CO₂ Sequestration via a Surface-Modified Ground Granulated Blast Furnace Slag Using NaOH Solution

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This study investigates the improvement of the CO₂ sequestration percentage of a ground granulated blast furnace slag (GGBF-slag) with surface modification using a NaOH solution. The amount of CO₂ sequestration of the GGBF slag increased via the surface modification with the NaOH solution in the direct carbonation method. The increase of the carbonation percentage of the GGBF slag resulted from the increase in the hydraulic activity of the GGBF-slag. The carbonation percentage on the basis of the total calcium oxide of the GGBF slag was approximately 10 times larger than that of the GGBF-slag without the surface-modification. The carbonation rate depended on the morphology of the calcium carbonates formed on the surface of the GGBF-slag. [doi:10.2320/matertrans.M2011110]

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1. Introduction

CO₂ sequestration by mineral carbonation using feedstocks including Ca and Mg silicate materials is a possible technology for the reduction of carbon dioxide emission to the atmosphere.1–3) In particular, mineral carbonations using industrial residues, such as combustion residues, steel slag and waste cement have the advantages of low cost and widespread availability in industrial areas when compared with ores.4) Among these, steel slag is a very attractive feedstock as it has a high calcium oxide content and high alkalinity, which should enhance the CO₂ mineralization during the carbonation process.

Mineral carbonation may be conducted by means of a direct or indirect method.5) The indirect method includes the chemical extraction of Ca and Mg from feedstocks using an effective selective solvent. Therefore, the indirect method can maximize the efficiency of the CO₂ sequestration in the formation of pure calcium carbonate. However, this method is complicated and has high costs compared with the direct method. The direct method is the simplest approach to CO₂ sequestration including crushing, grinding, and milling, as well as some mechanical separation for example, magnetic extraction of magnetite. In general, the direct method of mineral carbonation is the reaction of gaseous CO₂ with particulate Ca and Mg oxide bearing materials at suitable temperatures and pressure levels. However, the direct method of mineral carbonation without refined or modified materials is limited in capturing CO₂ because the direct gas-solid reactions are too slow to be practical.5) Steel slag is also known to have a low CO₂ carbonation rate in the direct carbonation method. Therefore, most published research on the CO₂ carbonation of steel slag using the direct carbonation method has focused on the improvement of environmental quality and the mechanical properties with regard to use in construction materials such like alternative aggregate.7–10)

This paper presents the systematic study to improve the CO₂ sequestration percentage of steel slag via its surface modification method in the direct carbonation method. In this study, ground granulated blast furnace (GGBF) slag was selected for use in the experiments and NaOH was used as the surface modification reagent, because NaOH is well known as an alkaline activator that accelerates the surface dissolution of the GGBF-slag.11,12)

2. Experimental Methods

2.1 Raw materials

The GGBF-slag used in this study was collected from H. Steel Co. Ltd. (Dang-gen, Republic of Korea). The chemical composition of the GGBF-slag is shown in Table 1. The GGBF-slag was rich in Ca. The CaO content, which forms calcium carbonates during the carbonation reaction, was 41.5 mass%. The contents of SiO₂ and Al₂O₃ were 33.7 mass% and 13.9 mass%, respectively. And MgO was also present at about 6.5 mass% in the raw GGBF-slag. The representative samples of the GGBF-slag used in this study were ground until all materials passed a predetermined sieve size of 200-mesh (d: <35 μm), and the surface area (Blaine) of prepared GGBF-slag was 4,100 cm²/g. 1 M and 2 M NaOH solutions were prepared for use in the surface modification process of the GGBF-slag. The GGBF-slag was added to the NaOH solution at a solution-to-solid ratio of 10 (mL/g). The prepared slurry was agitated for 24 h in controlled conditions with the temperature and relative humidity at 298 ± 0.5 K and 65%, respectively. The surface

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Table 1 Chemical composition of the GGBF-slag used in this study.

<table>
<thead>
<tr>
<th>Composition</th>
<th>mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>41.5</td>
</tr>
<tr>
<td>SiO₂</td>
<td>33.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13.9</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.3</td>
</tr>
<tr>
<td>MgO</td>
<td>6.5</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.0</td>
</tr>
<tr>
<td>MnO</td>
<td>0.5</td>
</tr>
</tbody>
</table>
modified GGBF-slag in the NaOH solutions was obtained through a filtration process. Table 2 shows the sample names used in the CO₂ sequestration experiment.

### Table 2 Sample names and descriptions designed for the CO₂ sequestration experiment.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGBF-slag</td>
<td>Ground granulated blast furnace slag</td>
</tr>
<tr>
<td>M1-GGBF-slag</td>
<td>The surface modified GGBF-slag in 1 M NaOH solution</td>
</tr>
<tr>
<td>M2-GGBF-slag</td>
<td>The surface modified GGBF-slag in 2 M NaOH solution</td>
</tr>
</tbody>
</table>

#### 2.2 Methods

The CO₂ carbonation experiments with the tested GGBF-slag were conducted in a 2 L closed Ti-lined pressure reactor. The carbonation reactor was charged with approximately 1 L of the specimen, which was prepared by mixing the tested GGBF-slag with distilled water at a water-to-solid ratio of 0.2 (mL/g). The specimen was carbonated for 6 h with 0.15 MPa at a CO₂ concentration of 100% and a temperature of 298 ± 0.5 K. The carbonated samples were analyzed using X-ray diffraction (XRD; Model D/Max 2200V/PC, Rigaku, Target: Cu Kα) and scanning electron microscopy (SEM; JEOL Model JSM-6380LA) measurements to identify the products and the morphologies during the CO₂ carbonation experiment. The amount of sequestrated CO₂ in the carbonated samples were calculated using eq. (1), where C, C₀, and Cᵥ are the amount of carbon dioxide in the carbonated sample, that in the non-carbonated sample (the initial carbonation ratio in the sample before the carbonation reaction), and the theoretical amount of carbon dioxide required for combination with the total calcium oxide in the sample to form the calcium carbonate, respectively.¹³)

\[
\frac{(C - C₀)}{(Cᵥ - C₀)} \cdot 100\% \tag{1}
\]

The carbonated specimen was heated to 1000°C in a TG-DTA instrument (Shimadzu Model DTG-60H). The amount of carbon dioxide in the carbonated specimen was determined using the weight loss of the specimen between 550°C and 950°C, which occurred due to the thermal decomposition of the calcium carbonate.¹⁴) The initial carbonation ratio (C₀) of CaO in the GGBF-slag before the carbonation experiment was estimated about 0.32 mass%.

#### 3. Results and Discussion

Figure 1 shows the XRD pattern of the GGBF-slag used in this study. The GGBF-slag includes highly crystalline phases of wollastonite and akermanite, and a large quantity of an amorphous phase. Figure 2 depicts the XRD patterns of the non surface-modified GGBF-slag as carbonation reaction at different times. The formation of calcium carbonate such as calcite was observed in the sample of GGBF-slag carbonated for 1 h. However, further increases in the formation of calcite and additional consumption of the raw composition of the GGBF-slag were not detected even through carbonating for 6 h. Figure 3 shows the XRD patterns of the surface-modified GGBF-slag with the 1 M and 2 M NaOH solutions. Ca(OH)₂, Ca₅(Si₆O₁₆)(OH)₂, and Ca₂Al(OH)₇ nH₂O, which are a hydration product of GGBF-slag activated by NaOH, were formed accompanying the consumption of the raw composition of the GGBF-slag such as wollastonite and akermanite. These results indicate that the surface of the GGBF-slag is hydraulically activated by the reaction with NaOH. It is reported that the initial carbonation reaction of feedstock is
accompanied by its hydration reaction. Therefore, the formation of hydrates through the surface modification process of the GGBF-slag indicates that the surface-modified GGBF slag has a surface condition that reacts easily with CO$_2$ gas. Figure 4 is the schematic diagram of the surface modification of the GGBF-slag in the NaOH solution. In general, when the GGBF-slag was percolated in water, an alumino-silicate gel with a high density on the GGBF-slag surface was formed. The gel layer plays a role as an impermeable layer, resulting in stopping further hydration of the GGBF-slag (Fig. 4, (A)). However, when the GGBF-slag was percolated in alkaline solution, the OH$^-$ ions destroy the alumino-silicate gel, and its hydration reaction progresses, resulting in the formation of hydrates, including calcium silicate hydrates, calcium alumino-silicate hydrates, and calcium hydroxide (Fig. 4, (B)). The hydration processes of GGBF-slag in alkaline solution are summarized as following:

(1) OH$^-$ ions destroy siloxane bond of alumino-silicate gel

\[ \equiv \text{Si-O-Si} \equiv + 3\text{OH}^- \rightarrow [\text{SiO(OH)}_3]^- \]  
\[ \equiv \text{Si-O-Al} \equiv + 7\text{OH}^- \rightarrow [\text{SiO(OH)}_3]^- + [\text{Al(OH)}_4]^- \]  

(2) Hydration & precipitation of hydrates

\[ x\text{Ca}^{2+} + y[\text{Si(OH)}_3]^- + (z-x-y)\text{H}_2\text{O} + (2x-y)\text{OH}^- \rightarrow x\text{CaO} \cdot y\text{Si}_2\text{O}_3 \cdot z\text{H}_2\text{O} \]  
\[ x\text{Ca}^{2+} + y[\text{Al(OH)}_4]^- + (z-x-y)\text{H}_2\text{O} + 2(x-y)\text{OH}^- \rightarrow x\text{CaO} \cdot y\text{Al}_2\text{O}_3 \cdot z\text{H}_2\text{O} \]  
\[ x\text{Ca}^{2+} + x\text{H}_2\text{O} \rightarrow x\text{Ca(OH)}_2 \]  

Figure 5 shows the XRD patterns of the carbonated samples of the surface-modified GGBF-slag in the 1 M NaOH solution at different times. A calcite with a high crystalline phase was formed in the M1-GGBF-slag through the carbonation reaction for 15 m. For the M2-GGBF-slag, calcite and vaterite which are a polymorphism of calcium carbonate were produced with an increase in the carbonation time, as shown in Fig. 6. From these results, the surface modification with the NaOH solution contributes to an increase in the carbonation reactivity of the GGBF-slag with CO$_2$ gas. Figure 7 shows the SEM photos of the sample surfaces: (A) GGBF-slag, (B) GGBF-slag carbonated for 6 h, (C) M1-GGBF-slag carbonated for 6 h, and (D) M2-GGBF-slag carbonated for 6 h.
slag carbonated for 6 h. There is not a large difference between the GGBF-slag and the GGBF-slag carbonated for 6 h. However, a cubic crystal structure, resulting from the formation of calcite, was observed in the M1-GGBF-slag sample carbonated for 6 h. In the M2-GGBF-slag sample carbonated for 6 h, the products with small particle size were observed when compared with the carbonated M1-GGBF-slag. The calcium carbonate with sphere shape was also observed, and it was expected as a vaterite-type calcite, detected in the XRD pattern, which is well known as a metastable phase of calcite. Figure 8 presents the carbonation percentages on the basis of the total calcium oxide of the GGBF-slag, M1-GGBF-slag, and M2-GGBF-slag with an increase in the carbonation time. The GGBF-slag without surface modification was only carbonated by approximately 2~3% after 6 h of carbonation time. However, the carbonation percentage of the surface-modified GGBF-slag; M1-GGBF-slag and M2-GGBF-slag reached approximately 27% and 21% after 6 h of carbonation time, respectively. In particular, the carbonation percentage of the M2-GGBF-slag reached nearly 20% within 20 m of carbonation time.

Figure 9 shows the solubility of Ca(OH)$_2$ with the concentration of Na(OH)$_2$ in the solution. As shown in the figure, the solubility of Ca(OH)$_2$ decreases with increase on the concentration of NaOH in the solution. Therefore, it is expected that the large number of nuclei of Ca(OH)$_2$ formed on the surface of M2-GGBF-slag during the surface modification process in 2 M NaOH solution comparing with that of M1-GGBF-slag caused by the low solubility of Ca(OH)$_2$. From the XRD pattern shown in Fig. 3, the large amounts of Ca(OH)$_2$ and the other hydrates (C-S-H, C-A-H) could be observed in the M2-GGBF-slag comparing with that of M1-GGBF-slag. Thereby, the large amount of calcite with small particle size is able to form on the surface of M2-GGBF-slag. However, the increase in the carbonation percentage was not great after the carbonation reaction. It
is considered that the later carbonation reaction of GGBF-slag after the formation of product layer depends on its morphology such like particle size, because the more carbonation reaction takes place with a diffusion-controlled reaction through product layer. The rate of permeation through the layer produced on the surface of reactant is expressed by the Poiseuille’s equation as follows:

\[ Q = \frac{\pi \cdot r^4 \cdot h}{8\eta \cdot l} \]  

Where

- \( Q \): Rate of permeation through a pore
- \( r \) and \( l \): Radius and length of single pore (cm)
- \( h \): Pressured difference (cm)
- \( \eta \): Viscosity of the fluid

The radius \( r \) and length \( l \) of single pore of formed layer depend on the particle size of which calcium carbonate is synthesized on the surface of reactant. The smaller the particle size is, the more the radius \( r \) of single pore of formed layer decreases, and on the other hand, the length \( l \) of single pore of formed layer increases. It was confirmed on the observation of Fig. 7 that the early carbonation reaction of M2-GGBF-slag was accompanied with the formation of calcium carbonates with small size on the surface of reactant. Thereby, when comparing with those of M1-GGBF-slag, the radius \( r \) and length \( l \) of single pore of layer formed on the surface of M2-GGBF-slag would be smaller and longer, respectively. Therefore, the formed layer of calcium carbonate on the M2-GGBG-slag would strongly interrupt the permeation of substances, such like CO₂ gas, water molecular and calcium ion. S. Goto et al. also reported that when calcium silicate compound was carbonated, the amorphous calcium carbonate with small size was produced on the surface of calcium silicate compounds, resulting into stopping the carbonation of calcium silicate. Therefore, the carbonation reaction of the M2-GGBF-slag was greatly reduced or completely halted despite showing a high carbonation percentage within 20 m of carbonation time.

However, the carbonation percentage of the M1-GGBF-slag steadily increased within 6 h of carbonation time. It is considered that the high carbonation percentage of the M1-GGBF-slag results from the formation of a high crystalline phase of calcite in the early stages of the carbonation reaction. These results demonstrate that the formation of calcium carbonates with high crystallinity in early stages of carbonation reaction is necessary to obtain the high carbonation percentage of GGBF-slag, because the later carbonation percentage of the GGBF-slag depends on the texture of the carbonates, such as the crystallinity and particle size, which are produced in the outer portion of the non-carbonated materials.

4. Conclusions

The surface modification using a NaOH solution contributed to the improvement of the amount of CO₂ sequestration of GGBF-slag in the direct carbonation method. The increase of the carbonation percentage of the GGBF-slag was due to the improvement of hydraulic activity of the GGBF-slag in the NaOH solution, resulting in the formation of hydrates such as Ca(OH)₂, Ca₂(Si₆O₁₈)(OH)₂, and Ca₂Al(OH)₆·nH₂O. The texture of calcium carbonates produced in early stages of carbonation reaction affected the further carbonations with a diffusion-controlled reaction of CO₂ gas, because the later carbonation reaction of the GGBF-slag depended on the crystallinity and particle size of calcium carbonates formed in the early stage of carbonation reaction.

REFERENCES