Carbonation of Chrysotile under Subcritical Conditions

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The carbonation of chrysotile $[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_4]$ under subcritical conditions was experimentally investigated in alkali solution, and the chemical composition as well as the morphological and structural changes were discussed. The starting material was hydrothermally treated by aqueous direct carbonation at a temperature of 100°C and a CO_2 partial pressure range of $0.5\text{ MPa}\sim 4\text{ MPa}$ at pH 13. Highly crystalline magnesite was synthesized under a CO_2 partial pressure of 3 MPa. The carbonation rate increased at the proportional rate according to the applied CO_2 pressure to approximately 57%. The surface morphology of chrysotile changed from the fibrous form to a round or oval shape at the initial stage and subsequently to magnesite with well-faceted rhombohedral planes.

The dissolution rate of Mg was higher than Si, such that the Mg : Si ratio of chrysotile decreased from 1.56 to $0.4\sim 0.6$ as the reaction time increased. The resultant silica-rich layer of the reaction product ultimately changed through the Mg-depleted skeletal phase to the amorphous silica phase. The experimental results suggest that carbonation in alkali solution under subcritical conditions is of great significance because an excessive amount of acid and alkali reagents can be eliminated in the carbonation process. [doi:10.2320/matertrans.M2011155]

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1. Introduction

Mineral carbonation has been recognized as a promising option for emission reduction of CO_2 as a mitigation measure of global warming.¹⁾ Carbon sequestration and utilization processes via carbonation reaction of materials containing alkaline earth metals such as calcium and magnesium have been developed. The utilization of magnesium and calcium silicate for the sequestration of carbon dioxide is already beyond the proof-of-concept stage, and it has great potential to sequester substantial amounts of CO_2 . This sequestration process offers a safe and permanent method of CO_2 disposal, since CO_2 is chemically incorporated into the mineral and is immobilized.^{2,3)} Magnesium-bearing deposits are frequently richer than deposits containing calcium oxide. Thus, magnesium silicate such as serpentine is more attractive for CO_2 sequestration.

The most comprehensively studied process for carbonation is aqueous carbonation involving leaching or dissolution of silicate in liquid media.⁴⁻⁶⁾ In a previous work, many researchers found that acids were much more efficient at leaching magnesium from serpentine than bases were.⁷⁾ However, the effect of carbonation for most silicate minerals is generally very weak in acidic to neutral solutions, but may be notable in alkaline conditions. Moreover, the pH swing process might be required to achieve a higher conversion of the CO_2 mineral carbonation. Therefore, the high energy cost due to the use of excessive amounts of acid and alkali reagents is a major obstacle to the practical applications of mineral carbonation.⁸⁾

In this study, the leaching of serpentine and carbonation to design a more effective mineral sequestration process were carried out in alkaline solution at an appropriate temperature and under subcritical conditions.

Fig. 1 XRD patterns of raw material (a) and heated chrysotile (b).

2. Experiment

2.1 Materials

The mineral chrysotile $[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_4]$ used in this study was obtained from Chungyang, Korea. X-ray diffraction (XRD) data indicated that the starting material was pure chrysotile (Fig. 1(a)). Thermal activation of hydrated Mg-silicate species was accomplished by the addition of a heat treatment stage in the mineral pretreatment process, with an objective of rendering the crystal structures unstable by dehydroxylation. Thermogravimetry/differential thermal analysis (TG-DTA) was used to investigate the heat-activation process of chrysotile, and Fig. 2 shows its TG-DTA profile. Its thermal decomposition follows a two-stage sequence where the first weight loss is attributed to absorbed water (71°C) and the second is attributed to dehydroxylation (642°C). During the heat treatment, the transformation of chrysotile into forsterite (Mg_2SiO_4) and enstatite (MgSiO_3) was achieved at 818°C . In the range of $550\sim 708^\circ\text{C}$, an

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Table 1 Chemical composition of heat-treated chrysotile from Chungyang, Korea.

Component	SiO ₂	MgO	CaO	Al ₂ O ₃	Na ₂ O	K ₂ O	Fe ₂ O ₃	MnO	TiO ₂	Total
%	43.3	39.5	0.05	1.55	0.08	0.02	6.77	0.06	0.03	87.45

Fig. 2 TGA-DTA patterns of chrysotile.

additional 10.6 mass% loss can be ascribed to the loss of OH groups. Hence, chrysotile used in this study contains 13.6 mass% of water. This result has been researched in several previous studies.^{9,10} Therefore, the starting material for the carbonation was heated at 650°C for 2 h in atmosphere. After activation, the chrysotile became metachrysotile, and forsterite and hematite (Fe₂O₃) peaks appeared (Fig. 1(b)). The major components of heated chrysotile were 39.5% MgO and 43.3% SiO₂, whereas the major impurities were 6.8% Fe₂O₃, 1.6% Al₂O₃, and 0.05% CaO (Table 1).

2.2 Methods

The starting material for carbonation was crushed in a Jet-mill to grains that could pass through a < 325 mesh sieve. The grain size was measured by a particle-size analyzer (KMC-1B, KME Co.). The chemical composition of chrysotile was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (JY 38 Plus, France Jobin Yvon).

All carbonation experiments were performed in a 1 L cold-seal-type stainless vessel. The following experimental conditions were maintained unless otherwise specified: the reaction temperature was 100°C, the reaction time was 1 h, and the CO₂ partial pressure was varied from 0.5 to 4 MPa. The initial alkalinity of the solution was adjusted at pH ~ 13, and the final pH was always ~7.5. The pH of the solution was controlled by adding 1 M NaOH solution (OCI, extra pure). 0.5 M NaHCO₃ was added as a more effective CO₂ carrier. The mineral/water/liquid CO₂ mixture was continuously agitated to prevent settling of the solid.

After carbonation, the reaction products were collected and analyzed by XRD (X'pert MPD X-ray diffractometer with graphite-monochromatized CuK α radiation, Phillips Co). The microstructure of the synthesized products was examined by a transmission electron microscope (TEM, JEM 2200FS, JEOL) coupled with an energy dispersive X-ray spectrometer (EDS, Oxford) and a scanning electron micro-

scope (FE-SEM, S-4700, Hitachi). TEM samples were dispersed in distilled water by an ultrasonic probe. They were air dried after they were placed on a holder. Scanning electron microscopy (SEM) examination was carried out at a working voltage of 15 KeV. The sample powder was sedimented on a Cu-microgrid and coated with osmium tetroxide (OsO₄).

The carbonation rate of chrysotile to magnesite was calculated by thermogravimetric analysis (TG-DTA) at atmospheric pressure (DTG-60H, Shimadzu). Profiles were obtained for a temperature range of 30–900°C with a constant heating rate of 10°C/min under argon.

3. Results and Discussion

The carbonation reaction of heated chrysotile was successfully investigated under subcritical conditions. The FT-IR spectra provided valuable information on the chrysotile carbonation reaction (Fig. 3). The IR spectrum of chrysotile exhibits three well-defined spectral regions. The first band appears in the 3800–3600 cm⁻¹ region, the second appears in the 1200–800 cm⁻¹, and third region included the bands below 800 cm⁻¹. Two bands observed at 3688 cm⁻¹ and 3645 cm⁻¹ are assigned to in-phase outer and inner Mg-OH stretch, respectively. Two broad bands observed at 3440 cm⁻¹ and 1638 cm⁻¹ are due to the stretching and bending vibrations of water molecules adsorbed to the chrysotile tubes.^{11,12} Two bands at 1078 and 952 cm⁻¹ are attributed to the Si-O-Si stretching vibrations perpendicular to the basal plane and the Si-O-Si vibrations in the basal plane, respectively.^{11,13} A strong IR band at 613 cm⁻¹ attributed to inner Mg-OH vibration and a shoulder at 555 cm⁻¹ arising from the perpendicular Si-O bending vibration were observed. The IR band at 442 cm⁻¹ is assigned to the bending vibration of Si-O-Si (Fig. 3(a)).¹⁴

After heat treatment of chrysotile, especially the IR band at 3688 cm⁻¹ assigned to the surface Mg-OH stretch and bands at 1078, 952, and 442 cm⁻¹ attributed to the SiO₄ tetrahedra vibration became considerably weak and exhibited broadening. These results can be ascribed to the loss of OH groups by heat treatment of chrysotile (Fig. 3(b)). After carbonation under a CO₂ partial pressure 0.5 MPa, the spectrum of magnesite included a peak resulting from the out-of-plane CO₃²⁻ band at 885 cm⁻¹ (ν_2). A characteristic double peak at 1423 and 1485 cm⁻¹ appeared. The position and shape of the peaks correspond to the CO₃²⁻ group in silicate glasses after dissolution of CO₂ (Fig. 3(c)).^{15,16} Under 1 MPa, the in-plane CO₃²⁻ band at 747 cm⁻¹ (ν_4) was observed anew, and the double peaks at 1423 and 1485 cm⁻¹ decreased (Fig. 3(d)). With regards to the IR patterns, a well ordered magnesite was successfully obtained when reaction CO₂ partial pressure was increased to 1.5 MPa. After the carbonation under 1.5 MPa, the asymmetric CO₃²⁻ stretch at 1431 cm⁻¹ (ν_3) was formed newly (Fig. 3(e)). As CO₂ partial

Fig. 3 FT-IR spectra of starting material (a), heated chrysotile (b) and carbonation products under various CO_2 partial pressures: 0.5 MPa (c), 1 MPa (d), 1.5 MPa (e), 2 MPa (f).

pressure increased, the peaks of ν_2 , ν_3 , ν_4 were exhibited at 1435, 881, 748 cm^{-1} , respectively and peak intensity of magnesite became stronger. Highly crystalline magnesite was synthesized under 3 MPa (Fig. 3(f)), too.

The surface morphology was examined by SEM (Fig. 4). Most of the chrysotile was composed of acicular and cylindrical-like structure of the fibrils, which were under 100 nm (Fig. 4(a)). After the reaction under 0.5 MPa, magnesite crystals showed irregular morphology of a rather round shape surrounded by unreacted chrysotile. Moreover, the unreacted chrysotile crystals partially exhibited a lath-type morphology, but most of them were changed to an oval shape (Fig. 4(b)) although their chemical compositions coincided with that of chrysotile. After the reaction under 1 MPa, magnesite crystals exhibited irregular corners/edges (Fig. 4(c)), and under 1.5 MPa, well-faceted rhombohedral magnesite was exhibited, with the crystal size of magnesite of

approximately 2 μm (Fig. 4(d)). When the CO_2 partial pressure was increased up to 2.5 MPa, most of magnesite particles were found to be twin crystals, and unreacted chrysotile decreased considerably (Fig. 4(e)). Under 3 MPa, highly crystalline magnesite was observed (Fig. 4(f)). When the CO_2 partial pressure increased above 3.5 MPa, however, most of the edges and corners of the carbonate particles were eroded (Fig. 4(g)).

The extent of carbonation was determined by calcining the final product using TGA, as the weight change during calcination corresponds to the amount of CO_2 captured by carbonation (Fig. 5). The maximum carbonation rate was found to be approximately 57% at 100°C under 3 MPa. TGA analysis revealed that the amount of transformed magnesite increased rapidly up to 1 MPa. It increased at somewhat proportional rate to approximately 57% after carbonation up to 3 MPa, after which point it decreased slightly. From this result, it may be inferred that the dissociation of carbonic acids occurred with an increase in the CO_2 partial pressure above 3.5 MPa, and the pH of the solution was decreased.

Many studies on carbonation in the literature reported that mineral dissolution in the aqueous phase can be increased in the presence of anions, protons, organic ligands, and weak acids. Maroto-Valter *et al.* (2005)¹⁰ researched that the steam-activated serpentine underwent a 60% conversion to magnesite at 155°C and 12.6 MPa after 1 h in distilled water. O'Connor *et al.* (2005)¹⁷ proposed that the maximum carbonation rate achieved was no more than 57% at 155°C and 12 MPa. Considering that the carbonation rate in this study was obtained at 100°C under a CO_2 partial pressure of 3 MPa in alkali solution, we find that our results are comparable to the results of Maroto-Valter *et al.* and O'Connor *et al.*; our results suggest that carbonation in alkali solution is of great significance because excessive amounts of acid and alkali reagents can be eliminated in the carbonation process, and conversion under subcritical conditions may be applied practically.

The chemical composition as well as the morphological and structural changes related to the dissolution of chrysotile under CO_2 at a pressure of 3 MPa at reaction times from 15 min to 1 h was examined by TEM (Fig. 6). The TEM image of heated chrysotile maintained its typical morphology and periodic array of lattice points (Fig. 6(a)). EDS data of heated chrysotile showed a Mg : Si ratio of 1.56. After the reaction for only 15 min, the skeletal image of chrysotile surrounded by a succession of a silica-rich layer was shown, and the Mg content around the inner core of chrysotile was higher than that of the outside layers. The Mg : Si ratio was in the range of 1.0~1.2 (Fig. 6(b)). As the reaction time increased up to 30 min, the amount of Mg released from chrysotile increased, and the silica-rich layer exhibited parallel structural lines. Accordingly, a large number of Mg ions were leached out, and the range of Mg : Si ratio was 0.4~0.6 (Fig. 6(c)). After the reaction for 1 h, an amorphous silica phase was observed, which seemed to be separated from the host as the final stage of dissolution (Fig. 6(d)).

Si release during the dissolution was less than that of Mg; i.e., dissolution was non-stoichiometric for cations Si and Mg. The breakdown of $\text{Si-O-Si-} + 2\text{OH} + 2\text{Si-O-}$ is active in alkali solution at the initial stage.¹⁸⁻²⁰ As the reaction

Fig. 4 SEM image of chrysotile (a) and carbonation product according to CO_2 partial pressure: 0.5 MPa (b), 1 MPa (c), 1.5 MPa (d), 2.5 MPa (e), 3 MPa (f), 3.5 MPa (g).

progressed, the pH of the alkali solution decreased because the dissolved CO_2 formed carbonic acid, which likely dissociated to H^+ and HCO_3^- .²¹⁾ Moreover, as the proton concentration increased, the protonation of the oxygen atoms polarized and weakened the Mg-O-Si bonds,^{3,22)} thereby facilitating the preferential removal of magnesium atoms

from the crystal lattice and leaving the skeletal structure of the Si-rich layers. Eventually, the complete dissolution of Mg from chrysotile leads to the presence of only the amorphous silica phase. This mechanism provides the reason why the carbonation rate in alkali conditions is higher than that in a neutral or acidic solution.

Fig. 5 Carbonation rate of chrysotile at various subcritical conditions.

4. Conclusion

Chrysotile carbonation was experimentally performed under subcritical conditions in alkali solution. As the reaction proceeded, the surface morphology of chrysotile changed from an acicular and a cylindrical-like form to a round or oval shape at the initial stage and to a highly crystalline magnesite with well-faceted rhombohedral planes after carbonation. The carbonation rate increased proportionally according to the applied CO₂ pressure to approximately 57% at 3 MPa.

The dissolution rate of Mg was higher than Si, such that the Mg : Si ratio of the reacted chrysotile decreased from 1.56 to 0.4~0.6 as the reaction time increased under a pressure of 3 MPa, and the amorphous silica phase was observed at the final stage of dissolution. Mg was released preferentially from the crystal lattice in alkali solution and left the skeletal structure of Si-rich layers.

Fig. 6 TEM image of chrysotile obtained after reaction in alkali solution: heated chrysotile (a), 15 min (b), 30 min (c), 1 h (d).

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