The Conditions of Ettringite Formation by the Reaction of a Blast Furnace Slag with Aqueous Alkaline Solutions

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(Received on June 5, 2016; accepted on June 24, 2016; originally published in Tetsu-to-Hagané, Vol. 101, 2015, No. 11, pp. 566–573; J-STAGE Advance published date: August 25, 2016)

Blast furnace (BF) slags have been utilized in cement, concrete aggregate, roadbed materials, and earthwork materials. If an appropriate control of the elution and compound formation is developed under severer environmental conditions, their usage would be more diverse. Because the chemical composition of BF slag is similar to that of Portland cement, the possibility of ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O) formation from BF slag following a mechanism similar to that of cement hydration might be possible under a wet alkaline environment. Therefore, the effect of an alkaline solution on ettringite formation from BF slags was investigated by slag-leaching experiments and thermodynamic calculations using PHREEQC. The formation of ettringite was observed only for the high pH solutions in the experiments, whereas its thermochemical possibility from the air-cooled BF slags was always expected by the calculation. The kinetic analysis showed that the dissolution of alumina from the slag may control the whole reaction rate. The mixing of granulated BF slag with air-cooled ones tended to enhance the ettringite formation. Furthermore, a technique for removing the ettringite formed in the slag was also developed.

KEY WORDS: blast furnace slag; ettringite formation; alkaline solution; slag-leaching; thermodynamic calculation; PHREEQC; reaction kinetics.

1. Introduction

Iron and steelmaking slags, produced as by-products in the steel industry, are expected to be utilized more as recycling materials which can save resources and energy. In 2013, the production of steelmaking slags in Japan was about 39 million tons, and that of blast furnace slags was about 25 million tons. Almost 100% of the blast furnace slags are utilized in cement, roads, concrete aggregates, engineering works, and soil stabilization in Japan. For enhancing the added value of blast furnace slags and its utilization in a wide variety of ways, the development of technologies for adequately controlling the elution of components and formation of compounds from slags is an important research subject. With respect to the elution of components and formation of compounds from blast furnace slags, many studies have been performed since the latter half of the 1970s, mainly on the elution of sulfur and formation of sulfur compounds, and significant knowledge has been obtained on the generation of yellow water, vitriolization, behavior of sulfur, and morphological properties.

One of the important problems in the formation of compounds is related to ettringite. Ettringite is a needle-like crystal that is represented as 3CaO·Al₂O₃·3CaSO₄·32H₂O. It is known that ettringite is formed from the aluminate phase (3CaO·Al₂O₃) and gypsum (CaSO₄·2H₂O) during the early stage of cement hydration. One reason for the concrete deterioration, there is a phenomenon called “delayed ettringite formation (DEF),” which causes expansion and destruction of concrete. This happens when ettringite is formed extensively inside concrete, and the hardened body expands to cause destruction several years or several decades after steam curing of concrete. This expansion is caused by a volume increase that occurs when ettringite is formed. The chemical composition of blast furnace slag is similar to that of cement, so that ettringite can be formed from blast furnace slags when ettringite is set under a situation similar to the early stage of cement hydration. Therefore, for utilization of blast furnace slags in a wide variety of ways, it is necessary to consider the possibility of ettringite formation under an alkaline environment, similar to cement mixing.

We investigated the effect of the pH of environmental water that is in contact with blast furnace slags on ettringite formation by a slag-leaching experiment, and considered the mechanism of ettringite formation based on thermodynamic calculations using the geochemical code PHREEQC. Furthermore, we considered a convenient way to decompose the ettringite that is formed in slags.

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DOI: http://dx.doi.org/10.2355/isijinternational.ISIJINT-2016-347
2. Experimental

2.1. Slag-leaching Experiment

In general, the test method used for determining the amount of chemical materials eluted from slags is JISK0058-1, where fixed amounts of crashed samples below 2 mm diameter are mixed with 10 times water and the mixture is shaken in 200 times per minute for 6 hours to dissolve the materials. The purpose of this study was to investigate the formation of compounds from the slags in contact with the surrounding environmental water, so that the ratio of slag and solution was set as high as possible. The slags were prepared for below 2 mm diameter following the JIS method and 100 g of slag and 100 ml of aqueous solution, or 30 g of slag and 30 ml of aqueous solution were mixed and kept in the sealed glass containers. To prevent destruction of the formed ettringite crystals, they were not shaken or stirred, and were left at rest at 25°C for a maximum of 4 weeks. After the experiments, the samples were separated into solution and slag by filtration under reduced pressure with 0.45 μm pore size membrane filters. The slags obtained after filtration were dried carefully at 25°C to prevent decomposition of ettringite. The slags used for the experiments were two kinds of air-cooled slags A and B (after aging), and granulated slag G. The chemical compositions of the slags are shown in Table 1.

With respect to the filtered leaching solution, the concentration of Ca and total S (T.S) was analyzed using inductively coupled plasma-mass spectrometry (ICP-MS, 7700x, Agilent Technologies) after the pH was measured. Furthermore, with respect to the experimental samples using 100 ml of the solution, the concentration of Al was analyzed by ICP-MS using an internal standard method by adding yttrium, and analysis of SO₄²⁻ and S₂O₃²⁻ (thiosulfate ion) was conducted by ion chromatography (ICS-2100, Thermo Scientific).

The slags after drying were milled using a wet method with 2-propanol (Kanto Kagaku, special grade) and characterized using X-ray diffraction (XRD, Mini-flex II, Rigaku). The measurement was performed over a scan field of 7–12 deg. at a speed of 1 deg./min, CuKα target, 15 mA tube voltage, and the presence of an ettringite peak (2θ = 9.1 deg.) of crystal orientation (100) was confirmed. Since the ettringite crystal was oriented, the samples were not pressed together, the surface was flattened carefully, and the measurement was performed using a rotary sample stand. With respect to slags in which a peak of ettringite was observed, the amount of formed ettringite was calculated with a calibration curve prepared in advance. A standard addition method was used to prepare the calibration curve (addition rates of ettringite were 0, 2.5, and 5.0 mass%), and good linearity was obtained for all the slags.

2.2. Decomposition of Ettringite in Slags

For using slags safely and stably, not only clarifying the condition of ettringite formation in slags, but also the method for decomposing ettringite in slags is required. Since it is known that ettringite is decomposed when it is heated at high temperature in air, how much ettringite could be decomposed and removed by heating at high temperature was investigated.

Air-cooled slag C, in which about 3 mass% of ettringite was formed, was prepared in advance with a particle diameter of less than 2 mm. The chemical composition of slag C is shown in Table 1.

Experiments were performed assuming that slag treatment was carried out in either air or water. For the experiments under air atmosphere, 1.0 g of slag was placed in a drying furnace at 40–90°C for 2 h, and XRD measurements were performed. The degree of decomposition of ettringite was calculated using Eq. (1), where I₀ is the peak strength of ettringite before treatment and I is that after treatment.

In the case of experiments in water, 1.0 g of slag and 100 ml of pure water were mixed and kept at 40–90°C for 2 h. XRD measurement was performed on the slags after filtration, and the decomposition degree of ettringite was calculated using Eq. (1).

\[
\text{Decomposition degree} = \left(1 - \frac{I}{I_0}\right) \times 100 \quad \text{...... (1)}
\]

3. Thermodynamic Calculation

The possibility of ettringite formation from slag components dissolved in the leaching solutions was calculated using PHREEQC. PHREEQC is a geochemical code that was developed by the United States Geological Survey (USGS), and is available to the general public. It enables various chemical equilibrium calculations in solutions at a relatively low temperature. In this study, the saturation index (SI) of ettringite was calculated using the pH and concentration of Ca, Al, SO₄²⁻, and S₂O₃²⁻ in the solutions, obtained from the experiments. Lnt.dat, which contains a broad variety of material data for minerals like ettringite, was used as the database. However, since the thermodynamic data of ettringite in this database deviated from many reported equilibrium experiments, calculations in this study were performed specially with the solubility product data calculated by Perkins and Palmer. With respect to monosulfate hydrate (3CaO·CaSO₄·12H₂O), the value reported by Damidot and Glasser was used.

The dissolution-formation reaction of ettringite is given by Eq. (2).

\[
3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} = 6\text{Ca}^{2+} + 2\text{Al(OH)}_4^- + 3\text{SO}_4^{2-} + 4\text{OH}^- + 26\text{H}_2\text{O} \quad \text{...... (2)}
\]

Here, the ion activity product (IAP) of ettringite is defined as Eq. (3), and the value of the solubility product \( K_{sp} \) is given by Eq. (4). \( [X] \) in Eq. (3) represents the activity of component X.

Table 1. Chemical composition of the BF slags used for the experiment (mass%).

<table>
<thead>
<tr>
<th>Slag</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>MnO</th>
<th>T.Fe</th>
<th>T.S</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>41.9</td>
<td>34.2</td>
<td>15.4</td>
<td>5.67</td>
<td>0.43</td>
<td>0.33</td>
<td>0.51</td>
</tr>
<tr>
<td>B</td>
<td>41.8</td>
<td>34.8</td>
<td>14.3</td>
<td>5.7</td>
<td>0.37</td>
<td>0.32</td>
<td>0.64</td>
</tr>
<tr>
<td>C</td>
<td>41.6</td>
<td>34.1</td>
<td>14.4</td>
<td>5.81</td>
<td>0.32</td>
<td>0.33</td>
<td>0.86</td>
</tr>
<tr>
<td>G</td>
<td>42.6</td>
<td>34.5</td>
<td>14.6</td>
<td>6.36</td>
<td>0.21</td>
<td>0.2</td>
<td>0.86</td>
</tr>
</tbody>
</table>
IAP = \left[ Ca^{2+} \right]^6 \left[ Al(OH)_{3}^{-} \right]^2 \left[ SO_4^{2-} \right]^3 \left[ OH^{-} \right]^4 \left[ H_2O \right]^{26} 
........................................ (3)

\log K_{sp} = -\frac{10.689}{T} - 8.867 ............... (4) \quad (14)

Here, the SI is given by Eq. (5) using IAP and \( K_{sp} \). SI > 0 means precipitation, SI = 0 means equilibrium, and SI < 0 means dissolution.

SI = log \left( \frac{IAP}{K_{sp}} \right) ........................................ (5)

4. Results and Discussion

4.1. Slag-leaching Experiment in Pure Water

As a preliminary experiment, the dissolution behavior of slag components in pure water with leaching time was investigated. 100 g of slag A and B were extracted and leached in 100 ml of pure water at 25°C for a certain time. The results of the measurement of the Ca concentration and T.S in the solutions are shown in Fig. 1. Since both the Ca and S elute promptly 1 day after the start of leaching, and concentration does not change significantly, it was deemed that the dissolution concentration can be assessed well after 7 days of leaching. Hence, a leaching time of 7 days was set as the standard.

The measurement results of the pH and each concentration of the solution in which 100 g of slag A, B, G, A+G (weight ratio of 1:1), and B+G (weight ratio of 1:1) are leached, are shown in Table 2. At the right side in Table 2, the values of the SI of ettringite, monosulfate hydrate, CaSO₄·2H₂O (gypsum), and calcium hydrate Ca(OH)₂ (portlandite), which are calculated with PHREEQC using the compositions of the leaching solutions, are shown.

The pH of all the solutions increase after leaching, and mainly compounds of Ca and S are eluted. By comparing the T.S content, and the concentration of SO₄²⁻ and S₂O₃²⁻, it can be seen that about 90% of S eluting from the air-cooled slags exists as SO₄²⁻ or S₂O₃²⁻. The concentration of S₂O₃²⁻ and Ca from the air-cooled slag A is higher than slag B. It is estimated that S₂O₃²⁻ exists as a form of calcium thiosulfate (CaS₂O₃) in the slags. Since it is believed that the solubility product of calcium thiosulfate in water is large (16), although the approximate value has not been reported, it can be considered that the calcium thiosulfate in contact with water is dissolved completely. In both the experiments using slag A and slag B, the SI of ettringite is positive, and it is thermodynamically possible for ettringite to be formed. However, in XRD measurements, a peak of ettringite was not observed in all the experiments, and only a peak for CaSO₄·2H₂O was observed in the XRD measurements. In this experiment, since leaching is done in the completely closed condition, it can be assumed that the concentration of Ca in the solutions increases with the dissolution of calcium thiosulfate, so that the SI of slag A, in which the concentration of S₂O₃²⁻ is high, is larger than slag B. The SI of CaSO₄·2H₂O is almost 0, and it can also be confirmed by thermodynamic calculation that CaSO₄·2H₂O is saturated. The SI of both monosulfate hydrate and Ca(OH)₂ are negative, so that it can be considered that these chemical compounds do not precipitate.

Compared to the air-cooled slag A and B, in the case of granulated slag G, the concentration of T.S, SO₄²⁻, and S₂O₃²⁻ is low, and the pH and concentration of Al is high. By thermodynamic calculation, the SI of all the target chemical compounds is negative, and it is estimated that the precipitation of all of the chemical compounds cannot occur, and hence, peaks for all of them were not observed by XRD.

Compared to the case of air-cooled slag alone, in the case of slag A+G and B+G, where the slags are mixed, the pH and concentration of Al is high, and trends of air-cooled slag and granulated slags are seen at the same time. As a result, the SI of ettringite is higher than that of the air-cooled slag, and it is estimated that CaSO₄·2H₂O is saturated. However, an ettringite peak is not observed in XRD and only a peak of CaSO₄·2H₂O is observed.

![Fig. 1. Variation of Ca and total S concentrations in the leaching solution with time.](image-url)

**Table 2.** The concentration of dissolved components in the solution and pH after one week’s leaching in a pure water and the calculated saturation indexes.

<table>
<thead>
<tr>
<th>Slag</th>
<th>pH after leaching</th>
<th>Ca (ppm)</th>
<th>Al (ppm)</th>
<th>Total S (ppm)</th>
<th>SO₄²⁻ (ppm)</th>
<th>S₂O₃²⁻ (ppm)</th>
<th>SI of ettringite</th>
<th>SI of monosulfate</th>
<th>SI of gypsum</th>
<th>SI of portlandite</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>11.13</td>
<td>961</td>
<td>0.46</td>
<td>1 585</td>
<td>1 566</td>
<td>1 675</td>
<td>2.92</td>
<td>−2.57</td>
<td>0.08</td>
<td>−2.38</td>
</tr>
<tr>
<td>B</td>
<td>10.92</td>
<td>747</td>
<td>0.45</td>
<td>1 008</td>
<td>1 540</td>
<td>654</td>
<td>1.66</td>
<td>−3.74</td>
<td>0.03</td>
<td>−2.89</td>
</tr>
<tr>
<td>G</td>
<td>11.27</td>
<td>671</td>
<td>3.33</td>
<td>132</td>
<td>557</td>
<td>21.1</td>
<td>−3.11</td>
<td>−4.74</td>
<td>−1.86</td>
<td>−2.98</td>
</tr>
<tr>
<td>A+G</td>
<td>11.44</td>
<td>821</td>
<td>0.54</td>
<td>1 017</td>
<td>1 519</td>
<td>847</td>
<td>4.03</td>
<td>−1.40</td>
<td>0.04</td>
<td>−1.82</td>
</tr>
<tr>
<td>B+G</td>
<td>11.22</td>
<td>685</td>
<td>0.75</td>
<td>743</td>
<td>1 516</td>
<td>292</td>
<td>3.14</td>
<td>−2.22</td>
<td>0.01</td>
<td>−2.33</td>
</tr>
</tbody>
</table>

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4.2. Slag-leaching Experiment in Alkaline Solutions

4.2.1. Ettringite Formation from Air-cooled Slags

The measurement results of pH and the concentration of each compound in the solutions after leaching 100 g of slag A and slag B for 7 days in 100 ml NaOH solution is shown in Table 3. In all the solutions, the pH after leaching is lower than that before leaching. With the initial pH of the solution being higher, the concentration of Ca tends to decrease, that of SO$_4^{2-}$ tends to increase greatly, and that of S$_2$O$_3^{2-}$ tends to increase slightly. When the initial pH of the solution was 12.01, an ettringite XRD peak was not observed in both slags A and B, but when the initial pH is 12.63, a peak attributed to ettringite can be observed in both slags A and B.

The SI of each chemical compound determined by thermodynamic calculation is shown in Table 4. The numbers in the upper line show the SI calculated using the initial pH of the solutions after the experiments shown in Table 2. First, observing the values at the bottom line, the SI of ettringite and CaSO$_4$·2H$_2$O are positive in all the experiments, and the SI of monosulfate and Ca(OH)$_2$ are negative. In the experiments in which ettringite precipitation occurs, the peaks of ettringite and CaSO$_4$·2H$_2$O are also observed in the XRD measurement, and it corresponds to the results of the thermodynamic calculation.

On the other hand, the calculated values in the top line are the calculated results when the pH of the solutions of the compounds after leaching is assumed to be the initial pH for estimating the reaction path. This assumes that unreacted NaOH is supplied to the leaching solution near the slags, which corresponds to the largest driving force for ettringite formation. It can be seen that when the pH is high, the SI has a large positive value for ettringite precipitation. In the experiments in which ettringite precipitation is observed, the SI of CaSO$_4$·2H$_2$O is negative and that of the other compounds is positive. However, in fact, since the pH of the entire solution decreases rapidly to the value after leaching with the dissolution of new compounds from the slags, the SI of CaSO$_4$·2H$_2$O becomes positive while the SI of the monosulfate and Ca(OH)$_2$ become negative. Consequently, it can be considered that ettringite formation proceeds with the precipitation of CaSO$_4$·2H$_2$O.

4.2.2. Ettringite Formation from Mixed Slags

By leaching experiments in pure water, it became clear that when air-cooled slags were mixed with granulated slags, the SI of ettringite increased, since the pH and concentration of Al increased. Then, for determining the condition of ettringite formation when air-cooled slags and granulated slags are mixed, these slags, mixed at various ratios, were leached in pure water and NaOH solutions of various concentration. Since the main purpose was to analyze ettringite in the solid samples after the experiments, the weight of the slag was set at 30 g and the volume of the solution was set at 30 ml.

The XRD patterns of the solid samples after the experiments, when granulated slag G is mixed with air-cooled slag A at a mixing ratio of 50%, are shown in Fig. 2. In the case of pure water and at a NaOH concentration of 0.005 mol/l, an ettringite peak was not observed. When the NaOH concentration exceeds 0.01 mol/l, a clear peak can be observed at 2$\theta = 9.1$ deg. A peak at 2$\theta = 11.6$ deg. is for CaSO$_4$·2H$_2$O with a (020) crystal orientation.

The amounts of ettringite formed after the leaching experiments, in which slag A and slag G are mixed, are shown in Fig. 3 as a function of the initial pH of the solution. In Fig. 3, the numbers next to the names of the slags show the mixing ratio of that slag. For example, A70 means 70%A-30%G. In slag A (A100), ettringite formation starts with the dissolution of new compounds from the slags, the SI of ettringite increases, since the pH and concentration of Al increased. Then, for determining the condition of ettringite formation when air-cooled slags and granulated slags are mixed, these slags, mixed at various ratios, were leached in pure water and NaOH solutions of various concentration. Since the main purpose was to analyze ettringite in the solid samples after the experiments, the weight of the slag was set at 30 g and the volume of the solution was set at 30 ml.

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The amounts of ettringite formed after the leaching experiments, in which slag A and slag G are mixed, are shown in Fig. 3 as a function of the initial pH of the solution. In Fig. 3, the numbers next to the names of the slags show the mixing ratio of that slag. For example, A70 means 70%A-30%G. In slag A (A100), ettringite formation starts with the dissolution of new compounds from the slags, the SI of ettringite increases, since the pH and concentration of Al increased. Then, for determining the condition of ettringite formation when air-cooled slags and granulated slags are mixed, these slags, mixed at various ratios, were leached in pure water and NaOH solutions of various concentration. Since the main purpose was to analyze ettringite in the solid samples after the experiments, the weight of the slag was set at 30 g and the volume of the solution was set at 30 ml.
at an initial pH of 12.3. At a mixing ratio is 50%, it starts at a pH of 11.8. Thus, ettringite formation starts at a lower pH when the mixing ratio of granulated slag is higher. The concentration of ettringite tends to be higher when the mixing ratio is higher. In A100 and A90, in which the mixing ratio is low, the concentration of ettringite increases with increasing pH, while in A70 and A50, in which the mixing ratio is high, it becomes the highest at a pH of 12.4. From the results shown in Table 4, it can be considered that in the high pH region, since the SI of Ca(OH)$_2$ is a large positive value, the formation of Ca(OH)$_2$ proceeds prior to ettringite formation. In these experiments, the analytical data for the solution, which is required for thermodynamic calculation, cannot be obtained since the amount of solution is small. The competition between the formation of ettringite and other compounds is a topic of future study.

Similar to Fig. 3, the case for the mixing of slags B and G is shown in Fig. 4. As in the case of slag A, ettringite formation tends to start at lower pH with the mixing ratio of slag G being higher, and the concentration of ettringite is highest near pH 12.4. The concentration of the formed ettringite is lower than in slag A; however, it is possible that this difference originates from the presence of a mineral phase and heat history, in addition to the compounds. This is a point that should be considered in future.

The relation between the concentration of ettringite formed in the slags and the mixing ratio of the granulated slags in the NaOH solutions at various pH described in Figs. 3 and 4, is shown in Figs. 5 and 6. For example, from Fig. 5, it can be estimated that at pH = 12.0, ettringite formation occurs when the mixing ratio of granulated slag with slag A exceeds about 35%, whereas when the pH increases to 12.2, the critical mixing ratio at which ettringite formation does not occur decreased to about 18%. According to Fig. 6, in slag B, the acceptable mixing ratio of granulated slag is about 35% at pH = 12.0, however, at pH = 12.4, ettringite can be formed when slag B is used alone.

4.3. Determining the Mechanism of Ettringite Formation

In previous studies, two mechanisms were proposed for ettringite formation, a liquid phase reaction and a topochemical reaction. In the liquid phase reaction, it is assumed that nucleation and crystal growth occur randomly in the liquid phase, far from the solid phase, when the crystallization rate of ettringite is lower than the dissolution rates of
Ca\(^{2+}\), Al(OH)\(^{3+}\), and SO\(_4^{2-}\), and harmful expansion does not occur. On the other hand, in the topochemical reaction,\(^{18}\) it is assumed that crystal growth occurs at the surface of the solid phase when the crystallization rate of ettringite is higher than the dissolution rate of Ca\(^{2+}\), Al(OH)\(^{3+}\), and SO\(_4^{2-}\), and harmful expansion occurs, since the oriented growth exerts pressure on the surroundings.

In this study, in all of the experiments except for the case in which slag G alone is used, the SI of ettringite calculated using the compositions and the pH of the leaching solutions are positive and ettringite can be formed. However, in actual experiments, ettringite formation can be observed only when the pH of the initial solution is high. It is suggested that ettringite formation is kinetically controlled. Since the process of ettringite formation from the blast furnace slag can be divided into 3 stages: 1) dissolution of the constituents of ettringite from the slags, 2) transportation of the species to the site of ettringite precipitation, and 3) precipitation of ettringite from the solutions, the kinetic consideration of these stages was conducted.

In this study, considering that Ca\(^{2+}\) and SO\(_4^{2-}\) are dissolved in the bulk under all of the experimental conditions, in the dissolution of slag compositions (stage 1), the dissolution of Al(OH)\(^{3+}\) from melilite (solid-solution of gehlenite Ca\(_2\)Al\(_2\)SiO\(_6\)) and akermanite Ca\(_2\)Mg\(_2\)Si\(_2\)O\(_7\))\(^{19}\) can control the precipitation reaction of ettringite represented by Eq. (2). Although there is almost no research on the dissolution rate of gehlenite in alkaline solutions, Engstrom et al.\(^{20}\) measured the dissolution amounts of each mineral as slag components in aqueous solutions (pH = 4, 7, 10) continuously using granular reagents of 20–38 \(\mu\)m in diameter by automatic titration. Using the data obtained from a dissolution experiment of gehlenite in a NaOH aqueous solution of pH = 10 at 25\(^\circ\)C, the dissolution rate (flux) of Al(OH)\(^{3+}\) \(J_{\text{dissol}}\) was calculated and Eq. (6) was obtained.

\[
J_{\text{dissol}} = 3.2 \times 10^{-9} \text{[mol} - \text{Al}_2\text{O}_3 \cdot \text{m}^2 \cdot \text{s}^{-1}] 
\] .......................... (6)

With regard to the transportation of components in the solutions (stage 2), when there is no liquid flow, the diffusion of Al(OH)\(^{3+}\) can be the rate controlling step. Since the diffusion coefficient of Al(OH)\(^{3+}\) cannot be obtained from literature, the value of Al\(^{3+}\), \(D_{\text{Al}^{3+}} = 5.41 \times 10^{-10} \text{[m}^2 \cdot \text{s}^{-1}]\)\(^{21}\) was used. By assuming the concentration at the reaction interface as zero, the diffusion flux \(J_{\text{diff}}\) is given by Eq. (7), where \(\delta \text{[m]}\) is the diffusion distance. When the diffusion coefficient of Al(OH)\(^{3+}\) is estimated using the diffusion coefficient of other complex anions, the value is about twice as large as that obtained using Eq. (7).

\[
J_{\text{diff}} = \frac{1.0 \times 10^{-31} \text{(ppmAl)}}{\delta} \text{[mol} - \text{Al}_2\text{O}_3 \cdot \text{m}^2 \cdot \text{s}^{-1}] 
\] .......................... (7)

With regard to the precipitation rate of ettringite from solution (stage 3), Baur et al.\(^{22}\) measured the dissolution-precipitation reaction rate between the solid ettringite and the aqueous solution in equilibrium at 25\(^\circ\)C using the iso-tope exchange method. Since the chemical equilibrium is maintained, the precipitation rate and dissolution rate have the same value \(k_{eq} \text{[mol/m}^2 \cdot \text{s}^{-1}]\) in principle. Two experiments were performed with \(^{45}\text{Ca}\) and \(^{35}\text{SO}_4\) as the isotopes, and the values of \(\log k_{eq}\) are \(-12.15\) and \(-11.86\) for \(^{45}\text{Ca}\) and \(\log k_{eq} = -11.65\) and \(-12.12\) for \(^{35}\text{SO}_4\) were reported. Calculating the dissolution-precipitation reaction rate in equilibrium by averaging these 4 values, \(k_{eq} = -1.12 \times 10^{-12}\) was obtained.

On the other hand, for the formation rate of ettringite from solutions in the supersaturation range, an empirical formula at 20\(^\circ\)C was given by Damidot.\(^{23}\) Since 1 mol of alumina in slag is required to form 1 mol of ettringite, Eq. (8) can be introduced as the precipitation flux \(J_{\text{precip}}\) of ettringite, where SI is the saturation index of ettringite obtained by thermodynamic calculation.

\[
J_{\text{precip}} = 2.0 \times 10^{-5} (SI - 1) \left[ \frac{H_2^+}{0.05} \right]^{0.2} \left[ \text{SO}_4^{2-} \right]^{0.3} \left[ \text{mol} - \text{Al}_2\text{O}_3 \cdot \text{m}^2 \cdot \text{s}^{-1} \right]
\] .......................... (8)

The rates in the three controlling steps as described above are arranged as the alumina flux, and for comparing their controlling processes, they are shown in Fig. 7 as a function of SI. In Fig. 7, the horizontal broken line represents the dissolution rate of Al(OH)\(^{3+}\) from gehlenite in solution at pH = 10, and the horizontal dashed lines represent diffusion flux in the case where the diffusion distances are 1 \(\mu\)m and 0.1 \(\mu\)m when the Al concentration in the solution is 0.4 ppm. The filled circles in Fig. 7 represent the precipitation rates of ettringite calculated from the compositions of the solutions and the values of pH in the experiments in pure water, shown in Table 2 by Eq. (8). Open circles in Fig. 7 represent the same calculation for the experiments in NaOH aqueous solution shown in Table 3 using their initial values of pH, where the values of SI of ettringite in the upper low in Table 4 are used. Since it is required to evaluate the precipitation rate at the largest driving force of ettringite, the initial value of pH is used. While the actual experiments are performed at 25\(^\circ\)C, Eq. (8) is at 20\(^\circ\)C. However, temperature correction was not performed since the temperature dependence of the reaction rate is not clear. Plots surrounded by the broken lines are samples in which ettringite formation was actually observed. Since the precipitation rates measured

![Fig. 7. Comparison of the possible rate-determining steps as a function of the saturation index of ettringite SI.](image)
by the isotope exchange method is extremely small, they are not shown in Fig. 7. It is obvious from Fig. 7 that since the dissolution rate of $\text{Al(OH)}_4^-$ at $pH = 10$ is much lower than the diffusion flux and the precipitation rate of ettringite, the reaction of ettringite formation is likely to be controlled by the dissociation of $\text{Al(OH)}_4^-$ from the slags. In actual experiments, since the pH of the solution is higher than 10, it is estimated that the dissolution rate is larger than the broken lines in Fig. 7. The magnitude relationship between SI and pH is shown in the plots corresponds well, therefore, pH increases monotonically from left to right in the figure. According to the thermodynamic calculation, the SI values of gehlenite are always large negative values under every condition, so that it can be considered that $\text{Al}_2\text{O}_3$ in the slags tends to dissolve. Therefore, it can be explained that ettringite formation is observed in the experiment where the pH of the solution is the highest since the dissolution rate of $\text{Al(OH)}_4^-$ increases with increasing pH. From Fig. 7, it is estimated that the crystallization rate of ettringite is higher than the dissolution rate of $\text{Al(OH)}_4^-$, so that it is also estimated that topochemical ettringite formation proceeds at the surface of slags, and it is possible that harmful expansion occurs with oriented crystal growth. Considering the dissolution of $\text{Al(OH)}_4^-$ from the slags as the controlling step, with a multiplier effect of the supply of $\text{Al(OH)}_4^-$ from the granulated slags into solution, and the promotion of dissolution of $\text{Al(OH)}_4^-$ with increasing pH, the mechanism of promotion of ettringite formation with the addition of granulated slags to air-cooled slags can be explained.

The results of this study can also be applied in the case where the water content of slags is low like the slags that are utilized on land, when the region where the water content is high is formed at the bottom of the slag layer. For utilizing air-cooled slags under an alkaline environment at a higher concentration, technological development including the cooling method, which promotes precipitation of the mineral phase, in which the dissolution rate of $\text{Al(OH)}_4^-$ is low, is useful, and by measuring the dissolution rate of $\text{Al(OH)}_4^-$ from gehlenite and melilite over a wide pH range, a detailed evaluation of the environmental resistance of slags can be possible using a kinetic simulator combined with thermodynamic calculation.

### 4.4. Experiment on Decomposition of Ettringite

The temperature dependence of the decomposition degree of ettringite when slag C was kept in pure water and dry air for 1h is shown in Fig. 8. In water and dry air, the decomposition degree greatly increases near 60–70°C, and it increases with an increase in the temperature. At 90°C, in both cases, about 80% of the ettringite is decomposed. When Slag C is kept in pure water, it can be considered that since the solubility product $K_{sp}$ of ettringite increases with the temperature increase, dissolution of ettringite in water occurs and ettringite can be removed. Calculating the equilibrium between ettringite and pure water, 0.86 g of ettringite dissolves in 1 l of pure water at 90°C. Therefore, for completely dissolving ettringite in 1.0 g of slag containing 3 mass% of ettringite, it can be calculated that 34 ml of pure water is required. In experiments, 100 ml of pure water is used, and it can be considered that the reason why the decomposition degree of ettringite does not reach 100% arises from kinetics, the decrease in its solubility with the dissolution of Ca, $\text{SO}_4^{2-}$, and so on.

On the other hand, when slag C is kept in dry air, it can be considered that the structure of ettringite is destroyed by the detachment of water molecules from it. Ettringite is composed of $\{\text{Ca}_6[\text{Al(OH)}_6\cdot24\text{H}_2\text{O}]^{6+}\}$ columns and $\{\left[(\text{SO}_4)_3\cdot2\text{H}_2\text{O}\right]^{6-}\}$ channels, and the whole structure is held by their network of hydrogen bonds. The result of the thermogravimetric measurement (TG) of the synthesized ettringite for investigating its thermal stability is shown in Fig. 9. Detachment of water molecules starts near 50°C and 2 water molecules corresponding channel of ettringite at 75°C. Above that temperature, the number of detached water molecule continues to increase, and it is estimated that detachment occurs from the column. This sequential behavior shows a correspondence with the temperature dependence of the decomposition degree shown in Fig. 8. However, since a part of the water molecule detached in dry air can be reversibly integrated into the structure of ettringite, it can be reformed when the slags are in contact with water again after treatment, so that this cannot be considered as a desirable method. For verifying this problem, 1.0 g of synthesized ettringite, 94% of which is decomposed by keeping it in dry air for 2 h at 90°C, is placed in 100 ml of pure water at 25°C for 1–3 days. As a result, about
60% of the ettringite reforms in all the samples. Therefore, for decomposing and removing the ettringite in the slags completely, it can be considered that treatment with high-temperature water is effective and convenient.

5. Conclusion

In this study, we investigated the effect of the pH of environmental water in contact with blast furnace slag for ettringite formation by slag leaching experiments, and the following results were obtained.

(1) In air-cooled slag, granulated slag, and mixed slag, ettringite formation was not observed by leaching them in pure water.

(2) $\text{S}_2\text{O}_3^{2-}$ in air-cooled slag increases the concentration of Ca in the solution and the saturation index of ettringite.

(3) When air-cooled slag is leached in alkaline solution, ettringite formation is observed for a highly alkaline concentration. Upon increasing the mixing ratio of granulated slag with air-cooled slag, the critical pH of ettringite formation starts decreasing.

(4) The dissolution process of $\text{Al(OH)}_4^-$ from slags is estimated to be the controlling step of ettringite formation. Addition of granulated slag to air-cooled slag is considered to promote ettringite formation because of a multiplier effect of the supply of $\text{Al(OH)}_4^-$ and an increase in the pH.

(5) When slag containing ettringite is heated in pure water and dry air, ettringite decomposes. The decomposition degree increases with increasing temperature and it reaches about 80% at 90°C.

Acknowledgements

The authors wish to thank Professor Chiharu Tokoro, Waseda University, for her valuable lecture about PHREEQC, and Naofumi Fujita, Nippon Steel & Sumitomo Metal Corporation, for his suggestions on the decomposition of ettringite. All the slags and the synthesized ettringite used in the experiments were provided by Nippon Slag Association. A part of this research was financially supported by Nippon Slag Association and the Steel Foundation for Environmental Protection Technology.

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