Contribution of Mineralogical Phases on Alkaline Dissolution Behavior of Steelmaking Slag

Zuoqiao ZHU,1) Xu GAO,2)* Shigeru UEDA2) and Shin-ya KITAMURA2)

1) Department of Metallurgy, Graduate School of Engineering, Tohoku University, 6-6, Aramaki Aza Aoba, Aoba-ku, Sendai, Miyagi, 980-8579 Japan.
2) Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi, 980-8577 Japan.

(Received on January 22, 2019; accepted on April 17, 2019; J-STAGE Advance published date: July 26, 2019)

To suppress alkaline elution from steelmaking slag through microstructure control, in this study, several mineralogical phases identified in industrial steelmaking slag were synthesized, and their dissolution behaviors were investigated. The results indicated that in addition to free CaO and free MgO, 2CaO·SiO2·3CaO·P2O5 (C2S–C3P) is another reason for alkaline elution from steelmaking. To suppress the amount of C2S–C3P in steelmaking slag, reducing the slag basicity by the compositional modification of slag at the hot stage was considered. To determine the optimum composition, the contribution of newly formed primary crystalline phases must be clarified. Some primary crystalline phases in the CaO–SiO2–FeO–MgO–Al2O3 system were synthesized, and their dissolution behaviors were evaluated. The results indicated that the formation of α-CaO·SiO2 (α-CS), β-CaO·SiO2 (β-CS), 3CaO·2SiO2 (C3S2), 2CaO·MgO·2SiO2 (C2MS2), and 3CaO·MgO·2SiO2 (C3MS2) must be restrained in slag modification. Based on the results, a slag with multiple components and low basicity was synthesized, and the suppression of alkaline elution by reduction of slag basicity and microstructure control was confirmed. Moreover, a method to predict Ca dissolution and pH change during the dissolution of slag by the combination of each crystal phase was proposed.

KEY WORDS: steelmaking slag; mineralogical phase; alkaline elution; primary crystal phase; pH.

1. Introduction

During the steelmaking process, the generation of steelmaking slag is inevitable, and large quantities of steelmaking slag have been produced annually. Generally, steelmaking slag is used as a raw material for road construction and civil works. In Japan, approximately 14 million tons of steelmaking slag is generated annually, and more than 60% of it is used for road and civil constructions.1) Because of the high basicity (mass% CaO/mass% SiO2), alkaline elution is the most serious environmental issue when steelmaking slag is used near coastal areas or rivers. Therefore, treatments to suppress alkaline elution becomes necessary before slag utilization.

Among the slag treatment methods, slag aging can suppress the volume expansion of slag;2) however, this treatment cannot prevent alkaline elution as it changes free CaO (MgO) to Ca(OH)2 (Mg(OH)2). Slag carbonation has also been proposed3–5) to change the free CaO that is exposed at the surface of the slag particle into CaCO3. This method can suppress the alkaline elution from the surface of the slag particle, but the industrial operation is still limited. In addition, the hot stage modification of steelmaking slag has been developed to suppress volume expansion.6) In this process, silica sand is added to the molten slag through oxygen injection to lower the basicity. The heat generated by the oxidation reaction of metallic Fe and FeO maintains the slag at the molten state. This process has been industrialized7) and reported to be in operation in some steelmaking shops.8–10) Recently, this process has also been utilized to transfer steelmaking slag to a phosphate fertilizer through modification using sewage sludge ashes.11) Based on the methods introduced above, efforts are still required to develop some effective methods to suppress alkaline elution.

Steelmaking slag contains multiple oxides, and these oxides form various mineralogical phases after the slag is cooled. Among the mineralogical phases in steelmaking slag, free-CaO (f-CaO) and dicalcium silicate (2CaO·SiO2, C2S) are generally known as the water-soluble phases; however, to understand the alkaline elution mechanism, the contribution of all the mineralogical phases should be clarified. Therefore, several mineralogical phases that are typically observed in various industrial steelmaking slags were synthesized in this study, and their dissolution behavior and change in pH were studied. The phases that acted as the primary reason for the alkaline elution from the steelmaking slag were clarified.
Based on the results above, we considered applying the hot stage modification to change the slag composition and subsequently the slag microstructure. In the modified slag, some primary phases, which are different from the phases of steelmaking slag, would generate during solidification, and these phases would determine the alkaline elution behavior of the modified slag. This implies that, to properly modify the slag composition, the newly formed primary crystal phases that may cause alkaline elution should be specified in advance. Therefore, in this study, several primary crystalline phases in the CaO–SiO₂–FeOₓ, CaO–SiO₂–MgO, and CaO–SiO₂–Al₂O₃ systems were synthesized, and their dissolution behaviors and changes in pH were studied. Based on these results, the proper primary phases that were suitable for slag modification were specified. Moreover, to confirm the suppression of alkaline elution by hot stage modification, a slag, which consisted only with the proper primary phases, was synthesized, and its dissolution behavior was studied.

2. Experimental Method

2.1. Synthesis of Mineralogical Phases

In previous studies, the authors have analyzed the mineralogical phases that were identified in the commercial fertilizer made by industrial steelmaking slag. In this study, the same phases observed in the previous research were synthesized in a laboratory using reagents. Reagent-grade CaCO₃, SiO₂, Fe, FeO₂, Ca₃(PO)₄, MnO, MgO, and Al₂O₃ were used to synthesize the slag. The analyzed chemical composition of each phase is shown in Table 1 under the air atmosphere. The sintering temperature was determined as lower than the solidus temperature of each crystal phase according to the phase diagrams. The sintering temperature was slow at low temperatures. Such phases were synthesized by sintering, because the reaction between solid chemicals was slow at low temperatures. These phases were synthesized by heating the glassy phase that was obtained after the melting of reagents. Specifically, to create α-CS, CaO·SiO₂·3CaO·P₂O₅ (C₂S–C₃P), 1 773 K for 2CaO·Fe₂O₃ (C₂F), and 1 573 K for MgO·FeO (MF₂⁺). To synthesize the glassy phases, the mixture of regents was melted for 2 h at 1 723 K followed by water quenching. For the mixture containing FeO, melting was conducted using an Fe crucible and for the mixture containing Fe₂O₃, melting was conducted using an Al₂O₃ crucible.

For the C−S−F and MF phases, because the valence of iron oxide was not analyzed in the previous study, the total Fe content was converted into either FeO or Fe₂O₃. In addition, neither the f-CaO nor free-MgO (f-MgO) was listed among the phases, because the increase in pH by the leaching of f-CaO and f-MgO was studied well, and this study focuses on the effects of the other phases.

After synthesis, the chemical composition of each phase was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the crystalline phase was confirmed by X-ray diffraction (XRD).

In addition to the mineralogical phases identified from the steelmaking slag, some primary crystalline phases were selected from the phase diagrams of the CaO–SiO₂–FeOₓ, CaO–SiO₂–MgO, and CaO–SiO₂–Al₂O₃ systems and synthesized. The above-mentioned oxide systems were considered because they typically exist in steelmaking slag.

Table 2 shows the chemical composition of each primary crystalline phase. Sintering was conducted as the same method as that used to synthesize the mineralogical phases shown in Table 1 under the air atmosphere. The sintering temperature of α-CS, C₃S₂, C₃MS₂, and C₃MS₃ was 1 673 K, that of 2MgO·SiO₂ (M₂S) and CaO·MgO·SiO₂ (CMS) was 1 723 K, and that of CaO·Al₂O₃·2SiO₂ (CAS₂) was 1 773 K. Some phases with a low melting point such as β-CS (melting point of 1 398 K) were difficult to synthesize by sintering, because the reaction between solid chemicals was slow at low temperatures. Such phases were synthesized by the heat treatment of the glassy phase that was obtained after the melting of reagents. Specifically, to create β-CS, 2CaO·0.5MgO·0.5Al₂O₃·1.5SiO₂ (C₂M₀.5A₀.5S₁.₃),

Table 1. Chemical composition of each mineralogical phase identified from industrial steelmaking slag (mass%).

<table>
<thead>
<tr>
<th>Glassy phase</th>
<th>CaO</th>
<th>SiO₂</th>
<th>MgO</th>
<th>FeO</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>C−S−F⁺⁺</td>
<td>28.8</td>
<td>29.3</td>
<td>4.0</td>
<td>3.6</td>
<td>7.0</td>
</tr>
<tr>
<td>C−S−F⁺⁺</td>
<td>28.3</td>
<td>28.5</td>
<td>7.5</td>
<td>3.5</td>
<td>6.8</td>
</tr>
<tr>
<td>C−S−A</td>
<td>39.2</td>
<td>36.0</td>
<td>6.2</td>
<td>0.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

C: CaO; S: SiO₂; P: P₂O₅; F: FeO₂; M: MgO; A: Al₂O₃; F⁺⁺/F⁺⁺ means the phase uses FeO₂/FeO as iron oxide

Table 2. Chemical composition of each primary crystalline phase selected from phase diagrams (mass%).

<table>
<thead>
<tr>
<th>Phase</th>
<th>CaO</th>
<th>SiO₂</th>
<th>MgO</th>
<th>FeO</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-CS</td>
<td>48.3</td>
<td>51.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>β-CS</td>
<td>48.3</td>
<td>51.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₃S₂</td>
<td>58.3</td>
<td>41.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₃M₂S₁</td>
<td>29.8</td>
<td>31.9</td>
<td>38.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M₂S</td>
<td>-</td>
<td>42.9</td>
<td>57.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CMS</td>
<td>35.9</td>
<td>38.5</td>
<td>25.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₃M₂S₂</td>
<td>41.2</td>
<td>44.1</td>
<td>14.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₃M₂S₃</td>
<td>51.2</td>
<td>36.6</td>
<td>12.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CAS₂</td>
<td>25.9</td>
<td>55.6</td>
<td>18.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₂M₀.5A₀.5S₁.₃</td>
<td>20.1</td>
<td>43.2</td>
<td>-</td>
<td>36.7</td>
<td>-</td>
</tr>
</tbody>
</table>
and CaO-SiO$_2$-FeO (CSF$^{2+}$), their mixtures were melted for 1 h at 1 833 K, 1 873 K, and 1 573 K, respectively, followed by water quenching. Subsequently, the glassy phase was annealed for 48 h. The annealing was conducted in air for $\beta$-CS and C$_2$M$_{0.5}$A$_{0.5}$S$_{1.5}$ (Melilite) at 1 273 K and 1 523 K, respectively. The annealing of CSF$^{2+}$ was conducted at 1 423 K in Ar. After synthesis, all the synthesized primary phases were analyzed by ICP-AES and XRD.

### 2.2. Synthesis of Slag

To prepare the slag with low basicity (mass% CaO/mass% SiO$_2$:0.98), the reagents and synthetic CaO and FeO were mixed with a target ratio. The mixture was melted using a Pt crucible at 1 723 K for 2 h in air and after melting, the molten slag was slowly cooled in a furnace. The chemical composition of the synthetic slag was confirmed by ICP-AES and shown in Table 3. The mineralogical phases of the synthetic slag were observed by XRD and an electron probe micro analyzer (EPMA).

### 2.3. Leaching Test

The experimental apparatus of this leaching test is shown in Fig. 1, which is similar to previous studies.$^{16,17}$ Before performing the leaching test, 400 ml of deionized water was poured into a polyethylene container that was set in a thermostatic bath of 298 K. Subsequently, pH and ORP probes were immersed in the deionized water and the stirring of water was started (200 rpm). Before measuring the pH, the probe was corrected by a standard buffer solution of pH 4.01, 6.86, and 9.18 at 298 K.

After the temperature of the deionized water reached 298 K and the pH stabilized at approximately 6, 1 g of synthesized phase or slag was added into the deionized water. Before the leaching test, each phase and slag were ground into powder (< 53 µm). This time was set as the start of the experiment, and the change in both the pH and ORP of the leachate was recorded. In addition, 5 ml of the leachate was sampled using syringes at regular time intervals. After the solution pH reaches a maximum value, the leaching test and leachate sampling was continued for another 30 min. After the leaching test, the leachate and residue were separated by filtration with a vacuum suction system. The sampled solution was analyzed by ICP-AES, and the residue was analyzed by XRD. As a standard material to evaluate the degree of alkali dissolution of each mineralogical phase and slag, the maximum pH of CaCO$_3$ was measured using the same leaching test. Its measurement was stopped for 3 min when the pH reduced from the maximum.

### 3. Results

#### 3.1. XRD Observations for Synthesized Mineralogical Phases

The XRD results of the synthesized crystal phases and glassy phases, which were identified from the steelmaking slag, are shown in Figs. 2 and 3, respectively. As the objective peaks of the target crystalline phases and the broad peaks of the glassy phases were observed, these phases were considered to be synthesized successfully.

The XRD results of the selected primary crystalline phases from the CaO–SiO$_2$–FeO$_x$, CaO–SiO$_2$–Al$_2$O$_3$–5%MgO, and CaO–SiO$_2$–MgO systems are shown in Figs. 4 and 5. All the objective peaks for the synthesized were confirmed.

#### 3.2. Dissolution of Alkali and Change in pH by Synthetic Phases Identified in Steelmaking Slag

Because Ca and Mg are the major alkali elements existing in slag, this study focuses primarily on the dissolution behaviors of these two elements. The dissolved content of

### Table 3. Chemical composition of synthetic slag (mass%).

<table>
<thead>
<tr>
<th>CaO</th>
<th>SiO$_2$</th>
<th>MgO</th>
<th>P$_2$O$_5$</th>
<th>MnO</th>
<th>FeO</th>
<th>Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.8</td>
<td>29.3</td>
<td>4.0</td>
<td>3.6</td>
<td>7.0</td>
<td>24.8</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Ca and Mg in water as a function of time from the phases identified in steelmaking are shown in Figs. 6 and 7, respectively. In Fig. 6, the dissolved content of Ca from C$_2$S–C$_3$P and C$_2$AS were higher than that from CaCO$_3$, but the other phases indicated lower contents. In Fig. 7, the dissolved content of Mg from the synthesized phases indicated close to 1 mg/L at 20 min, except for MF$^{3+}$ whose results reached 2.5 mg/L at 30 min. Comparing the dissolved content of Ca and Mg, the dissolved content of Mg was much lower than that of Ca. Therefore, Ca was considered as the major alkaline element in the following discussions.

Figure 8 shows the change in pH during the dissolution of each synthetic phase identified in steelmaking slag. When the solid phase was placed into water, each phase indicated a sudden increase in pH and reached the maximum pH in 30 min. Comparing the dissolution behaviors of Ca and Mg, the dissolutions of both Ca and Mg continued although the pH reached a maximum value, and the phases with a large Ca dissolution indicated high values of the maximum pH. After reaching the maximum pH value, the pH value of some phases started to decrease slowly. This was caused by
the gradual dissolution of $O_2$ and $CO_2$ from air. However, the decrement in pH for $MF_2^{2+}$ was larger. From this phase, $Fe^{2+}$ was dissolved, and the oxidation of $Fe^{2+}$ in solution would decrease the pH according to Eq. (1). In addition, although the dissolved Ca content of $C_2AS$ was close to that of $C_2S$--$C_3P$ as shown in Fig. 8, the increment in pH by dissolving $C_2AS$ was not as high as that of $C_2S$--$C_3P$. During the dissolution of $C_2AS$, $Al$ was also dissolved, and the dissolution of $Al$ would decrease the pH according to Eq. (2).

\[
Fe^{2+} + 2H_2O = FeOOH + 3H^+ + e \quad \text{..............(1)}
\]

\[
(Al_2O_3)_{C_{2AS}} + H_2O = 2AlO_2^- + 2H^+ \quad \text{..............(2)}
\]

Figure 9 shows a comparison of the maximum pH measured for each phase of the steelmaking slag to that of CaCO$_3$. In this comparison, because CaCO$_3$ is a major component in natural stone, the phase that indicates a lower value than that of CaCO$_3$ can be recognized as this phase does not affect the increase in pH. From the result, $C_2S$--$C_3P$ indicated a much higher max pH value than CaCO$_3$, and the values of $C_2AS$ and $MF_2^{3+}$ were almost the same as that of CaCO$_3$. On the contrary, glassy phases, and $MF_2^{2+}$ were lower than that of CaCO$_3$. The max pH of $C_2F$ was slightly lower than CaCO$_3$, though the Ca concentration after leaching of $C_2F$ was about $1/3$ of CaCO$_3$. This is because the value of pH is the logarithm of $OH^-$ activity, and the $OH^-$ concentration is determined by charge balance to cations such as $Ca^{2+}$.

Based on the results above, to suppress the pH increase in an aqueous environment by steelmaking slag, in addition to $f$-CaO and $f$-MgO, the amount of $C_2S$--$C_3P$ in the steelmaking slag should be restrained. In addition, the other mineralogical phases were less responsible for the alkaline elution. $C_2S$--$C_3P$ is a major mineralogical phase in steelmaking slag that exhibits a large volume ratio in slag; therefore, the removal of $C_2S$--$C_3P$ from slag is difficult.

### 3.3. Dissolution Behavior of Ca and Mg from Synthetic Primary Phases

The contents of Ca and Mg dissolved from the synthesized primary crystalline phases that were selected from the phase diagrams are shown in Figs. 10 and 11, respectively. As shown in Fig. 10, the dissolutions of $\alpha$-$CS$, $\beta$-$CS$, $C_3S2$, $C_2MS2$, and $C_3MS2$ indicated high contents of Ca, and the other phases indicated low values. The dissolved contents of Ca from $C_3S2$ and $C_3MS2$ were close to those of $C_2S$--$C_3P$ and $C_2AS$. Regarding the content of dissolved Mg as shown in Fig. 11, $C_3MS2$, CMS, and $C_2MS2$ indicated an obvious dissolution of Mg. Similar to the results of the phases in the steelmaking slag, the dissolved Ca was larger than that of Mg for primary phases; therefore, the removal of $C_2S$--$C_3P$ from slag is difficult.

Figure 12 shows the comparison on the maximum pH between the synthesized primary crystalline phases and CaCO$_3$. From this comparison, $\alpha$-$CS$, $\beta$-$CS$, $C_3S2$, $C_2MS2$, and $C_3MS2$ indicated higher values of maximum pH than that of CaCO$_3$, while the pH value of CMS was almost the same to that of CaCO$_3$. On the contrary, the maximum pH values of Melilite, CMS2, $CSF_2^{2+}$, $CAS2$, and $MS$ were lower than that of CaCO$_3$. Therefore, to suppress the alkaline elution, in addition to $f$-CaO and $C_2S$--$C_3P$, the formations of $\alpha$-$CS$, $\beta$-$CS$, $C_3S2$, $C_2MS2$, and $C_3MS2$ should be controlled in a modified steelmaking slag as well.

Fig. 8. Change in pH during the dissolution of the synthetic mineralogical phases in steelmaking slag.

Fig. 9. Comparison of maximum pH between mineralogical phases and CaCO$_3$. 

Fig. 10. Max pH of CaCO$_3$(pH=9.98)
3.4. Dissolution Behavior of Synthetic Slag

The analysis results by XRD and EPMA are shown in Figs. 13 and 14, respectively. The XRD results revealed that the slag was composed primarily of CAS₂, CSF₂, and iron oxide. The observation by EPMA, the same mineralogical phases were confirmed. In addition, neither XRD nor EPMA confirmed the existence of C₂S–C₃P.

The dissolution behaviors of Ca and Mg from the synthetic slag, and the change in pH during dissolution are shown in Fig. 15. The Ca content increased rapidly to approximately 2.6 mg/L at 0.5 min and increased gradually to approximately 2.7 mg/L at 5 min. The Mg content increased to approximately 0.14 mg/L after 0.5 min, and remained at the same level. The pH increased rapidly to 9.1 after the addition of the slag for 0.5 min, and increased slightly to a maximum value of approximately 9.7 after 1.5 min. The maximum pH was lower than that of CaCO₃. Comparing to the leaching of CSF²⁺ and CAS₂, the maximum pH after leaching of synthetic slag was higher. This was probably because that the grain size of both phases in synthetic slag was smaller than the particle size used to measure the individual phase. Thus, the dissolution rate of both phases in slag would be large and the Ca concentration in leachate increased. In addition, because the Ca content
was much larger than that of Mg, the increase in pH was caused by the dissolution of Ca. Therefore, through a hot stage modification to decrease the basicity followed by slow cooling, the dissolution of Ca and the pH increase would be suppressed as the formation of C2S–C3P could be restrained.

The calculated lines of Ca content and pH are shown in Fig. 15, and the details are described in Discussions.

4. Discussions

4.1. Relation between Maximum pH Values and Ca Content in Leachate

When a mineralogical phase dissolves into aqueous solution, the charge balance between cations and anions in solution must be balanced to maintain electric neutrality, as expressed by Eq. (3). In this study, only OH⁻ was considered as the anion, because the content of other anions such as CO₃²⁻ could be low when the maximum pH was reached in a short leaching time. In Eq. (3), X is the molar ratio of cation A⁺ in the leachate (mol/L); X₉H⁺ is the molar ratio of OH⁻ in the leachate (mol/L). Because pH is defined as -logΧH⁺, and the sum of logΧH⁺ and logΧOH⁻ is -14 at 298 K, Χ₉H⁺ can be written as 10⁻¹⁴. Because Ca in an aqueous solution could exist as either CaOH⁺ or Ca²⁺ or both, the relation between Ca content in solution and pH can be correlated by a parameter α, as shown in Eq. (4), where α is the total charge number of CaOH⁺ and Ca²⁺ that ranges from 1 to 2.

Subsequently, Eq. (4) is rewritten as a linear relation between pH and log(Χ₉Ca), as shown in Eq. (5). According to this equation, the relation between pH and log(Χ₉Ca) is linear with the slope as unity, and the value of α is obtained by the pH value at log(Χ₉Ca) = 0.

The relation between the measured maximum pH and Ca content is shown in Fig. 16, together with the fitting result as a linear relation. The slope of the line was close to unity and the pH at log(Χ₉Ca) = 0 was 13.8. Thus, the α was estimated as 1.58 by Eq. (5), which was considered as a reasonable value as it was within the range between 1 and 2. Previously, the relation between Ca content and pH was investigated by S. Tauchi et al. and Eq. (6) was proposed, where M₉Ca indicates the atomic weight of Ca. Compared with Eq. (5), this equation can be written as Eq. (7).

In this figure, the relation by Eq. (7) is plotted. Although the difference is small, the value of α by Eq. (7) is 0.75 and this value is not in the theoretical value range of α. Further, in Fig. 16, the experimental results deviated from the linear line when its maximum pH was smaller than 9. This could occur because as phases such as CAS₂ released...
only a small amount of Ca due to their low NBO/Si (NBO: Non-Bridging Oxygen) degree mentioned in previous studies, the influences of O2 and CO2 gas from air could demonstrate stronger effects on the pH, and the pH values would be underestimated.

4.2. Methods for Estimating the Dissolution Behavior of Slag

Because steelmaking slag was composed of various mineralogical phases, the dissolution behavior of slag implied the competitive dissolution among phases. If the dissolution behavior of a slag can be predicted using the dissolution of each phase, the proper slag composition to suppress alkaline elution can be designed by controlling the combination of phases.

Hence, the dissolution rate of each phase was evaluated first. For the leaching solid particles in an aqueous solution, many studies reported that the diffusion through an intermediate product layer or porous layer at the surface controls the dissolution rate. In this study, the formation of a surface layer on the particle of synthetic slag was considered, and the formation of a surface layer after the detachment of Ca can be considered. Thus, in this study, we assumed the formation of a surface layer on the particle of synthetic phase, and the diffusion through this layer controlled the leaching rate. In this case, the dissolution rate of Ca from each synthetic phase is defined as Eq. (8). Here, $A$ is the interfacial area between the solid particle and leachate ($m^2$), and it depends on the crystal because the behaviors of crack formation, disintegration, and agglomeration are different in each crystal; $V$ is the volume of the leachate ($m^3$); $D$ is the diffusion coefficient in the surface layer ($m^2s^{-1}$); $C_{Ca}^0$ is the concentration of Ca in the solid phase; and $t$ is the leaching time ($min$).

$$\frac{dC_{Ca}}{dt} = \frac{A}{V} D \left( \frac{C_{Ca}^0 - C_{Ca}^*}{x} \right) \quad (8)$$

$$x = \frac{D \left( C_{Ca}^0 - C_{Ca}^* \right)}{\rho t^*} \quad (9)$$

Substituting Eq. (9) in Eqs. (8), (10) is obtained after a time integration from 0.5 min to $t^*$ (min). Here, $C_{Ca}^{0.5}$ and $C_{Ca}^*$ indicate the concentrations of Ca at the interface between the layer and leachate at 0.5 min and $t^*$, respectively. In this calculation, as the concentration of Ca in the leachate was measured after 0.5 min, the initial time of integration was set as 0.5 min.

$$\sqrt{C_{Ca}^0 - C_{Ca}^{0.5}} - \sqrt{C_{Ca}^0 - C_{Ca}^*} = \frac{A}{V} \sqrt{D\rho \left( t^* - \sqrt{0.5} \right)} \quad (10)$$

Summarizing the quotes before $\sqrt{t^* - \sqrt{0.5}}$ in Eq. (10), the apparent rate constant $k'$ of leaching was defined as Eq. (10). Because $A$ and $\rho$ depend on the synthetic phase, the value of $k'$ is different in each crystal. The relation of Eq. (10) for CAS2 and CSF2+ observed in the synthetic slag are shown in Fig. 17. In this case, the time when the maximum pH was recorded was used as $t^*$, and the $k'$ for each synthetic phase was determined through a linear regression. In the regression, the equilibrium content of Ca when leaching a synthetic phase in an aqueous solution was used for $C_{Ca}^0$. The values have been calculated by pHREEQC using the Lnl database to be 3.3 mg/L for CAS2 and 4.5 mg/l for CSF2+. The values of $k'$ regression was 0.013 and 0.107 for CAS2 and CSF2+, respectively.

The calculated Ca content from each phase was added together to estimate the Ca content from the synthetic slag, and the pH was estimated by Eq. (5) using 1.58 as the value of $\alpha$. To calculate the Ca content, the mass of each phase in 1 g of the synthetic slag, calculated by mass balance, was considered.

The calculated Ca content and pH are shown in Fig. 15. As aforementioned, because calculation of Ca content from the synthetic slag does not consider the actual interfacial area of each phase, the calculated values of both Ca content and pH would be lower than the observed values.

5. Conclusions

To understand the alkaline elution mechanism of steelmaking slag, several mineralogical phases that have been identified in industrial steelmaking slag were synthesized, and their alkaline elution behaviors were investigated. In addition, to obtain the proper mineralogical structure after a hot stage slag modification, some primary crystal phases from the CaO–SiO2–FeO–Al2O3–MgO system were synthesized and their dissolution behaviors were investigated.
The conclusions are drawn as follows:

(1) Under current experimental conditions, for the mineralogical phases identified in steelmaking slag, the solid solution of C$_2$S–C$_3$P indicates a higher maximum pH than CaCO$_3$ (a primary component from natural stone). Other crystal phases of C$_3$F, C$_2$AS, MF, and the glassy phases of the C–S–A and C–S–F systems indicated lower maximum pH values than that of CaCO$_3$. Therefore, in addition to free CaO and free MgO, the amount of C$_2$S–C$_3$P in steelmaking slag should also be restrained, to suppress the alkaline elution.

(2) By the leaching test of the primary crystal phases of the CaO–SiO$_2$–FeO$_x$–Al$_2$O$_3$–MgO system, α-CS, β-CS, C$_3$S$_2$, C$_2$S$_2$M$_2$, and C$_3$S$_2$M$_2$ indicated higher values of maximum pH than CaCO$_3$; CMS indicated the similar maximum pH values than that of CaCO$_3$. Therefore, in addition to free CaO and free MgO, the amount of C$_2$S–C$_3$P in steelmaking slag should also be restrained, to suppress the alkaline elution from a modified slag, the amounts of CaO and free MgO, the amount of C$_2$S–C$_3$P in steelmaking slag should also be restrained, to suppress the alkaline elution.

(3) A slag with low basicity was synthesized and a leaching test was conducted. The results revealed that the major mineralogical phases were CAS$_2$ and CSF$_2$+, while C$_2$S–C$_3$P and other soluble primary crystal phases were not formed. The dissolved Ca was small, and the maximum pH was lower than that of CaCO$_3$.

(4) Based on the leaching results of each mineralogical phase, the relation between Ca content in the leachate and pH was determined. Moreover, by combining the dissolution of the synthetic phases, a method to predict the increase in Ca content and pH of leachate during the dissolution of a synthetic slag was proposed.

Acknowledgments

The authors appreciate the financial support by the Iron & Steel Institute of Japan (ISIJ) from the research group on “The control of solidification structure of steelmaking slag for suppressing alkaline elution”, and from the 27th ISIJ Research Promotion Grant.

REFERENCES