Physical Chemistry of Dissolution of Nutrients From Steelmaking Slag into Aqueous Solution Containing Organic Acids

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INTRODUCTION

Steelmaking slag is one of the major by-products generated during the steelmaking process; thus the stable utilization of steelmaking slag is essential to establishing a sustainable steelmaking process and maintaining a stable steelmaking operation. Steelmaking slag has been mainly consumed as concrete aggregate, roadbed material, and so on. However, such application of steelmaking slag as an alternative material of natural stone would shrink in near future in Japan because of the saturated development of society and declining public works. To maintain the steelmaking process, the stable recycling of steelmaking slag is an essential condition.

Recently, sea desertification has extended along the Japanese coast with the gradual destruction of the coastal ecological system year by year. It is pointed out that there are various causes of the sea desertification such as the increase of seawater temperature or the ingestion by herbivorous animals (e.g. sea urchins). Among those, one of the most important factors for the barren ground is the lack of nutrient elements in seawater, especially iron,1 since iron is indispensable for the chlorophyll synthesis and the respiration of various seaweeds as a micronutrient. Steelmaking slag is one of the prominent candidates as a source of iron considering various oxides such as FeO, SiO₂, and CaO as constituents. It has been clarified that steelmaking slag buried at the seacoast exhibited a significant enhancement effect on the growth of marine phytoplankton or the recovery of the disappeared seaweed beds.2 While the solubility of iron in oxic seawater is extremely small at the normal pH range3 and the dissolution of iron from steelmaking slag is significantly little. To overcome such facts, a simultaneous supply of organic acid acting as a chelating agent is one of the solutions to stabilize the dissolved iron in seawater and increase its solubility.

Authors have investigated the dissolution behaviors of steelmaking slag into seawater with various conditions such as slag/water ratio, dissolution time, or the organic acid concentrations, and have found the positive effect of the addition of organic acid.4-6 However, through numerous experiments, measured dissolution behavior was very complex owing to the influence of originally dissolved elements in seawater; thus, the quantitative analyses were limited.

In the present study, the effect of organic acid on the dissolution of various elements from steelmaking slag into freshwater was studied by the addition of gluconic acid as one of the natural organic acids. Laboratory scale dissolution experiments were conducted and the changes of pH, oxidation-reduction potential (ORP), and concentration of elements with dissolution time were measured. The dissolution mechanisms were discussed from experimental results and available thermodynamic data.7
EXPERIMENTAL

According to the previous study reported by Gao et al.,\(^8\) most Fe elution occurs from the amorphous phase in steelmaking slag. Therefore, samples simulating the amorphous phase in steelmaking slag were prepared to investigate the effect of organic acids on the leaching behavior of the CaO-SiO\(_2\)-FeO amorphous phase in an aqueous solution. Compositions of the prepared amorphous samples are shown in Table 1. The CaO-SiO\(_2\)-FeO slag with mass%CaO/mass%SiO\(_2\) = 1.0 and 30 mass%FeO was prepared as a reference (Sample O), and samples A and P contained 5 mass%Al\(_2\)O\(_3\) and 5 mass%P\(_2\)O\(_5\), respectively. CaO prepared by calcining CaCO\(_3\) reagent at 1273 K for 12 h, FeO obtained by reducing Fe\(_2\)O\(_3\) reagent with electrolytic iron powder, and SiO\(_2\), Al\(_2\)O\(_3\), Ca(H\(_2\)PO\(_4\))\(_2\)⋅H\(_2\)O, and CaHPO\(_4\)⋅2H\(_2\)O reagents were mixed to be the target composition. The mixed powder was charged into an iron crucible, melted and held in an electric furnace in an Ar atmosphere at 1673 K for 3 h, and the amorphous phase was obtained by water quenching. The obtained sample was dried in a desiccator for 12 h, then crushed to a particle size of 150 \(\mu\)m or less and used for the dissolution experiments.

Table I: Compositions of Synthesized Amorphous Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>CaO (mass%)</th>
<th>SiO(_2) (mass%)</th>
<th>FeO (mass%)</th>
<th>Al(_2)O(_3) (mass%)</th>
<th>P(_2)O(_5) (mass%)</th>
<th>%CaO/%SiO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>35.0</td>
<td>35.0</td>
<td>30.0</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>A</td>
<td>32.5</td>
<td>32.5</td>
<td>30.0</td>
<td>5.0</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>P</td>
<td>32.5</td>
<td>32.5</td>
<td>30.0</td>
<td>-</td>
<td>5.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

To confirm that the obtained sample was amorphous, it was analyzed using an X-ray diffractometer (Rigaku Miniflex 600). The measurement conditions were Cu-K\(\alpha\) radiation, tube voltage 40 kV, tube current 15 mA, and measurement speed 5.0 deg/min.

One hundred cm\(^3\) of prepared distilled water or gluconic acid aqueous solution was poured in 250 cm\(^3\) volume polypropylene bottle, and pH and oxidation-reduction potential (ORP) were measured. One gram of slag sample was put in the bottle and sealed for the dissolution experiment. Experiments were conducted with 30 mm shaking amplitude and 160 cycles per min at 298 K. After the prescribed time, the pH and ORP of the solution were immediately measured. The solution was collected by filtering with 0.45 \(\mu\)m pore membrane filter. Concentrations of Ca, Si, Al, and Fe of the filtrate were measured by inductively coupled plasma optical emission spectroscopy, and that of P by absorptiometry.

RESULTS AND DISCUSSION

1. Dissolution behavior

In all cases, the pH of the solution increased gradually with dissolution time, which is owing to the dissolution of CaO by the following reaction.

\[
\text{CaO (in slag) + H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2 \text{OH}^- \quad (1)
\]

Therefore, the type, the stability, and the solubility of dissolved species change with time. Figure 1 shows the change in Fe concentration of the solution with dissolution time in the case using Sample O.\(^7\) Considerable positive influence of gluconic acid addition in the solution on the Fe concentration was observed. Other species, namely Ca, Si, Al, and P also exhibited the same phenomena.

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2. Estimation of dissolved species

By using analyzed concentrations of solutions, equilibria of hydration and chelation reactions of Ca, Si, Al, Fe, and P with gluconic acid (hereafter described as “HGH₄”) were calculated at 298 K. Considered inorganic ions of those elements were Ca²⁺, CaOH⁺, H₂SiO₄⁻, H₃SiO₄²⁻, HSiO₄³⁻, SiO₄⁴⁻, Al³⁺, Al(OH)²⁺, Al(OH)₃⁺, Al(OH)₄⁻, Fe²⁺, FeOH⁺, Fe(OH)₃⁺, Fe(OH)₄⁻, HFeO₂⁻, Fe³⁺, Fe(OH)₂⁺, Fe(OH)₃⁺, Fe(OH)₄⁻, H₃PO₄⁻, H₂PO₄⁻, HPO₄²⁻, and PO₄³⁻. Equilibrium between inorganic ions and hydration reactions are expressed by equations (2) to (4). Chelation reaction equations of Ca, Al, and Fe with gluconic acid, and equilibrium constants of those reactions are shown in equations (5) to (10). The dissolution reaction of gluconic acid in water and the acid dissociation constant is shown in the equation (11). Equilibrium constants were calculated using standard Gibbs energies of formation reported by Pankow. Activity coefficients of ions were mainly calculated by extended Debye-Hückel equation and ion diameter parameters reported by Klotz. When the parameter was unknown, it was assumed that its activity coefficient is the same as those with the same valence. More detail can be found in the authors’ recent publication.

\[
\begin{align*}
A^{n+} + m H_2O &= A(OH)_m^{(n-m)+} + m H^+ \\
B^{n-} &= B^{(n-m)-} + m H^+ \\
H_\omega XO_4^0 &= H_\omega XO_4^{\omega-} + n H^+ \\
Ca^{2+} + GH_4^- &= Ca(GH_4)^+ & \log K(5) = 1.22 \\
Al^{3+} + GH_4^- &= Al(GH_4)_{2+} & \log K(6) = 1.98 \\
Al(GH_4)_{2+} &= Al(GH_3)^+ + H^+ & \log K(7) = -2.87 \\
Al(GH_3)^+ &= Al(GH)^+ + 2 H^+ & \log K(8) = -9.29 \\
Fe^{2+} + GH_4^- &= Fe(GH_4)^+ & \log K(9) = 1.0 \\
Fe^{3+} + 4 OH^- + GH_4^- + 4 H_2O &= Fe(G)^{2+} + 4 H_2O & \log K(10) = 37.2 \\
HGH_4 &= H^+ + GH_4^- & \log K(11) = -3.60
\end{align*}
\]

The calculation fraction of HGH₄-originating species in the solution in the case using Sample O is shown in Fig. 2. More than 60% of added HGH₄ exists as GH₄⁻ ion and HGH₄ molecule did not exist. The fraction of Ca(GH₄)⁺ and Fe(G)²⁺ ions gradually increased with increasing the dissolution time. Figure 3 shows the ratio of chelated Fe ions against the pH of the solution. It is clearly seen that the fraction of chelated Fe ions increases with increasing HGH₄ concentration and the pH of the solution. According to our recent study, the influence of the pH of the solution on the chelation efficiency depends on the type of organic acids, where some types show the opposite trend with the pH. Since it is naturally expected that the pH of the solution increases by the dissolution of steelmaking slag as discussed above, the appropriate choice of the type of organic acids as chelating agent is necessary.
CONCLUSIONS

The dissolution behavior of elements from steelmaking slag into an aqueous solution containing gluconic acid has been studied, particularly focusing on the dissolution of the amorphous phase. The influence of gluconic acid addition on the enhancement of elements dissolution from steelmaking slag has been confirmed. Utilizing available thermodynamic data on the formation reactions of chelated species in solutions, existing chemical species and their fractions have been quantitatively estimated. A clear tendency to enhance the formation of chelated Fe-containing species with increasing pH was found in the case of gluconic acid addition. Since some organic acids have shown the opposite tendency, the appropriate choice of the type of organic acids as a chelating agent is necessary.

REFERENCES


