1. Introduction

Over 10 million tons of steelmaking slags is produced every year in Japan.1) Steelmaking slag is a useful material to save natural resources2) and is expected to be used for a variety of purposes. The use of the slags as an aggregate for civil engineering has a long tradition and it comprises approximately 70% of all the products.1) In addition, steelmaking slag is recently used as fertilizer that enhances rice productivity in paddy fields damaged by seawater3) or constructs nursery ground in the sea.4) It is also used as a material for the development of biofuels.5)

A steelmaking slag may contain appreciable amounts of free lime (f-CaO) and small amounts of free magnesia or periclase (f-MgO), which cause expansive self-destruction by about 100% volume increase due to their reactions with water.6) Consequently, f-CaO and f-MgO in slag samples has not been reported yet. In the present work, we developed a method for determination of f-MgO in the slags by hydration of f-MgO with microwave digestion followed by thermogravimetry (TG). The microwave assisted hydration with hot water over 100°C makes f-MgO to rapidly and completely convert into Mg(OH)2, the amount of which, in turn, can be determined by TG. The developed method was successfully applied to the determination of f-MgO in synthetic and real steelmaking slag samples.

KEY WORDS: free magnesia; steelmaking slags; microwave hydration; thermogravimetry.
to convert f-MgO to Mg(OH)₂. Even pure MgO could not completely be converted to Mg(OH)₂ by the hydration with steam at 200°C for 20 h.

There are many successful examples of microwave application including grinding a hard material, drying a sample, and rapid hydration of cements. Under an appropriate microwave irradiation condition, it is thus expected that hydration of MgO can be accelerated by offering several advantages over conventional heating such as instantaneous deep inside heating with high temperature homogeneity. In the present work, we examine the conditions of microwave heating for rapid and complete hydration of f-MgO in several slag samples. Based on the results, the microwave-assisted-hydration/TG method for determination of f-MgO in slag samples was developed. The method presented was successfully applied to the determination of f-MgO in synthetic and real steelmaking slag samples.

2. Experimental

2.1. Materials

Steelmaking slag samples used in this study are listed in Table 1. Four of them are synthetic slags, while the others are actual slag samples. Analytical reagent-grade hydrochloric acid and MgO (99.9%) were purchased from Wako Pure Chemicals (Tokyo, Japan). Yttrium standard solution (1 000 mg L⁻¹) was obtained from Kanto Chemicals (Tokyo, Japan). Water was purified with a Direct-Q (Merck Millipore, Tokyo, Japan).

2.2. Sample Preparation

A 1.0 g of a granulated slag sample was placed in a PTFE digestion vessel. After the addition of 10 mL of degassed water to the slag sample, it was treated with a microwave digestion system ETHOS PRO (Milestone General, Kawasaki, Japan). The sample was heated at the heating rate of 13°C min⁻¹. After the temperature has reached the prescribed temperature, it was kept constant for a definite time. Then the vessel was cooled in air, and the content was filtrated with a membrane filter (OMNIPOR, 0.45 µm pore size, Merck Millipore, Tokyo, Japan). The residue was dried at 80°C in an oven for 4 h in an atmosphere of dry nitrogen.

2.3. Determination of the Content of f-MgO in Steelmaking Slag

A Hitachi High-Tech Science TG/DTA30 (Tokyo, Japan) was employed to evaluate a mass loss of Mg(OH)₂ by the thermal decomposition. TG was performed in dry nitrogen atmosphere at a constant heating rate of 10°C min⁻¹ from 30°C to 1 000°C. The weight of sample, Wₚ, used for TG was about 20 mg for all the measurements and the flow rate of dry nitrogen over the sample was 300 mL min⁻¹. From the mass loss of Mg(OH)₂, Wₘg(OH)₂, for the hydrated slag sample, the total amount of Mg present as f-MgO and Mg(OH)₂ in the original slag was calculated as the content of MgO, CₘgO, according to

\[
C_{\text{MgO}}(\%) = \left( \frac{W_{\text{Mg(OH)₂}}}{18.0 \times 40.3} / W_p \times 100 \right) \tag{1}
\]

The amount of Mg(OH)₂ that exists originally in the raw steelmaking slag sample was also determined by TG and was then converted to the content of MgO, CₘgO'. A content of f-MgO in the raw steelmaking slag, Cₐ-MgO, was calculated as

\[
C_{\text{f-MgO}}(\%) = C_{\text{MgO}} - C_{\text{MgO'}} \tag{2}
\]

The concentrations of Mg and Ca in the filtrate after microwave digestion of slag samples were determined by ICP-AES after the measurement of pH of the filtrate solutions. To prepare a sample solution for measurement of Mg in the filtrate, 2.5 mL of the filtrate and 2.5 mL of (1 + 1) HCl were pipetted into a measuring flask. The solution was made up to 25 mL with pure water after yttrium was added as an internal standard to compensate for changes in analytical signal of ICP-AES with sample matrix; the concentration of yttrium in the final solution was 100 ppb. For the measurement of Ca, 50 µL of the filtrate was used and the other procedure was the same as given above for the determination of Mg. The pH meter and the ICP-AES instrument used were Horiba (Kyoto, Japan) F-51 and a Hitachi High-Tech Science (Tokyo, Japan) SPS-3000, respectively. The operating conditions of ICP-AES are shown in Table 2.

2.4. X-ray Diffraction

A Rigaku RINT Ultima III and a Rigaku SmartLab were employed for X-ray diffraction measurements in this work. The operating conditions are shown in Table 3.

3. Results and Discussion

3.1. Microwave Assisted Hydration of Reagent-grade MgO

To evaluate the effect of a microwave heating for hydra-
tion of MgO. 0.1 g of a reagent-grade MgO (99.9%) was digested with 10 mL of pure water at 200°C for 30 min. After filtration and drying, the residue was examined using a Rigaku Rint Ultima III XRD instrument. As shown in Fig. 1, the XRD pattern of MgO completely disappeared and that of Mg(OH)₂ was observed after the microwave hydration. This indicates that the microwave heating is effective for rapid hydration of MgO.

3.2. The Influence of CO₂ on Hydration of f-MgO

Figure 2 shows TG curves obtained for a raw slag sample and hydrated slag samples digested in the air and nitrogen atmospheres. In the TG curve of the raw slag, the distinct decreases of the sample mass at around 400°C and 630°C were observed. These are caused by the thermal decompositions of Ca(OH)₂ and CaCO₃, respectively. On the other hand, in the TG curves of the hydrated slags, significant decreases in the mass were observed at around 350°C corresponding to the thermal decomposition of Mg(OH)₂, which had been converted from f-MgO. When the hydration of the slag sample was carried out in air, the mass loss at around 630°C was larger than that for the sample digested in nitrogen atmosphere. This indicates that f-CaO in the slag sample was converted to CaCO₃. Similarly, the smaller mass loss at around 350°C for the sample hydrated in nitrogen than that for the sample digested in air overlaps that of CaCO₃, which means that the formation of MgCO₃ makes it difficult to accurately determine f-MgO by TG. Therefore we carried out the microwave hydration in nitrogen atmosphere. Figure 2 shows that the mass loss of CaCO₃ in the slag sample hydrated in nitrogen is much less than that for the sample digested in air.

3.3. The Optimum Condition of Microwave Heating

The effects of temperature and time of microwave heating on the hydration of f-MgO in steelmaking slag were investigated. Figure 3 shows the dependence of the amount of hydrated MgO in slag C (wt%) on hydration temperature. Hydration time: 80 min. 

Table 3. Operating conditions of XRD.

<table>
<thead>
<tr>
<th></th>
<th>RINT Ultima III</th>
<th>SmartLab</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>Cu Co</td>
<td></td>
</tr>
<tr>
<td>Target power</td>
<td>40 kV/40 mA</td>
<td>40 kV/36 mA</td>
</tr>
<tr>
<td>2θ</td>
<td>10–90°</td>
<td>5–120°</td>
</tr>
<tr>
<td>Scanning speed/° min⁻¹</td>
<td>4.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Slit/mm</td>
<td>0.3</td>
<td>13</td>
</tr>
<tr>
<td>Counting angle/°</td>
<td>0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Fig. 1. XRD pattern of a reagent-grade MgO obtained after hydration by microwave heating. Temperature: 200°C. Heating time: 30 min.

Fig. 2. TG curves for slag A: (a) raw, (b) hydrated in air, and (c) hydrated in N₂. Heating rate: 10°C min⁻¹.

Fig. 3. Dependence of the amount of hydrated MgO in slag C (wt%) on hydration temperature. Hydration time: 80 min. n = 2.

Fig. 4. Dependence of the amount of hydrated MgO in slag C (wt%) on hydration time at 220°C. n = 2.

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temperature and time, respectively.

It should be noted that a reagent-grade MgO was completely converted to Mg(OH)₂ under milder conditions (200°C, 30 min) than the optimal conditions for hydration of f-MgO in a slag sample as shown in Fig. 1. This indicates that f-MgO in steelmaking slag cannot easily be hydrated compared to reagent-grade MgO.

3.4. Thermogravimetry of Steelmaking Slag Samples Treated by Microwave Hydration

Figure 5 represents TG curves of six slag samples before and after the hydration by microwave heating. A steep decrease in mass caused by thermal decomposition of Mg(OH)₂ was observed around 350°C for each of the synthetic slag samples. Although the mass losses at the same temperature were also observed for the actual slag samples, they were relatively small.

![Figure 4](image1.png)

Fig. 4. Dependence of the amount of hydrated MgO in slag C on hydration time. Hydration temperature: 220°C. n = 2.

![Figure 5](image2.png)

Fig. 5. TG curves of thermal decomposition of four synthetic slags and two actual products before and after microwave assisted hydration in N₂. (a) slag A, (b) slag B, (c) slag C₁, (d) slag C, (e) slag S₁, (f) slag S₂. Heating rate: 10°C min⁻¹. The solid and broken lines are the TG curves of the raw and hydrated slag samples, respectively. The arrow represents the mass loss due to the thermal decomposition of Mg(OH)₂.
The scheme of the determination of f-MgO in a slag sample by microwave-assisted-hydration/TG is shown in Fig. 6. As shown in Figs. 5(e) and 5(f), the TG curves for actual steelmaking slags show a continuous decrease in mass in the whole temperature range examined. Therefore the background corrections were made for the quantification of f-MgO in slag samples according to Eq. (3).10)

\[
\text{The content of f-MgO} \% = \frac{M_1 - \frac{m_1 + m_2}{2}(T_e - T_s)}{M_0} \times \frac{40.3}{18.02} \times 100 \quad \ldots (3)
\]

where \( M_1 \) is the mass loss (mg) by the thermal decomposition of Mg(OH)\(_2\), \( M_0 \) is the sample mass (mg), \( T_s \) and \( T_e \) are the temperatures of the start and end of the decomposition of Mg(OH)\(_2\), and \( m_1 \) and \( m_2 \) are the rates of decrease in mass (mg°C\(^{-1}\)) in the temperature ranges of 200°C to 220°C and 500°C to 520°C, respectively. The contents of f-MgO in the steelmaking slag samples determined by the microwave-assisted-hydration/TG method are summarized in Table 4. The low standard deviation values of measurements indicate good precision of the developed method.

Table 4. Quantification results of f-MgO in steelmaking slag samples (\( n = 3 \)).

<table>
<thead>
<tr>
<th>slag</th>
<th>( C_{f-MgO} ) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4.58 ± 0.36</td>
</tr>
<tr>
<td>B</td>
<td>1.03 ± 0.04</td>
</tr>
<tr>
<td>C</td>
<td>1.02 ± 0.05</td>
</tr>
<tr>
<td>S1</td>
<td>0.36 ± 0.04</td>
</tr>
<tr>
<td>S2</td>
<td>0.17 ± 0.03</td>
</tr>
</tbody>
</table>

We validated the accuracy of the microwave-assisted-hydration/TG method for determination of f-MgO in slag samples by investigating the species change of magnesium by microwave hydration using XRD. Figure 7 shows the XRD patterns obtained with Rigaku SmartLab for the raw slag (a), the slag sample hydrated by the microwave method (b), and the slag sample hydrated and then submitted to TG (c). It can clearly be seen that the peaks for MgO diminish by the hydration of the slag sample, while those for Mg(OH)\(_2\) become larger. For the sample submitted to TG after hydration, on the contrary, the peaks for Mg(OH)\(_2\) were not detected, whereas the peak for MgO was as large as that observed for the raw slag sample. This result also reveals that f-MgO in the slag can completely be converted to Mg(OH)\(_2\) by the microwave hydration developed in this study.

Table 5 shows the amounts of Mg and Ca in the filtrate solutions after the microwave hydration treatment of the slag samples together with the pH values of the solutions. The amounts of Mg in the solution dissolved from 1 g of the slag sample are less than 1 \( \mu \)g, which indicates that the dissolution of MgO into water during the hydration process does not affect the determination of f-MgO in slag samples by the present method. On the other hand, the amounts of dissolved Ca in the filtrate solutions are much higher than those of Mg. Assuming that the dissolved Ca in the solutions arises from Ca(OH)\(_2\) in the slag samples, the pH values were

<table>
<thead>
<tr>
<th>slag</th>
<th>Mg (( \mu )g/10 mL H(_2)O)</th>
<th>Ca (mg/10 mL H(_2)O)</th>
<th>pH measured</th>
<th>pH calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.04</td>
<td>4.9</td>
<td>12.4</td>
<td>12.4</td>
</tr>
<tr>
<td>B</td>
<td>0.05</td>
<td>1.7</td>
<td>11.9</td>
<td>11.9</td>
</tr>
<tr>
<td>C</td>
<td>0.27</td>
<td>4.2</td>
<td>12.4</td>
<td>12.3</td>
</tr>
<tr>
<td>S1</td>
<td>0.12</td>
<td>5.5</td>
<td>12.4</td>
<td>12.4</td>
</tr>
<tr>
<td>S2</td>
<td>0.38</td>
<td>2.6</td>
<td>11.5</td>
<td>12.1</td>
</tr>
</tbody>
</table>

Fig. 6. Procedure for determination of f-MgO in a steelmaking slag sample by microwave-assisted-hydration/TG.

Fig. 7. The XRD patterns of a raw slag (a), a slag treated by microwave assisted hydration (b), and a slag sample submitted to TG after microwave assisted hydration (c). Sample: slag A.
calculated from the concentrations of Ca. As shown in Table 5, the calculated pH values agree well with the observed values. This means that the high basicity of the filtrate solutions is attributed to the dissolution of Ca(OH)₂ in the slag samples, resulting in the depression of the dissolution of MgO into water. Since MgO is converted to Mg(OH)₂ by the reaction with water, the dissolution of Mg(OH)₂ will be suppressed in alkaline solutions. However, there is no need to consider the effect of dissolution of Mg(OH)₂ on the determination of f-MgO in slag samples even if the water would not be alkalized, because the solubility of Mg(OH)₂ is negligibly small even in pure water (0.9 mg in 100 g of water²²)). The solubility of MgO calculated from that of Mg(OH)₂ is 0.6 mg in 100 g of water, which agrees with the literature value (0.62 mg in 100 g of water²²)).

4. Conclusions

We developed the microwave-assisted-hydration/TG method for accurate and precise determination of f-MgO in steelmaking slag. This method is based on TG with the microwave assisted hydration of the slag samples. f-MgO in slag samples is converted to Mg(OH)₂ by microwave digestion in water. Subsequently Mg(OH)₂ formed in the slag samples is determined by TG from the mass loss due to the thermal decomposition of Mg(OH)₂. The amounts of f-MgO in synthetic and actual slag samples were successfully determined by the present method and the reproducible quantification results were obtained.

Acknowledgements

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REFERENCES