Influence of amount of oxidizing slag discharged from stainless steelmaking process of electric arc furnace on elution behavior into fresh water

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Abstract. Fundamental study was carried out for provision for acidification of soil due to acid rain. The influence of weight of the additive slag on elution behavior of the slag into water was studied in this study. Elution experiment was carried out on a basis of JIS K 0058-1. Generally, the pH in the aqueous solution increased with an increase in weight of the additive slag. The pH converged to approximately eight. Calcium, magnesium and manganese, which were essential elements for plants, were eluted from the slag irrespective to elution condition. The eluted concentrations of Ca and Mg increased with an increase in weight of the additive slag. Silicon and zinc were also eluted depending on the conditions. Aluminum that was harmful for plants was not eluted from the used slag.

1. Introduction
A large quantity of slag has been formed in steelmaking process yearly. Because final disposal yard is tight in Japan, re-use of the slag in coastal water where the environmental quality standards are not strict have been studied [1-10]. On the other hand, steelmaking slag contains the substances that are essential for plants. The slag is expected to be a supply source of minerals to soil [11-14]. A certain slag has been already used as a fertilizer. In these studies, field-tests of the slag were mainly performed. However, only a few researchers studied fundamentally the elution from the slag [15-17]. In our previous works [18, 19], we studied the elution behaviour of the slag that was discharged from oxidizing process of normal steel in an electric arc furnace (EAF). It was found that the elution concentration of the used slag was less than the environmental quality standards (EQSs). The elution behaviour of calcium and magnesium were expressed by the parabolic law. The elution rate increased with a decrease in the initial pH in the aqueous solution. The slag has buffering action to pH of water and is anticipated to be neutralization effect on acid rain. According to the ministry of the environment in Japan, the average hydrogen ion exponent (pH) of rainfall in Japan is 4.68. Rain of which pH was
less than four fell sometimes and somewhere in Japan. The pH of rainfall at Lake Ijira is 4.51, and it is the lowest in Japan [20]. The damage to ecosystem with the acid rain has not been reported until now, but the monitoring has been continued. Addition of the slag to soil may ease the acidification of soil and effusion of minerals from soil due to the acidification. Then, in this work, as a series of fundamental study of elution of the slag into water, we studied the elution behaviour of the small quantity of slag in water.

2. Experiment

2.1. Slag
The used slag in this experiment was the oxidizing slag which was discharged from stainless steel making in an electronic arc furnace (EAF). The slag was ground, and then sieved. The slag of which size was 1-2 mm was used for the experiment. Table 1 shows the chemical compositions of the slag. The chemical compositions of the oxides were converted from the composition of the metallic components which were determined by an inductively-coupled plasma atomic emission spectrometry (ICP-AES) after alkali fusion of the slag. As shown in figure 1, the X-ray diffractometer (XRD) revealed that the slag was mainly composed of $2\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and $\text{CaO} \cdot \text{SiO}_2$.

| Element | Mass% |
|---------|-------|
| CaO     | 33.0  |
| SiO$_2$ | 44.1  |
| Al$_2$O$_3$ | 5.39 |
| MgO     | 7.68  |
| CaS     | 0.33  |
| Cr$_2$O$_3$ | 3.29 |
| MnO     | 4.09  |
| TiO$_2$ | 1.02  |
| FeO     | 0.74  |
| NiO     | 0.06  |
| CuO     | 0.24  |
| ZnO     | 0.01  |

2.2. Procedure
Because the experimental apparatus and procedure were described in detail in the previous paper [18], a brief account for them was given here. Elution experiment was carried out on a basis of JIS K 0058-1 (Test method for chemicals in slags- Part 1: Leaching test method). Figure 2 shows the schematic of the experimental apparatus. The parts of the apparatus which were contact with water were made of PTFE. The apparatus was set in a simple globe box that was made of vinyl sheet to prevent interfusion of suspended dust in the vessel. The slag of 0.1-100 g in weight set in the vessel. A pH of the purified water was pre-adjusted to be 6.0 by addition of super precision analysis grade HCl. The purified water of 1 L in volume was softly poured in the vessel. Subsequently, the water in the vessel was mixed at a rotating speed of 100 rpm. The slag was laid silently in the container during mixing. The aqueous solution was sucked by a whole pipette, and it was passed through the filter of which pore size was 0.45 μm. The filtrate was analyzed with an ICP-AES. The pH of the aqueous solution in the container was also measured by a pH meter.
3. Results and discussions

3.1. Change in pH with time

Figure 3 shows the change of pH in the aqueous solution with time. In the case of the slag weight of 100 g, the pH increased steeply in the early stage of the elution, and, subsequently, it gradually decreased. In the case of the slag weight of 10 g and below, the pH also increased steeply in the early stage of the elution, and, subsequently, it gradually increased. Generally, the pH increased with an increase in the slag weight. The pHs seem to converge to approximately eight.

The behavior of pH may be determined by the following three reactions. One is adsorption and desorption of H$^+$ to and from surface hydroxyl of the slag and decomposition of the surface hydroxyl [21]. Another is the dissolution of components of the slag into water. Basically, these reactions give the buffering action the slag-water system. The other is formation of H$^+$ by following dissolution of CO$_2$ contained in the air.

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} &= 2\text{H}^+ + \text{CO}_3^{2-} \tag{1} \\
\text{CO}_2 + \text{H}_2\text{O} &= \text{H}^+ + \text{HCO}_3^- \tag{2}
\end{align*}
\]

The increase in the weight of the additive slag implies the increase in the interfacial area of slag-solution. Therefore, pH is influenced by the interfacial area. The pH is mainly determined by adsorption and desorption of H$^+$ to and from surface hydroxyl of the slag and decomposition of the surface hydroxyl. The threshold value of pH is approximately eight. When the pH in the solution is below eight, H$^+$ adsorbs on the slag surface. Oppositely, when the pH is above eight, H$^+$ desorbs into the aqueous solution. This gives the slag – water system buffering action. In north Europe and Canada, acidification of lake becomes problem. Addition of a small amount of the slag into acid lake may improve the pH in acid water in lake.

![Figure 3. Change in pH with time.](image)

3.2. Elution behavior

3.2.1. Main substances

Figure 4 and Figure 5 show the elution behavior of Ca and Mg from the slag into the aqueous solution respectively. Generally, the eluted concentrations of Ca and Mg increased steeply at an early stage of the elution. Subsequently they gradually increased with time. In addition, the eluted concentration of Ca and Mg increased with an increase in the weight of the additive slag. In comparison with the eluted concentration of Mg, the eluted concentration of Ca was higher than that of Mg. The increase in the weight of the additive slag implies the increase in the interfacial area between slag and aqueous solution. However, the eluted concentration does not increase tenfold even if the interfacial area becomes large tenfold. As mentioned above, pH in the aqueous solution became large with an increase
in weight of the additive slag. In previous work [18,19], it was found that the elution rate decreased with an increase in the pH. Therefore, the eluted concentration did not increase proportionally with the interfacial area.

Figure 4. Change in eluted Ca with time.

Figure 5. Change in eluted Mg with time.

Figure 6. Solubility of Ca(OH)$_2$ and CaCO$_3$.

Figure 6 shows the solubility of Ca(OH)$_2$ and CaCO$_3$. Here, the partial pressure of CO$_2$ was $3.85 \times 10^{-4}$ atm in the air. The each solubility was calculated with both Debye-Hückel theory and the combination of the following thermodynamic data [22].

\[
\begin{align*}
\text{CaCO}_3 + 2\text{H}^+ &= \text{Ca}^{2+} + \text{CO}_2(g) + \text{H}_2\text{O} & \log K = 9.74 \quad (3) \\
\text{Ca(OH)}_2 + 2\text{H}^+ &= \text{Ca}^{2+} + 2\text{H}_2\text{O} & \log K = 22.8 \quad (4) \\
\text{CaCO}_3 &= \text{CaCO}_3^0 & \log K = -5.27 \quad (5)
\end{align*}
\]

where $K$ is the equilibrium constant. In addition, the relation between the eluted concentration of Ca and pH, which were obtained experimentally, was also shown in figure 6. In the case of weight of the additive slag of 10 g and below, the eluted concentrations of Ca were lower than the solubility of CaCO$_3$. In the case of weight of the additive slag of 100 g, the eluted concentrations of Ca ranged in the solubility of CaCO$_3$. If Ca in the slag existed as CaCO$_3$, Ca cannot be eluted in aqueous solution. In addition, the XRD revealed that no CaCO$_3$ formed after experiment. Although the eluted Ca concentration existed in the region of formation of CaCO$_3$, it could be said that the reverse reaction of eq. (3) did not proceed. The concentration of Mg was below the solubility of Mg(OH)$_2$ and MgCO$_3$.

Figure 7 shows the elution behavior of Si. In the case of weight of the slag of 100 g, the eluted concentrations of Si increased steeply at an early stage of the elution, and, subsequently, it gradually increased with time. In the case of weight of the slag of 10 g, the eluted concentrations of Si were
lower than the detection limit of the ICP-AES at an early stage of the elution, and, then, it increased gradually. It may be said that the elution of Si occurred when the pH is smaller than approximately 7.5, but further study is necessary for understanding the elution behavior of Si. In the case of weight of the additive slag of 1 g and below, the eluted concentrations of Si were lower than the detection limit of the ICP-AES. Generally, the eluted concentration of Si increases with an increase in weight of the additive slag. Here, the eluted Si concentration was below the solubility of $H_2SiO_3$. Accordingly, it is thought that the elution of Si of the slag proceeds after the formation of $H_2SiO_3$ on the slag surface [18].

Figure 7. Change in eluted Si with time.

Figure 8. Change in eluted Mn with time.

Figure 8 shows the elution behavior of Mn. Generally, the eluted concentration of Mn increased steeply at an early stage of the elution. Subsequently they gradually increased with time. However, when 100 g of the slag was eluted, Mn was not almost eluted at an early stage of the elution. In addition, the concentration of Mn increased with an increase in the weight of the additive slag except for the result of 100 g of the additive slag.

Figure 9. Solubility of MnO, Mn(OH)$_2$ and MnCO$_3$.

Figure 9 shows the solubility of MnO, Mn(OH)$_2$ and MnCO$_3$. Here, as mentioned above, the each solubility was calculated with the combination of the following thermodynamic data [22].

$$\begin{align*}
\text{MnO} + 2\text{H}^+ &= \text{Mn}^{2+} + \text{H}_2\text{O} \\
\text{log } K &= 18.39 \\
\text{Mn(OH)}_2 + 2\text{H}^+ &= \text{Mn}^{2+} + \text{2H}_2\text{O} \\
\text{log } K &= 15.19 \\
\text{MnCO}_3 + 2\text{H}^+ &= \text{Mn}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \\
\text{log } K &= 8.08 \\
\text{Mn}^{2+} + \text{H}_2\text{O} &= \text{MnOH}^+ + \text{H}^+ \\
\text{log } K &= -10.95
\end{align*}$$

\[\text{pCO}_2 = 3.85 \times 10^{-4}\text{atm}\]
In addition, the relation between the eluted concentration of Mn and pH, which were obtained experimentally, was also shown in figure 9. In the case of weight of the additive slag of 10 g and below, the eluted concentrations of Mn were lower than the solubility of MnCO$_3$. In the case of weight of the additive slag of 100 g, the eluted concentrations of Mn ranged in the solubility of MnCO$_3$ at an early stage of the elution, and, subsequently, the concentration increased along the solubility of MnCO$_3$. Although the XRD revealed that there was no MnCO$_3$ in the slag, MnCO$_3$ seemed to be at the surface of the slag. The elution of Mn proceeded when the pH in aqueous solution became lower that the solubility of MnCO$_3$.

Here, the concentrations of Al and Fe were not detected with the ICP-AES. It is favorable for plant that Al is not eluted from the slag, because Al is harmful for plants. The elution of Fe was preferable because Fe was essential element for plants. However, the elution of Fe did not occur.

Table 2 shows extraction ratio from the slag to the aqueous solution. Here, the extraction ratio was the ratio in weight of a substance contained in the additive slag to a substance extracted in aqueous solution. In addition, the eluted concentrations at the end of the elution experiment were used for calculation. The extraction ratios for Ca, Mg and Mn decreased with an increase in weight of the additive slag, whereas the extraction ratio of Si increased with an increase in weight of the additive slag. These results can be explained qualitatively as follows. The increase in the additive weight of the slag means the increase in the interfacial area. The elution rate increased proportionally with an increase in the weight of additive slag. On the other hand, the elution was also influenced by pH. The smaller the pH, the larger the elution rate. Accordingly, in the case of the elution of Ca, Mg and Mn, the elution of them is considered to be influenced by pH than interfacial area. Oppositely, the elution of Si is considered to be strongly influenced by interfacial area. The extraction ratio for Ca was almost the same as the ratio for Mg. This result implied that elution of Ca and Mg occurred depending on the amounts of them contained in the slag.

**Table 2. Extraction ratio from slag to aqueous solution. [%]**

| Weight of additive slag [g] | 0.1 | 1 | 10 | 100 |
|---------------------------|-----|---|----|-----|
| Ca                        | 1.8 | 0.32 | 0.21 | 0.053 |
| Si                        | 0.0 | 0.0 | 0.07 | 0.018 |
| Mg                        | 1.9 | 0.28 | 0.15 | 0.057 |
| Mn                        | 1.6 | 0.46 | 0.41 | 0.022 |

### 3.2.2. Minor substances

Figure 10 shows the elution behavior of Cr. The eluted concentration of Cr increased at an early stage of the elution. Subsequently, the eluted concentration of Cr decreased and, then, was not detected with the ICP-AES. The environmental quality standard (EQS) for soil pollution in Japan regulates the eluted concentration of hexavalent Cr. The eluted concentration of Cr detected with the ICP-AES was lower than the solubility of Cr(OH)$_3$. Accordingly, the eluted Cr was estimated to be trivalent Cr. In addition, the environmental quality standard refers only the eluted concentration of Cr six hours after the elution test. The eluted concentration of Cr obtained experimentally was lower than EQS.

Figure 11 shows the elution behavior of Zn. In the case of weight of the additive slag above 10 g, after the eluted concentration of Zn increased at an early stage of the elution, it decreased. Subsequently, the eluted concentration of Zn increased and decreased again. In the case of weight of the additive slag of 1 g, after the eluted concentration of Zn increased at an early stage of the elution, it decreased. After that, the eluted concentration of Zn was not detected. In the case of weight of the additive slag of 0.1 g, the eluted concentration of Zn was not detected through the elution.
It is estimated that the decrease in the eluted concentrations of Cr and Zn are caused by coprecipitation and adsorption of them on the slag. However, further study of this behavior of Cr and Zn is needed.

Table 3. Eluted concentrations of elements essential for plant. [mg/L]

| Weight of additive amount of slag [g] | Elution for 6h | Elution for 24h | Elution for 120h |
|-------------------------------------|----------------|----------------|-----------------|
| Total N                             | -              | -              | -               |
| Total P                             | -              | -              | -               |
| Total K                             | 0.226          | 0.209          | 2.028           |
| Total Ca                            | 0.316          | 0.308          | 10.5            |
| Total Mg                            | 0.0317         | 0.0154         | 0.144           |
| Total S                             | -              | -              | -               |
| Total Mn                            | 0.0502         | 0.0963         | 0.362           |
| Total Fe                            | 0              | 0              | 0               |
| Total Cu                            | -              | -              | -               |
| Total Zn                            | 0              | 0              | 0               |
| Total Cl                            | -              | -              | -               |
| Total Mo                            | -              | -              | -               |
| Total Si                            | 0.0176         | 0.0176         | 0.00176         |

3.3. Essential elements for plant

Table 3 shows the essential elements for plants and the eluted concentrations. Here, silicon is not an essential element usually, but is an essential element for gramineous plants. This slag can supply water with Ca, Mg and Mn irrespective to the elution conditions. Depending on elution condition, this slag can supply Zn and Si, too. This slag contains no P, K and so on. However, a certain steelmaking slag contains a lot of them. These slag may supply soil with various minerals. This slag satisfies the environmental quality standard for soil in Japan, but, as mentioned above, the eluted concentration of Cr was high at an early stage of the elution. Therefore, adding of this slag into soil directly seems to have the risk of pollution of soil. However, the eluate from the slag can be used for soil because of monitoring the substances and the concentration of them. This eluate can be used as a fertilizer.

4. Conclusions

We studied the influence of weight of the additive slag on elution behavior of the slag into water. The obtained main results can be summarized as follows:

(1) The pH in the aqueous solution increased with an increase in weight of the additive slag.
Calcium, magnesium and manganese, which were essential elements for plants, were eluted from the slag irrespective to elution condition. Silicon and zinc were eluted depending on the conditions. Irrespective to elution condition, iron was not detected in the aqueous solution, and aluminum, which was harmful for plants, was not detected.

The extraction ratio of calcium was almost the same as the ratio of Mg. The elution of them proceeded depending on the amounts of them in the slag.

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