Enhancement of Chrysotile Carbonation in Alkali Solution

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The carbonation of chrysotile [Mg₃Si₂O₅(OH)₄] was studied at various temperatures in order to examine the carbonation rate and Mg leaching properties in an alkali solution and distilled water using the direct method. For the efficient carbonation reaction, the chrysotile was converted to metachrysotile by heating at 630°C for 2 h. The carbonation rate was found to increase with the reaction temperature: 5 and 31% at 100°C and 45 and 53% at 260°C in distilled water and alkali solution, respectively. The carbonation in the alkali solution was faster producing well-faceted rhombohedral magnesite (MgCO₃) in comparison to the case in the distilled water. Highly crystalline magnesite could be obtained after the carbonation for 1 h at 260°C under a CO₂ pressure of 3 MPa in the alkali solution.

The additional object of this study was to convert the fibrous chrysotile to a non-hazardous material. During carbonation, the magnesite exhibited the typical rhombohedral morphology while the unreacted chrysotile changed primarily to aggregations of chrysotile crystals. This result has an important implication for the elimination of toxicity through the transformation of chrysotile asbestos into a non-hazardous material.


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1. Introduction

Chrysotile is one of the serpentine group and its crystal structure is characterized by the spiraling of both the silicate (SiO₄)²⁻ tetrahedral sheet as an inner layer and the magnesium hydroxide [Mg–(OH)₂] as an outer layer.¹ Thus, the fibers can also be represented by a tubular scroll-like morphology.

Owing to their outstanding technological properties, such as fire protection, moisture control, and thermal insulation, asbestos minerals have been extensively used since the beginning of the last century for innumerable industrial applications. Most of these applications involve products that contain chrysotile asbestos, which accounted for over 90% of worldwide asbestos production.²

However, on account of its asbestiform morphology, chrysotile is considered to be a carcinogenic health hazard. Consequently, asbestos must be removed and properly managed in accordance with the safety regulations. The most common method of dealing with hazardous asbestos is disposing of it in a suitable landfill, but the disposal of this kind without pre-treatment is forbidden. However, their pre-treatment involves many disadvantages, including high cost, long intervention times, large production of toxic waste, and risk of environmental pollution during and after the operation.³ Most of the chemical processes involve the covering of the surface of the asbestos fiber with organic or inorganic substances; in addition, strong acids can be used to destroy the fiber structure. Unfortunately, such acids are considered to be even more hazardous than chrysotile asbestos itself.⁴,⁵ Other popular natural treatments that convert chrysotile asbestos into non-hazardous substances are the thermal conversion⁶ and physical conversion using microwave radiation and mechanical methods.⁷–¹⁰

The increasing atmospheric concentration of CO₂, attributed to fossil fuel combustion, is a serious problem that leads to the global warming. A variety of options for reducing CO₂ emissions have been extensively studied; among them, mineral carbonation has recently attracted much interest because of its ability to sequester CO₂ indefinitely as chemically stable carbonates through a spontaneous exothermic reaction.¹¹–¹³ Serpentine is an attractive mineral reactant for mineral sequestration on account of its reserves and its relatively high magnesium content. The reserves of serpentine are much greater than any other Ca, Mg minerals.

Most of the carbonation of chrysotile was carried out in neutral or acidic pH because this is advantageous for the mineral extraction reaction to occur. It is well known that acids destroy the fiber structure of chrysotile asbestos. In contrast, the carbonation reaction should be carried out under the appropriately basic pH conditions requiring the pH swing reaction. Nevertheless, to the best knowledge of the authors, the dissolution and carbonation of chrysotile through the direct method in an alkali solution have never been attempted.

The aims of this study were to investigate the direct mineral carbonation in terms of the carbonation rate, Mg leaching properties, and the conversion of fibrous chrysotile to a non-hazardous material under economically viable and safe conditions through a comparative study using an alkali solution and distilled water.

2. Experiments

2.1 Materials

The chrysotile asbestos fibers used in this study were obtained from ChungYang, Korea. XRD data indicated that the starting material was pure chrysotile (Fig. 1(a)). The chemical composition of the chrysotile was 39.4 SiO₂ and 38.8 mass% MgO (Table 1). The ignition crystalline water content was estimated to be 13 mass%. Most chrysotile is crystallized as bundles or has a cylindrical structure for the fibrils, which are 20–50 nm in diameter (Figs. 2(a), 3(a)). Chrysotile exhibits complete order with respect to [100], but it exhibits no order with respect to [010].¹⁴

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At 600 to 650°C, chrysotile undergoes dehydration (endothermic dehydroxylation)\(^1,15\) to metachrysotile, according to the following reaction:

\[
\text{Mg}_3\left(\text{OH}\right)_2\text{Si}_2\text{O}_5 \xrightarrow{650\text{°C}} \text{Mg}_3\text{Si}_2\text{O}_7 + 2\text{H}_2\text{O}.
\]

As heating chrysotile is expected to facilitate its formation of carbonate, the chrysotile was heated at 630°C for 2 h in atmosphere. The formation of metachrysotile as amorphous phase was confirmed by XRD analysis;\(^1,15\) the chrysotile peaks disappeared completely and forsterite and hematite peaks were observed (Fig. 1(b)). The TEM image of heated chrysotile also revealed its typical morphology and structure (Fig. 2).

### 2.2 Methods

The starting material for the carbonation was the heat-treated chrysotile. The activated chrysotile was crushed in a jet mill into grains that would pass through a 200 mesh sieve. The grain size was measured by a particle size analyzer (KMC-1B, KME Co.). The chemical composition of chrysotile was measured by ICP-AES (JY 38 Plus, France Jobin Yvon).

All carbonation experiments were performed in a 1 L cold-seal type stainless steel vessel. Unless otherwise specified, the following experimental conditions were maintained: the CO\(_2\) partial pressure was 3 MPa, reaction time was 1 h, and reaction temperature was varied from 80 to 260°C. The reaction was carried in distilled water and alkali solution. The pH of the alkali solution was controlled by adding 1 M NaOH solution (OCI, extra pure). The mineral/water/liquid CO\(_2\) mixture was continuously agitated to prevent settling of the solids.

After carbonation, the reaction products were collected and analyzed by XRD (X’pert MPD X-ray diffractometer with graphite monochromatized CuK\(_\alpha\) radiation, Phillips Co.). The microstructure of the synthesized products was examined using a transmission electron microscope (TEM, JEM 2200FS, JEOL) coupled with an energy dispersive X-ray spectrometer (EDS, Oxford) and a scanning electron microscope (FE-SEM, S-4700, Hitachi). TEM samples were dispersed in distilled water using an ultrasonic probe. They were air dried after being placed onto a holey carbon Cu grid.

### Table 1 Chemical composition of the starting material (mass%).

<table>
<thead>
<tr>
<th>Component</th>
<th>SiO(_2)</th>
<th>MgO</th>
<th>CaO</th>
<th>Al(_2)O(_3)</th>
<th>Na(_2)O</th>
<th>K(_2)O</th>
<th>Fe(_2)O(_3)</th>
<th>MnO</th>
<th>TiO(_2)</th>
<th>Total</th>
</tr>
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<tbody>
<tr>
<td>%</td>
<td>39.36</td>
<td>38.80</td>
<td>0.05</td>
<td>1.96</td>
<td>0.65</td>
<td>0.13</td>
<td>6.42</td>
<td>0.06</td>
<td>0.02</td>
<td>87.45</td>
</tr>
</tbody>
</table>

### Fig. 1 XRD patterns of raw material (a), activated chrysotile (b), and carbonation products after at 80°C (c), at 140°C (d), at 260°C (e).

### Fig. 2 TEM image of heated chrysotile. A fibrous heated chrysotile with a tubular morphology for each fibril (a) and the electron diffraction pattern (b).

### Fig. 3 SEM image of carbonation products after reaction at various temperatures in distilled water and alkali solution: 80°C (a) (a-1), 100°C (b) (b-1), 140°C (c) (c-1), 260°C (d) (d-1).
and coated with osmium tetraoxide (OsO4).

The carbonation rate of chrysotile to magnesite was calculated by thermo-gravimetric analysis (TG-DTA) at atmospheric pressure (DTG-60H, Shimazu). 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 X-ray diffraction patterns of carbonated samples at temperatures of 80, 140 and 260°C are shown in Fig. 1. XRD patterns of carbonation samples from different pH at weak acidic and alkali condition were almost identical. Therefore, only patterns from alkali Solutions are presented here. The reaction time was 1 h and the pH was 6–7 for weak acidic and pH 13 for alkali solutions, respectively. After the carbonation reaction at 80°C, rather poorly crystallized magnesite appeared suggesting that the reaction was not pronounced. At this condition, very small amount of chrysotile was recrystallized and a peak at low angle is suggested by the formation of saponite \[ \text{M}_6^{+}\text{(Mg}_6\text{Si}_8\text{Al}_4\text{Si}_4\text{O}_{22}\text{(OH)}_8}\cdot n\text{H}_2\text{O} \] based on the octahedral Mg layers was also noticed (Fig. 1(e)). At 140°C, the synthesis of highly crystalline magnesite was evident after the carbonation (Fig. 1(d)). At 260°C, saponite became more stable at the expense of transformed mangesite (Fig. 1(e)).

The surface morphology of the synthesized magnesite samples carbonated in weak acidic and alkali solution was examined by SEM (Fig. 3). The micrographs appear to suggest that the carbonation products reacted more in alkali solutions than in distilled water at all temperatures in view of the morphological changes. Thus, after the reaction at 80°C in distilled water, magnesite crystals are hardly observed suggesting that the starting materials were not reacted with CO2 (Fig. 3(a)). In contrast, after the reaction at 80°C in alkali solution, few magnesite crystals finer than 1 µm with a more regular morphology were observed, which is typical for the carbonate particles. Here, the unreacted chrysotile crystals exhibited partially lath-type morphology; most of them were agglomerated to irregular shapes (Fig. 3(a-1)) after the reaction thus maintaining the chemical composition of chrysotile.

After the reaction at 100°C in distilled water, the aggregation of chrysotile crystals with irregular edges/corners under 10 µm was formed by partial dissolution and the crystal face of magnesite was poorly developed. The size of magnesite was about 1.5 µm (Fig. 3(b)). On the contrary, at 100°C in alkali solution, the crystal faces of magnesite were observed well-developed and some chrysotile crystals were still seen to remain unreacted (Fig. 3(b-1)).

After carbonation at 140°C in both solutions, well-faceted rhombohedral magnesite crystals appeared and the size of the magnesite crystals was about 2–3 µm. However, the unreacted chrysotile crystals were more after the reaction in distilled water than that in alkali solution (Fig. 3(c), (c-1)). This observation suggests that carbonation rate in the alkali solution was much higher. After increasing the reaction temperature to 260°C, most of the edges and corners of the carbonates were eroded by the partial dissolution. On the surface of magnesite crystals, the cavity and so called ‘curled habits’ were also observed and their chemical composition was found to be comparable to that of saponite (Fig. 3(d), (d-1)).

So far, it has been demonstrated that the fibrous shape of chrysotile was transformed to rhombohedra or agglomerates of chrysotile with the partial leaching of Mg2+ during the carbonation reaction. Here, the morphological modification of chrysotile during the transformation is worthy of further study in relation to the possible reduction of its toxicity.

The extent of the carbonation was determined by calcining the final product using TGA, since the weight change during calcination corresponds to the amount of CO2 captured by carbonation (Fig. 4). The result shows that the carbonation reaction of heated chrysotile was significantly higher in more alkali solution (pH 13) than in distilled water. The carbonation rate was found to be approximately 0 and 11% at 80°C, 5 and 31% at 100°C, 38 and 50% at 180°C, and 45 and 53% at 260°C in distilled water and alkali solution, respectively.

TGA result suggests that the amount of transformed magnesite increases very rapidly up to 140°C. Afterwards, it increases at a much slower rate up to 260°C. O’Connor et al. (2005) reported that the maximum carbonation rate was 57% at 155°C and 12 MPa. The carbonate rate in this study obtained at 260°C under CO2 partial pressure of 3 MPa in the alkali solution is comparable to the results of O’Connor et al. The initial stage of Mg-silicate dissolution is always nonstoichiometric with preferential Mg release at pH < 8, but preferential Si release occurs at pH ≥ 10. At high pH, where Si surface sites are deprotonated and therefore carry negative charge, detachment of silicon appears to control the overall silicate dissolution rates. Si is preferentially released from the chrysotile surface in an alkali solution consistent with its surface structure: isolated SiO4 tetrahedra can be easily removed from the surface, leaving Mg octahedra branched together via Mg–O–Mg bonds, as in brucite or Mg-bearing sheet silicate. The formation of the Mg-rich layer on the meta-chrysotile surface can be described as:

\[ \text{Mg}_3\text{Si}_2\text{O}_5(\text{surface}) + 7\text{H}_2\text{O} \rightarrow \text{Mg}_3\text{(OH)}_6(\text{surface}) + 2\text{H}_2\text{SiO}_4(\text{aq}) \]

The dissolution of the Mg-rich layer requires the breaking of Mg–O–Mg bonds, which is promoted by the hydration of metachrysotile surface with the formation of \( \text{MgO}_2\text{H}^+ \) species, as is the case of oxides or carbonates.

The pH determines which steps dominate the reaction sequence and, accordingly, the proportions of the carbonic
species. At low pH (~4), the production of H$_2$CO$_3$ dominates; in the middle of the pH range (~6), HCO$_3^-$ production dominates; and at a high pH (~9), CO$_3^{2-}$ production dominates.

In turn, the magnesium hydroxide can be carbonated according to

$$\text{Mg}^{2+} + \text{CO}_3^{2-} = \text{MgCO}_3 + \text{H}_2\text{O}.$$  

The amounts of Mg$^{2+}$ residue in the solution after the carbonation reaction at various reaction temperatures in distilled water and in alkali solution are presented in Fig. 5. After carbonation up to 100°C Mg$^{2+}$ residue in distilled water is almost an order higher than that in alkali solution. However, it decreased sharply after carbonation at 140°C. In contrast, residual Mg$^{2+}$ in alkali solution dropped rapidly at 100°C.

Regarding the carbonation, it was generally accepted that the mineral dissolution in aqueous phase can be increased by the presence of anions, protons, organic ligands, and weak acids. Park et al. (2004) examined various solvents to enhance the dissolution of magnesium, and suggested that a pH swing is needed to achieve a higher overall conversion for the CO$_2$ aqueous sequestration process. Similarly, in this study, the high amount of Mg$^{2+}$ dissolved in weak acid (distilled water) remained unreacted during the carbonation at 100°C. In contrast, in alkali solution, the reaction of dissolved was almost completed at 100°C as shown in Fig. 5. However, in weak acid, significantly conversion of residual Mg$^{2+}$ for mineral carbonation was possible only after the reaction temperature was increased to 140°C suggestive of the higher energy consumption. These results suggest that the direct carbonation method in alkali solution is of great significance in spite of the lower Mg$^{2+}$ dissolution rate. Therefore, the carbonation reaction in alkali solution is considered to be economically more viable than the neutral and acid conditions when one considers the cost for the higher energy operation and pH swing process.

4. Conclusion

The carbonation of heated chrysotile was studied to examine the feasibility of converting carbon dioxide to a thermally stable form of magnesite in both alkali and weak acid solutions. The conversion rate of chrysotile to magnesite in the alkali solution was higher than that in the distilled water. The carbonation rate was found to be 5 and 31% at 100°C and 45 and 53% at 260°C in distilled water and alkali solution, respectively. The amount of Mg$^{2+}$ residue in reaction solution after carbonation up to 100°C was much higher in distilled water than in alkali solution. Therefore, a pH swing and high energy should be provided to achieve a higher overall conversion in distilled water. On the contrary, the suggested direct method in alkali solution has an advantage over the conventional method since it can be operated at lower temperature without the pH swing process.

In addition, the morphological change of chrysotile during the carbonation is of another significance in view of the reduction of chrysotile’s toxicity. Fibrous chrysotile transformed to agglomerate at 80°C in alkali solution, and to well-faceted rhombohedral magnesite crystals at 140°C in both solutions. The morphological alteration is expected to convert chrysotile asbestos into a non-hazardous material.

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REFERENCES