Alkali Elution Behavior of Steelmaking Slag into Seawater by Continuous Stirred Tank Reactor

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In order to understand the alkali elution behavior of steelmaking slag under continuous flow, a kinetic study was carried out by continuous stirred tank reactor (CSTR). Tap water and seawater were used for measurements of circumferential velocity and temporal change in pH, respectively. Liquid was fed into the vessel and flowed constantly during the impeller rotation operation in the vessel. The effect of the various operating factors such as vessel inner diameter, slag size, slag composition, ratio of liquid volume to mass of slag, seawater feed rate, impeller height from the slag, impeller rotation speed etc. were investigated.

The circumferential velocity in the vessel was not affected by seawater feed rate but by the impeller rotation speed. The alkali elution rate increased with the increase in the circumferential velocity. The alkali elution rate was not influenced by the ratio of liquid volume to mass of slag and impeller height from the slag surface. The alkali elution rate decreased with the decrease in diameter of slag particle below 0.01 m due to the insufficient penetration of seawater between slag particles. The alkali elution rate increased with the increase in seawater feed rate at the same circumferential velocity. The non-dimensional correlation equation of alkali elution rate was shown by

\[ Sh = 8.26 \times 10^{-4} Re_p^{0.62} (Nt)^{-0.37} \]

where \( Sh \): Sherwood number, \( Re_p \): Particle Reynolds number and \( (Nt) \): the product of impeller rotation speed and residence time.

KEY WORDS: alkali elution; steelmaking slag; seawater; continuous stirred tank reactor.

1. Introduction

Utilization of steelmaking slag in the ocean area1-2) has attracted increasing attention from its feature to control the seawater contamination3-6) or to dissolve the nutrition elements into seawater.7-11) On the other hand, there are several studies on the elution of environmentally-controlled fluorine into the seawater.12-14)

When steelmaking slag is being dropped into the seawater or when it has been piled on the sea bottom, the surrounding sea area might become cloudy due to Mg(OH)₂ generated by the reaction of Mg²⁺ originally existed into the seawater and OH⁻ dissolved from the steelmaking slag. Thus, the alkali elution behavior of steelmaking slag in the ocean area must be understood in a careful manner.

As a test to determine the white turbidity easily, there exists a method to observe milky spot after the stirring of real or artificial seawater on the steelmaking slag.1) Kanayama et al.15) observed the white precipitate and turbidity due to Mg(OH)₂ formation after one to seventy two hours and showed that it was suppressed by the mixing of the steelmaking slag with the dredged soil. However, the effects of slag nature and operating factors on the alkali elution behavior were not found out within one hour when the alkali dissolution might reach a peak. Tamaki et al.16) carried out the kinetic study on the alkali elution behavior for one hour and found that the several operational factors such as impeller rotation speed, diameter of slag piece, etc. affect the alkali elution behavior. Kanayama et al.17) also built an analytical model on the alkali elution through slag layer. However, it might be difficult for the above batch-type column test to predict the alkali elution behavior in the real continuous flow of the ocean. Thus, a kinetic study on the alkali elution from steelmaking slag into the seawater was carried out by using the vessel with completely-mixed flow where seawater was fed continuously.

2. Experimental

2.1. Experimental Method

Figure 1 shows the schematic view of experimental apparatus. There is a liquid inflow hole at the upper part of cylindrical vessel made of acryl and a liquid outflow hole at the lower part. The inner diameter of both of the inflow and outflow holes is 2.0 × 10⁻² m. Tap water was used for liquid velocity measurement, whereas the seawater at Ushimado-cho, Setouchi City, Okayama, Japan was used for the alkali

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elution experiment. After setting the steelmaking slag and the seawater in the vessel, fluid was rotated by an impeller of \(7.5 \times 10^{-2} \text{ m}\) in diameter \((d_{\text{impeller}} = 7.5 \times 10^{-2} \text{ m})\). No slag was placed for fluid velocity measurement. Three kinds of vessels were used with inner diameters of \(15.6 \times 10^{-2}\) (base), \(22.6 \times 10^{-2}\) and \(30.0 \times 10^{-2} \text{ m}\), respectively. Fluid circumferential velocity was measured by an electromagnetic velocity meter (KENEC, VM-1001). The velocity sensor tip was set at a quarter of inner diameter apart from the vessel wall and at the height of 0.5 m from the slag surface. The pH value was measured at the outflow hole after it was confirmed that it agreed with the pH value near the outflow hole inside the vessel.

### 2.2. Samples and Experimental Conditions

The photographic image of steelmaking slag used for experiment is shown in Fig. 2. The diameter range and the average diameter of the slag particles are given in Table 1 and the chemical compositions in Table 2. The average diameter, \(<d>\) (m), of slag B, C or D assumed as a spherical shape was obtained from sampling a portion of each slag pieces, measuring their number, \(n_{\text{slag}}\), and mass, \(w_{\text{slag}}\) (kg), and then calculating by Eq. (1).

\[
<d> = \left(\frac{6w_{\text{slag}}}{\rho \pi n_{\text{slag}}}\right)^{1/3}
\]

where \(\rho\): slag density (kg/m³). On the other hand, the average diameter of slag A was assumed to be half of the maximum diameter, that is, \(4.8 \times 10^{-2} \text{ m}\) shown in Table 1 due to its fineness. Slags A, B and C have the same chemical compositions with the different diameters and slags C and D had the same diameter range with the different chemical compositions as shown in Tables 1 and 2.

The experimental conditions of alkali elution experiment are shown in Table 3. The standard is shown in Run 1 as follows, vessel diameter, \(\varphi\): \(15.6 \times 10^{-2}\) m, slag: C, ratio of liquid to solid, \(L/S\): \(5.0 \times 10^{-3}\) m³/kg, seawater feed rate, \(Q\): \(8.0 \times 10^{-3}\) m³/s, impeller height from the slag surface, \(H\): \(5.0 \times 10^{-2}\) m, impeller rotation speed, \(N\): 2.7 s⁻¹. On the other hand, \(L/S\) was varied from \(2 \times 10^{-2}\) to \(5 \times 10^{-3}\) m³/kg shown in Run 1, 2–4, \(N\) from 0 to 5.0 s⁻¹ denoted in Run 1, 5–8, <\(d>\) from \(0.48 \times 10^{-2}\) to \(2.18 \times 10^{-2}\) m as Run 1, 9–10, \(H\) from \(5.0 \times 10^{-2}\) to \(15.0 \times 10^{-2}\) m as Run 1, 11–12, \(\varphi\) from \(15.6 \times 10^{-2}\) to \(30.0 \times 10^{-2}\) m as Run 13–15 and \(Q\) from \(0.83 \times 10^{-5}\) to \(3.3 \times 10^{-5}\) m³/s as Run 1, 16–20.

### 3. Results and Discussion

#### 3.1. Effect of Impeller Rotation Speed and Seawater Feed Rate to Vessel on Seawater Circumferential Velocity in Vessel

Figure 3 shows the relationship between circumferential velocity, \(u\), and impeller rotation speed, \(N\), when tap water feed rate, \(Q\), was changed from 0 to \(2.5 \times 10^{-5}\) m³/s, \(\varphi\) fixed to \(15.6 \times 10^{-2}\) m and \(3.0 \times 10^{-2}\) m shown in Table 1 because \(15.6 \times 10^{-2}\) m is the standard diameter range shown in Table 3. The u values did not change much with the Q values, although \(u\) increased with increasing \(N\).

The relationship between \(u\) and impeller rotation speed is shown in Fig. 4. \(V\) was \(5.0 \times 10^{-3}\) m³ at \(\varphi=15.6 \times 10^{-2}\) m, \(10.0 \times 10^{-3}\) m³ at \(\varphi=22.6 \times 10^{-2}\) m and \(15.0 \times 10^{-3}\) m³ at \(\varphi=30.0 \times 10^{-2}\) m. Smaller \(\varphi\) increased \(u\). At the same impeller rotation speed, the u values increased with the decrease in vessel diameter, \(\varphi\). The \(u\) value instead of the impeller rotation speed will be used for the following alkali elution analysis.

#### 3.2. Temporal Change in pH and \([\text{OH}^-]\)

Figure 5 shows the typical examples of temporal changes in pH and \([\text{OH}^-]\) when rotation speed, \(N\), was changed and the other conditions such as slag C, \(\varphi=15.6 \times 10^{-2}\) m, \(L/S=5.0 \times 10^{-3}\) m³/kg, \(Q=0.83 \times 10^{-5}\) m³/s, \(H=5.0 \times 10^{-2}\) m, were kept constant (Run 1, 5–8). The pH values as shown

### Table 2. Chemical compositions of slag used for experiment.

<table>
<thead>
<tr>
<th>Slag</th>
<th>(%TiO₂)</th>
<th>(%MgO)</th>
<th>(%CaO)</th>
<th>(%FeO)</th>
<th>(%Fe₂O₃)</th>
<th>(%Al₂O₃)</th>
<th>(%MnO)</th>
<th>(%P₂O₅)</th>
<th>(%f.CaO)</th>
</tr>
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<tbody>
<tr>
<td>A, B, C</td>
<td>19.7</td>
<td>2.21</td>
<td>16.8</td>
<td>44.4</td>
<td>13.4</td>
<td>2.75</td>
<td>5.88</td>
<td>1.97</td>
<td>2.98</td>
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<tr>
<td>D</td>
<td>20.0</td>
<td>2.30</td>
<td>13.1</td>
<td>44.0</td>
<td>11.7</td>
<td>3.47</td>
<td>6.10</td>
<td>2.20</td>
<td>2.50</td>
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Both of the pH and $[\text{OH}^-]$ values without rotation varied more widely than those with rotation. It seems to be due to a lack of complete mixed state in the vessel. The longitudinal pH distribution in the vessel is shown in Fig. 6 under the standard conditions (Run 1). The radial position was at the half of vessel radius from the inner wall. The almost constant pH values at the upright direction in the upper part of Fig. 5 increased with the increase in time in the early stage and became constant or decreased slightly after that. The $[\text{OH}^-]$ (mol/m$^3$) values as shown in the lower part of Fig. 5 had also showed the same tendency. Both of the pH and $[\text{OH}^-]$ values without rotation varied more widely than those with rotation. It seems to be due to a lack of complete mixed state in the vessel.

The longitudinal pH distribution in the vessel is shown in Fig. 6 under the standard conditions (Run 1). The radial position was at the half of vessel radius from the inner wall. The almost constant pH values at the upright direc-

<table>
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<th>Table 3. Experimental conditions.</th>
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<tr>
<td>Run No.</td>
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</table>
tion led to the constant [OH\(^-\)] due to [H\(^+\)][OH\(^-\)] = 10\(^{-14}\) (mol/m\(^3\))^2 and the constant [Ca\(^{2+}\)] (mol/m\(^3\)) because of [Ca\(^{2+}\)]/[OH\(^-\)] = const.\(^{10}\) in the alkali elution such as [Ca\(^{2+}\)], [OH\(^-\)] from steelmaking slag into seawater. It resulted in a uniformly-mixed flow of fluid inside the vessel.

### 3.3. Effect of Operational Factors on Alkali Elution

#### 3.3.1. Evaluation of Alkali Elution for Continuous Operation

When liquid side mass transfer is a rate-determining step for alkali elution of steelmaking slag into seawater as revealed by batch reactor,\(^{16}\) the alkali elution rate is expressed by Eq. (2) where its driving force is the difference between saturated [Ca\(^{2+}\)] (mol/m\(^3\)) on the slag surface and [Ca\(^{2+}\)] (mol/m\(^3\)) in bulk seawater.

\[
d(V[Ca^{2+}])/dt = k'a([Ca^{2+}]_e - [Ca^{2+}]) \quad \text{......... (2)}
\]

where V: vessel volume (m\(^3\)), k': mass transfer coefficient (m/s), a: total surface area of slag (m\(^2\)). As [Ca\(^{2+}\)]\(_e\) > [Ca\(^{2+}\)] is accepted as shown by Tamaki et al.,\(^{16}\) Eq. (2) results in Eq. (3).

\[
d(V[Ca^{2+}])/dt = k'a[Ca^{2+}]_e \quad \text{............... (3)}
\]

The schematic view of the alkali elution behavior in the vessel is shown in Fig. 7. Alkali ion such as Ca\(^{2+}\) and OH\(^-\) of the steelmaking slag dissolves into bulk seawater and OH\(^-\) reacts with several ions in the seawater according to alkalinity change and two step dissociation of carbonic acid.\(^{15,16}\) As a completely-mixed flow is formed in the vessel as shown in section 3.2, mass balance\(^{10}\) of [Ca\(^{2+}\)] becomes Eq. (4).

\[
Q[Ca^{2+}]_w + k'a[Ca^{2+}]_e - Q[Ca^{2+}] = Vd[Ca^{2+}]/dt \quad \text{......... (4)}
\]

where Q: seawater feed rate (m\(^3\)/s), [Ca\(^{2+}\)]\(_w\): Ca\(^{2+}\) concentration in the seawater (mol/m\(^3\)), Integration of Eq. (4) under the initial condition of Eq. (5) results in Eq. (6).

\[
[Ca^{2+}] = [Ca^{2+}]_w \text{ at } t = 0 \quad \text{.............. (5)}
\]

\[
([Ca^{2+}]_w + k'a[Ca^{2+}]_e)/Q - [Ca^{2+}])/\{k'a[Ca^{2+}]_w/Q\} = \exp\{-t/\tau\} \quad \text{........... (6)}
\]

where \(\tau\): residence time (=V/Q) (s)

As the [Ca\(^{2+}\)] value in Eq. (6) increases with an increase in time and at steady state it is the same as [Ca\(^{2+}\)] at \(t \rightarrow \infty\), the following equation is accepted.

\[
[Ca^{2+}] - [Ca^{2+}]_w = k'a[Ca^{2+}]_e/Q \quad \text{......... (7)}
\]

According to Tamaki et al.,\(^{10}\) \(k\) and \(\alpha\) obtained from buffer effect of pH by carbonic acid in the seawater are defined as Eqs. (8) and (9), respectively.

\[
k = (\alpha/[Ca^{2+}]_w)/[OH^-]_w k' \quad \text{............... (8)}
\]

\[
([OH^-] - [OH^-]_w) = \alpha([Ca^{2+}] - [Ca^{2+}]_w) \quad \text{......... (9)}
\]

where \(\alpha\): constant for alkali elution from steelmaking slag into seawater. Thus, Eq. (7) is rearranged to Eq. (10), using Eqs. (8) and (9).

\[
[OH^-] - [OH^-]_w = k'a[OH^-]_w Q \quad \text{........... (10)}
\]

where [OH\(^-\)]\(_w\): hydroxyl-ion concentration in seawater (mol/m\(^3\)), [OH\(^-\)]\(_w\): saturated hydroxyl-ion concentration (mol/m\(^3\)). The [OH\(^-\)]\(_e\) value became 10\(^{-14}\) due to solubility product of Ca(OH)\(_2\) given by pH = 12.4.\(^{19}\)

#### 3.3.2. Effect of Operational Factors on Alkali Elution Rate

The relationship between liquid side mass transfer coefficient, \(k\), and \(\alpha\) obtained from buffer effect of pH by carbonic acid in the seawater are defined as Eqs. (8) and (9), respectively.

Figure 9 shows that the relationship between \(k\) and L/S (Run 1–4). The values of \(\phi, <d>\), Q, H and N were fixed to be 15.6×10\(^{-2}\) m, 2.17×10\(^{-2}\) m, 5.0×10\(^{-5}\) m\(^3\)/kg, 8.3×10\(^{-5}\) m\(^3\)/s and 5.0×10\(^{-2}\) m respectively. It was found that the alkali elution rate was not affected by L/S in these conditions.

The relationship between \(k\) and the average slag diameter, \(<d>\), is shown in Fig. 10 (Run 1–10). The values of \(\phi, <d>\), Q, H and N were fixed to be 15.6×10\(^{-2}\) m, 2.17×10\(^{-2}\) m, 5.0×10\(^{-5}\) m\(^3\)/kg, 8.3×10\(^{-5}\) m\(^3\)/s and 5.0×10\(^{-2}\) m respectively. It was found that the alkali elution rate was not affected by L/S in these conditions.
Q, L/S, H and N were fixed to be $15.6 \times 10^{-2}$ m, $0.83 \times 10^{-5}$ m$^3$/s, $5.0 \times 10^{-3}$ m$^3$/kg, $5.0 \times 10^{-2}$ m, 2.7 s$^{-1}$, respectively. The penetration ratio, P (%), resulted from the value, $<d>$, shown in Fig. 11, which resulted in the smaller k value for larger vessel diameter.

3.3.3. Non-dimensional Correlation Equation Effect of Alkali Elution Rate

The relationship between k and u is shown in Fig. 13. Q was fixed to be $0.83 \times 10^{-5}$ m$^3$/s, and both of slags C and D were involved in these conditions. The significant difference of k between slag C of (%f.CaO)=3.65 and D of (%f.CaO)=6.11 was not recognized. The regression expression of k was given by Eq. (11).

$$k = 2.90 \times 10^{-8} u^{0.35}$$

Although the exponent of u was almost the same as the batch experiment shown in Fig. 13, the k values were slightly higher at the same u value.

When u was fixed to be $13.0 \times 10^{-2}$ m/s by regulating the impeller rotation speed, the relationship between k and Q is shown in Fig. 14 (Run 1–4, 11–13, 16–20). The k value of batch experiment at u=$13.0 \times 10^{-2}$ m/s was involved in Fig. 14. The empirical equation of k was given by Eq. (12).

$$k = 1.09 \times 10^{-6} Q^{0.37}$$

Subsequently, the non-dimensional correlation equation of alkali elution rate was examined by using the data shown in Figs. 13 and 14. Sherwood number including the mass transfer coefficient of Ca$^2+$, k’, is given by Eq. (13).

$$Sh = k’ <d>/D_{Ca^{2+}}$$

where $D_{Ca^{2+}} = 0.76 \times 10^{-7}$ (m$^2$/s$^{20}$) denotes the diffusion coefficient of Ca$^2+$, $\alpha = 1.24 \times 10^2$ (mol/m$^3$) and $[Ca^{2+}] = 8.7$ (mol/m$^3$) were used for the calculation of k in Eq. (8)’. The particle Reynolds number defined by Eq. (14) is introduced because the u values correlate with the impeller rotation speed, N.

$$Re_p = \rho N d_{impeller} <d>/\mu \ \ \ \ \ \ \ \ (14)$$

where $d_{impeller}$: the impeller diameter (m) and $\mu$: viscosity (Pa·s). Moreover, non-dimensional number, $N\tau$, is used instead of Q as shown in Eq. (15).
in the impeller rotation speed, that is, the circumferential velocity.
(3) The alkali elution rate was not influenced by the ratio of liquid volume to mass of slag and impeller height from the slag surface.
(4) The alkali elution rate decreased with the decrease in diameter of slag particle below 1.0 cm due to the insufficient seawater penetration between slag particles.
(5) The alkali elution rate increased with the increase in seawater feed rate at the same circumferential velocity.
(6) When seawater was fully penetrated between slag particles, the relationship of the mass transfer coefficient, \( k \) (m/s), circumferential velocity, \( u \) (m/s), and seawater feed rate, \( Q \) (m\(^3\)/s) was expressed by \( k = 8.26 \times 10^{-4} R e_p^{0.62} (N_r)^{−0.37} \), where \( Sh \): Sherwood number, \( Re_p \): Particle Reynolds number, and \( N_r \): the product of impeller rotation speed and residence time.

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