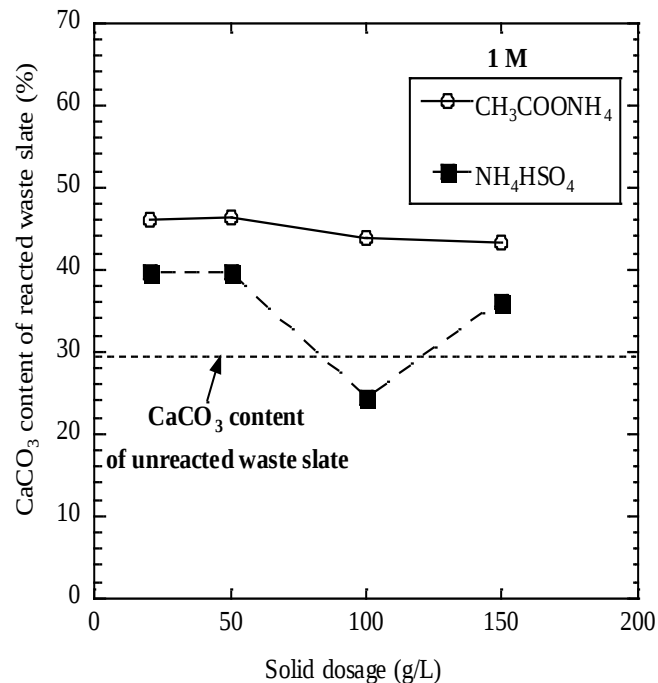


Figure 7. CaCO₃ content of reacted waste slate samples determined using TGA as a function of the solid dosage with the 1.0 M CH₃COONH₄ and NH₄HSO₄ solutions.

After the carbonation tests using 1 M CH₃COONH₄ and 1 M NH₄HSO₄ solutions, the calcite peak intensity increased at all the solid dosages (Figure 8). For both 1 M CH₃COONH₄ and 1 M NH₄HSO₄ solutions, a chrysotile peak was still observed in the reacted materials after the carbonation tests. For the 1 M CH₃COONH₄ and 1 M NH₄HSO₄ solutions, almost similar XRD results were obtained, except for the formation of gypsum (CaSO₄ · 2H₂O) for the 1 M NH₄HSO₄ solution (Figure 8).

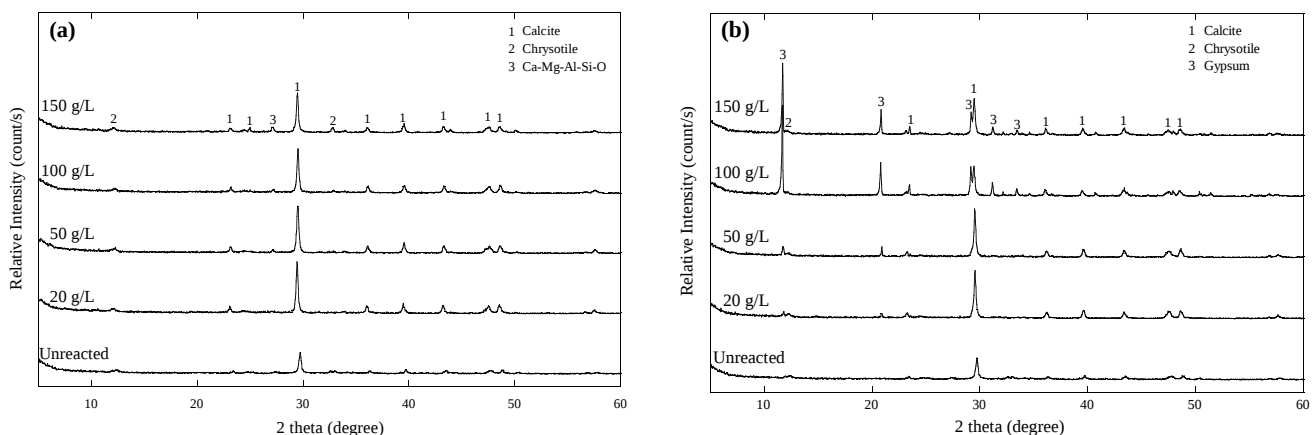


Figure 8. X-ray diffraction (XRD) patterns of unreacted waste slate (Unreacted) and reacted waste slate samples obtained from carbonation tests using (a) 1 M CH₃COONH₄ and (b) 1 M NH₄HSO₄ solutions at various solid dosages (20, 50, 100, and 150 g/L).

The images of SEM analysis on the as-received and reacted materials obtained after the carbonation tests using 1 M CH₃COONH₄ and 1 M NH₄HSO₄ solutions are shown in Figures 9 and 10, respectively. No carbonates were observed on the surface of needle-like chrysotile in the as-received

waste slate, as shown in Figure 9a, even though carbonates were formed by natural carbonation due to the long atmospheric exposure of the slate panels. In addition, the SEM images confirmed that the chrysotile originally contained in the waste slate was not fully decomposed after the carbonation tests.

Mg ions from chrysotile can be dissolved at high pressure (>3 MPa) and temperature (>600 °C) conditions or moderate temperature (>70 °C) with very strong acid solutions (e.g., hydrochloric acid, oxalic acid, and sulfuric acid), e.g., [33,34]. However, cubic calcite was precipitated on the surface of needle-like chrysotile at all solid dosages for both 1 M $\text{CH}_3\text{COONH}_4$ and 1 M NH_4HSO_4 solutions after the carbonation tests (Figures 9 and 10). Health impact of asbestos is mainly caused by its needle-like morphological characteristics. The mobility of needle-like chrysotile coated by carbonates might be decreased, which probably mitigated the chrysotile's toxicity by changing its morphology. The carbonates also changed chemical composition of asbestos surface. Aust *et al.* [35] reported that the asbestos toxicity is strongly related to surface chemical composition of respirable elongated mineral particles (e.g., Fe associated with the fibers). The carbonates coated chrysotile may inhibit the Fe-related reaction between chrysotile and biological molecules [35]. These results suggest that the aqueous mineral carbonation of asbestos-containing waste slate may reduce toxicity of asbestos.

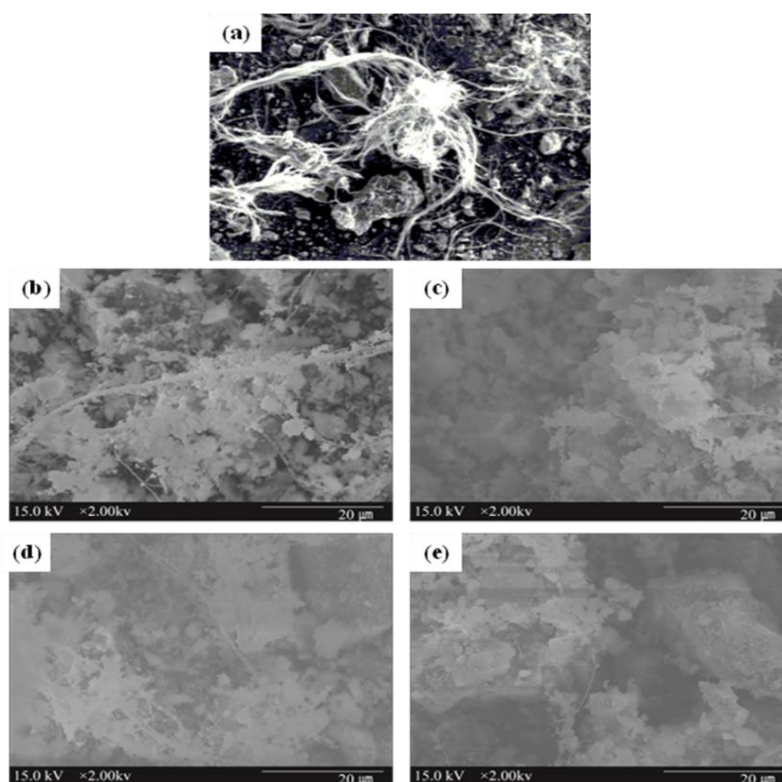


Figure 9. Scanning electron microscope (SEM) images of (a) unreacted waste slate and reacted waste slate samples obtained from carbonation tests using the 1 M $\text{CH}_3\text{COONH}_4$ solution at solid dosages of (b) 20 g/L, (c) 50 g/L, (d) 100 g/L, and (e) 150 g/L.

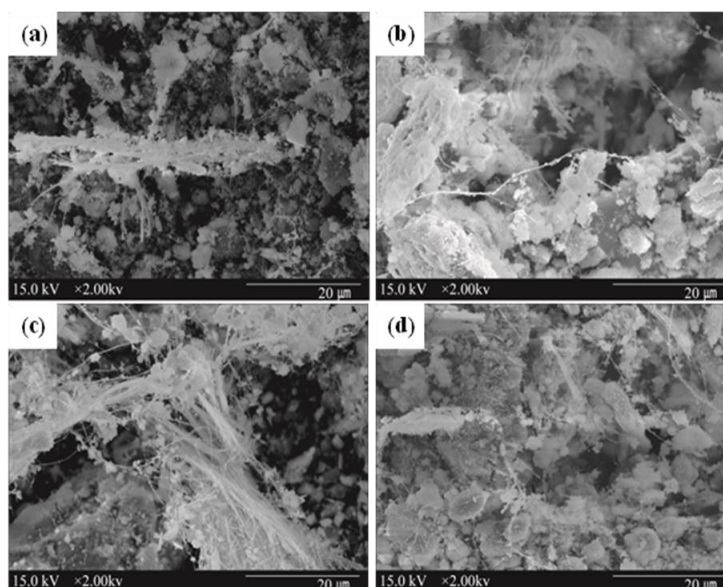


Figure 10. Scanning electron microscope (SEM) images of reacted waste slate samples obtained from carbonation tests using the 1 M NH_4HSO_4 solution at solid dosages of (a) 20 g/L, (b) 50 g/L, (c) 100 g/L, and (d) 150 g/L.

4. Conclusions

Leaching and carbonation tests on asbestos-containing waste slate using ammonium salt ($\text{CH}_3\text{COONH}_4$, NH_4NO_3 , and NH_4HSO_4) solutions were conducted at room temperature and atmospheric pressure conditions. The Ca and Mg-leaching efficiencies increased with decreasing the solid dosage and increasing the solvent concentration. The $\text{CH}_3\text{COONH}_4$ solution had the highest Ca-leaching efficiency (17%–35%) and the NH_4HSO_4 solution had the highest Mg-leaching efficiency (7%–24%). The NH_4HSO_4 solution had the lowest Ca-leaching efficiency, probably due to precipitation of gypsum.

The carbonation efficiency determined using the Ca concentrations of the filtrate obtained before and after the carbonation tests was correlated to the Ca-leaching efficiency. The carbonation efficiency in the $\text{CH}_3\text{COONH}_4$ solution ranged between 14 and 27%. The carbonation efficiency was lower in the NH_4HSO_4 solution due to its lower Ca-leaching efficiency. However, the carbonation efficiency based on the CaCO_3 content of the reacted materials was approximately 10%–17% higher than the carbonation efficiency determined using the Ca concentration of the leachate for both the 1 M $\text{CH}_3\text{COONH}_4$ and the 1 M NH_4HSO_4 solutions because further Ca^{2+} ions were dissolved from the waste slate during the carbonation tests. These results suggest that a maximum CO_2 sequestration capacity of ~ 0.07 kg CO_2 /kg waste slate was obtained at a solid dosage of 50 g/L using the 1 M $\text{CH}_3\text{COONH}_4$ solution. The cost of $\text{CH}_3\text{COONH}_4$ in this direct aqueous carbonation procedure using 1 M $\text{CH}_3\text{COONH}_4$ solution and a solid dosage of 50 g/L can be estimated to be about US\$4000 to sequester one ton of CO_2 assuming that the price of $\text{CH}_3\text{COONH}_4$ is US\$200/ton, which is too expensive. Thus, further study on reducing the cost of chemical is necessary.

The carbonates were precipitated on the surface of chrysotile, which was contained in the reacted materials obtained after the carbonation tests. However, no carbonates were observed on the surface of chrysotile in the as-received waste slate, even though natural carbonation had been occurred in the

slate. Consequently, the aqueous mineral carbonation changed the morphology and the surface composition of the needle-like chrysotile by coating it with carbonates. The results of this study suggest that the direct aqueous mineral carbonation of waste slate can be used to sequester CO₂ and to reduce the human body risk of asbestos-containing waste slate. However, the results should be verified by conducting multiple tests because a single test for leaching and carbonation was conducted in this study. In addition, further studies are necessary to investigate the human body risk of the solid particles obtained after the carbonation tests and the potential effectiveness of more appropriate conditions to further mitigate the toxicity of asbestos-containing waste slate.

Acknowledgments

This research was supported by the Basic Research Project (Study on the mineral carbonation of the alkaline industrial products, GP2015-009) of the Korea Institute of Geoscience and Mineral Resources (KIGAM) funded by the Ministry of Science, ICT and Future Planning and also supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2012R1A1B3002473).

Author Contributions

Ho Young Jo designed and managed the research and co-wrote and edited the paper. Hwanju Jo characterized the materials, interpreted the data, and co-wrote the paper. Sunnwon Rha conducted leaching and carbonation tests and characterized the materials. Pyeong-Koo Lee conceptualized the experiment and analyzed interpreted the data.

Conflicts of Interest

The authors declare no conflict of interest.

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