

Pb adsorption by air-cooled blast furnace slag as an intermediate cover soil after termination of post-closure care

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Abstract

To utilize air-cooled blast furnace slag (ABFS) as an intermediate soil for trapping Pb dissolved by the degradation of chelated Pb compounds after the termination of PCC, batch adsorption experiments were performed to clarify the Pb adsorption characteristics of ABFS at two pH levels (8 and 12), and the effect of Na, K, and Ca on these characteristics was investigated. The Henry model could be applied at the both pH with and without the addition of a cation at the total Pb concentration ($C_{e,total}$) as well as the available Pb concentration ($C_{e,av}$), which comprised Pb^{2+} and $[Pb(OH)]^+$ at the equilibrium concentration. Na, K, and Ca had no effect on the Pb adsorption characteristics of ABFS within the investigated concentration range. The distribution coefficient $K_{d,total}$ at pH 12 was 1/50 of the $K_{d,total}$ at pH 8 when $C_{e,total}$ was used, whereas the $K_{d,av}$ at pH 12 was 120 times higher than the $K_{d,av}$ at pH 8 when $C_{e,av}$ was used. Therefore, the decrease in $K_{d,total}$ with pH indicates that the influence of the formation of Pb–OH complexes on Pb adsorption by ABFS is higher than that of an increase in the negative charge density of ABFS.

Keywords: Pb adsorption, air-cooled blast furnace slag, intermediate cover soil, terminated landfill

1. INTRODUCTION

Because fly ash generated from municipal solid waste incineration (MSWI) contains a large amount of heavy metals, the Japanese Waste Management and Public Cleansing Law stipulates specific pre-treatment methods before landfilling can be done in order to prevent the leaching of heavy metals from MSWI fly ash¹⁾. Although chemical treatment with a liquid chelating agent is a common method for the pre-treatment of MSWI fly ash in Japan, Tujimoto et al. pointed out that chelated Pb compounds might degrade after landfilling²⁾. After post-closure care (PCC) is terminated at landfill sites, the leachate from landfill is not treated further. Therefore, if chelated Pb compounds are degraded after the termination of PCC, the dissolved Pb might be discharged into the environment. The discharging of Pb from leachate can be prevented by trapping it using an intermediate soil.

Blast furnace slag (BFS) is a by-product obtained during the production of iron and steel and is primarily used in cement production and road construction. Some researchers have reported that BFS can be utilized as an adsorbent for purification of water containing heavy metal ions³⁻⁸⁾. Therefore, the use of BFS as an intermediate soil for trapping Pb discharged after the degradation of chelated compounds is reasonable. The majority of research on Pb removal using BFS has been conducted at pH levels lower than 6 because at a pH greater than 6, which is expected during PCC⁹⁾, Pb removal is affected by the formation

of $Pb(OH)_2$ precipitate in addition to adsorption¹⁰⁾; thus, it is difficult to determine the dominant reaction mechanism responsible for the removal of Pb. In addition, although Na and K ions are present in the leachate during PCC¹¹⁾ and ion-exchange reactions have been reported as a mechanism of metal-ion adsorption using BFS¹²⁾, research on the effect of such cations on Pb adsorption has been limited⁵⁾.

The purpose of this study was to investigate the Pb adsorption characteristics of air-cooled BFS (ABFS) at pH 8 and 12 in the presence of Na, K, and Ca cations. This was done to utilize ABFS as an intermediate cover soil for trapping Pb dissolved by the degradation of chelated Pb compounds after PCC termination; pH values of 8 and 12 were used because the pH of the leachate after PCC termination is greater than 8. Additionally, the concentration of Pb in the pH range of 9–11 is less than 0.1 mg/L¹³⁾. Since this value conforms to the Japanese effluent standard, hence no Pb-trapping mechanism is required.

2. EXPERIMENTAL

2.1 ABFS

The ABFS used in this study was a commercial product obtained from the JFE Steel Corporation in Japan. ABFS was sieved to separate out grains with a size of 4.75–19 mm. It was then rinsed with distilled water to remove the remaining fine particles and impurities and was dried at 105 °C. In the final step, it was sieved again and stored in a pail. Figure 1 shows the particle-size distribution of the ABFS used in this study. Most particles are smaller than 15 mm and constituted 60% of the sample.

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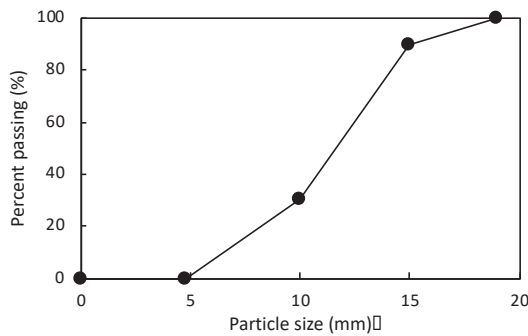


Fig. 1. Particle-size distribution of ABFS.

2.2 Adsorption studies

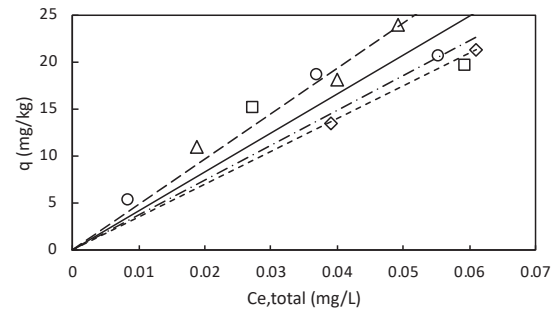
Stock solutions of Pb, Na, K, and Ca were prepared as chlorides at concentrations of 1000 mg-Pb/L, 100000 mg-Na/L, 100000 mg-K/L, and 50000 mg-Ca/L, respectively. For the experiment conducted at pH 8, 10 g of ABSF was introduced into a plastic bottle with 0.5 L, 2 L, or 4 L of raw water (Pb concentration = 0.1 mg/L), whereas for the experiment conducted at pH 12, 10 g ABSF was introduced into a plastic bottle with 0.5 L raw water (Pb concentration = 10 or 20 mg/L). These Pb concentrations do not form precipitates at the desired pH. To evaluate the effect of cations on the Pb adsorption characteristics of ABFS, raw water was prepared at concentrations of 3500 mg-Na/L, 2000 mg-K/L, or 650 mg-Ca/L using the stock solutions. Although these concentrations were higher than those found in leachate during PCC¹¹⁾, they were chosen to clearly determine the effect of cation addition. Raw water was prepared with 1M HCl or NaOH to obtain pH 8 or 12 after the batch adsorption experiment. Batch adsorption studies were performed at a shaking rate of 200 rpm for 6 h at room temperature (25 °C). After adsorption, the pH of the mixtures was measured, and the mixtures were separated via filtration using a membrane filter with a pore size of 0.45 μm. Concentrated nitric acid was then added to the filtrates in 0.5 % (v/v). The concentrations of Pb, Na, K, and Ca were then determined using atomic adsorption spectrometry (Hitachi, Z-2000).

3. RESULTS AND DISCUSSION

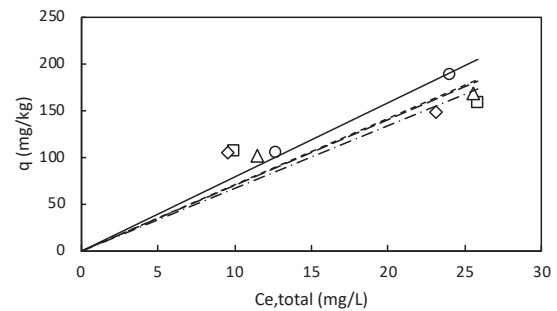
3.1 Adsorption isotherm

Figure 2 shows Pb adsorption isotherms at pH 8 and 12 with or without the addition of a cation. The observed concentration of Pb ($[t-Pb]$) was adopted as the equilibrium concentration. Straight lines in the figure show the Henry isotherm equation (Eq. 1) for the following condition:

$$q = K_{d,total} * C_{e,total} \quad (1)$$



a) pH 8



b) pH 12

Fig. 2. Adsorption isotherms of Pb using $C_{e,total}$ (○—: without addition, □—: Na addition, △—: K addition, ◇—: Ca addition).

Table 1. Obtained R^2 using $C_{e,total}$

pH	No addition	Na	K	Ca
8	0.90	0.59	0.95	1.00
12	0.99	0.64	0.89	0.67

where q (mg/kg) is the amount of adsorbed Pb, $C_{e,total}$ (mg/L) is the equilibrium concentration of observed Pb ($[t-Pb]$), and $K_{d,total}$ (L/kg) is a distribution coefficient for $C_{e,total}$. Table 1 shows the correlation coefficient (R^2) obtained. Since the R^2 values obtained are higher than 0.5, the Henry model is applicable at pH 8 and 12 with or without the addition of a cation. However, at a pH less than 6, the Langmuir and/or Freundlich model for BFS have been shown to be applicable within the equilibrium concentrations of 500-800 mg/L^{10), 14)}. This difference would be caused by the difference in the equilibrium concentration range between this study and their works.

3.2 Effect of cations on Pb adsorption

Figure 3 shows the effect of cations on $K_{d,total}$. In this figure, the total cation concentration was observed in equilibrium and expressed in meq/L. The observed concentrations of Na, K, and Ca were 120-140 meq/L (2800-3300 mg/L), 43-45 meq/L (1700-1900 mg/L), and 13-16 meq/L (560-630 mg/L), respectively. The values of $K_{d,total}$ with cation addition were almost the same as those obtained without cation addition at both

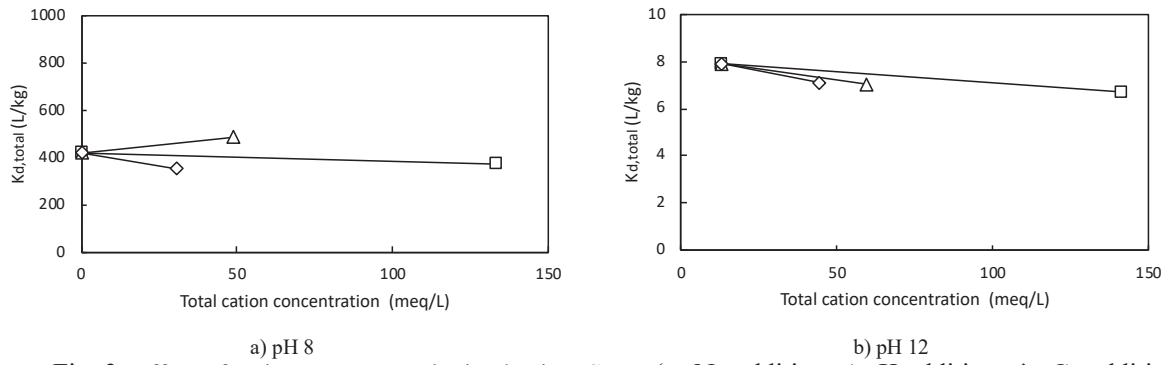


Fig. 3. Effect of cations on $K_{d,total}$ obtained using $C_{e,total}$ (\square : Na addition, \triangle : K addition, \diamond : Ca addition).

pH 8 and 12. This result indicates that the cations have no effect on $K_{d,total}$; however, Dimitrova reported the influence of Na (230 mg/L) and Ca (52 mg/L) on Pb adsorption at pH 4 [5].

3.3 Evaluation of the effect of Pb complexes on Pb adsorption

As shown in Figure 3, without cation addition, the $K_{d,total}$ obtained at pH 12 decreased to 1/50 of the $K_{d,total}$ at pH 8. An increase in pH leads to the formation of Pb hydroxyl complexes¹⁵⁾, and this implies that an increase in the amount of hydroxyl complexes could lead to a decrease in the number of positively charged Pb ions; thus, $K_{d,total}$ would decrease with pH. The effect of Pb complexes with OH^- on Pb adsorption was estimated. The Pb–OH complex reactions are given in Table 2. The total concentration of Pb is expressed as follows:

$$\begin{aligned}
 [t\text{-Pb}] &= [\text{Pb}] + [[\text{PbOH}]] + [[\text{Pb}(\text{OH})_2]] + \\
 &\quad [[\text{Pb}(\text{OH})_3]] \\
 &= [\text{Pb}] \{1 + \beta_{\text{OH}, 1}[\text{OH}] + \beta_{\text{OH}, 2}[\text{OH}]^2 \\
 &\quad + \beta_{\text{OH}, 3}[\text{OH}]^3\} \quad (2)
 \end{aligned}$$

The concentrations of Pb^{2+} and $[\text{PbOH}]^+$, which are expected to be adsorbed onto ABFS, were calculated from the measured pH and $[t\text{-Pb}]$. Figure 4 shows the isotherm for the available Pb concentration $C_{e,av}$ calculated using Eq.3 (where the concentrations of Pb^{2+} and $[\text{PbOH}]^+$ are used as equilibrium concentrations).

$$C_{e,av} = [\text{Pb}] + 0.5[[\text{PbOH}]] \quad (3)$$

In Eq.3, it is assumed that the electrical charge of $[\text{PbOH}]^+$ is half of that of Pb^{2+} .

Table 3 shows the R^2 values obtained using the Henry isotherm equation. Since the R^2 values obtained are higher than 0.5, the Henry model is applicable at pH 8 and 12 with or without the addition of a cation. Figure 5 shows the effect of cation addition on the $K_{d,av}$ obtained using $C_{e,av}$. The cations have no effect on K_d when $C_{e,av}$ is also used as the equilibrium

Table 2. Pb–OH complex reactions and equilibrium constants

Reaction	β
$\text{Pb}^{2+} + \text{OH}^- \rightleftharpoons [\text{Pb}(\text{OH})]^+$	$10^{6.3}$ [16]
$\text{Pb}^{2+} + 2\text{OH}^- \rightleftharpoons [\text{Pb}(\text{OH})_2]$	$10^{10.90}$ [16]
$\text{Pb}^{2+} + 3\text{OH}^- \rightleftharpoons [\text{Pb}(\text{OH})_3]^-$	$10^{13.66}$ [16]

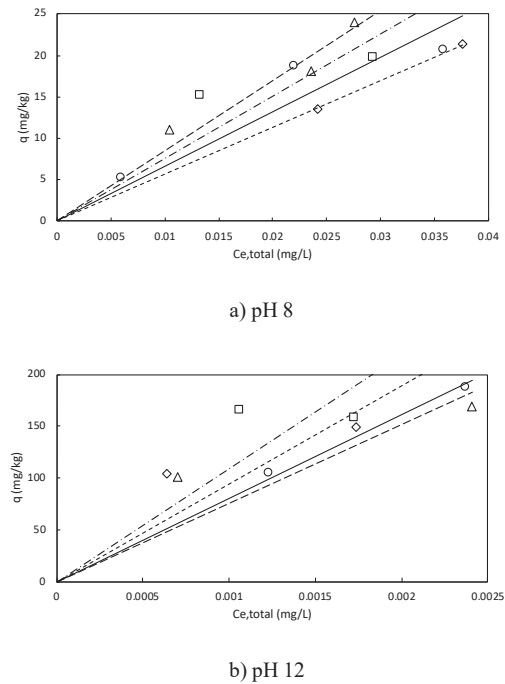


Fig. 4. Adsorption isotherms of Pb using $C_{e,av}$ (\circ —: without addition, \square —: Na addition, \triangle —: K addition, \diamond —: Ca addition).

concentration. The K_d obtained at pH 12 was 120 times higher than that obtained at pH 8 when $C_{e,av}$ was used.

This increase in $K_{d,av}$ with pH agrees with the result reported by Srivastava et al.¹⁷⁾. Therefore, the decrease in $K_{d,total}$ with an increase in the pH indicates that at an increasing pH, the influence of the formation of Pb–OH complexes on Pb adsorption by ABFS is

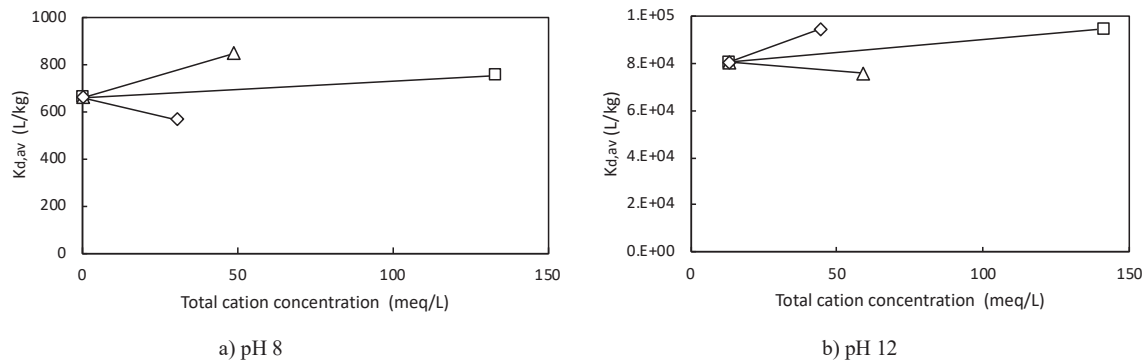


Fig. 5. Effect of cations on $K_{d,av}$ obtained using $C_{e,av}$ (□: Na addition, △: K addition, ◇: Ca addition).

greater than that of an increase in the negative charge density of ABFS.

These results suggest that the adsorption capacity of ABFS under the conditions of high pH in leachate can be estimated by considering Pb–OH complexes, and the ability of ABSF as an intermediate cover soil for trapping Pb after PCC termination can be evaluated.

4. CONCLUSION

In order to utilize ABFS as an intermediate cover soil for trapping Pb discharged by the degradation of chelated Pb compounds after the termination of PCC, the Pb adsorption characteristics of ABFS were determined at pH 8 and 12 with or without the addition of Na, K, and Ca cations.

The Henry model could be applied at both pH 8 and 12 with or without the addition of cations when using both $C_{e,total}$ and $C_{e,av}$ as equilibrium concentrations. The addition of Na, K, and Ca cations had no effect on Pb adsorption by ABFS within the concentration range investigated in this study. When using $C_{e,total}$ as the equilibrium concentration, the $K_{d,total}$ at a pH of 12 was 1/50 of the $K_{d,total}$ at a pH of 8. When using $C_{e,av}$ as the equilibrium concentration, the $K_{d,av}$ at a pH of 12 was 120 times higher than that at a pH of 8. Therefore, the decrease in $K_{d,total}$ with an increase in pH indicates that with increasing pH, the influence of the formation of Pb–OH complexes on Pb adsorption by ABFS is greater than that of the increase in the negative charge density of ABFS. These results suggest that the viability of ABFS as an intermediate cover soil for trapping Pb after PCC termination can be evaluated by considering the behavior of Pb–OH complexes.

Acknowledgement

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|----|-------------|------|------|------|
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| 12 | 0.99 | 0.97 | 0.72 | 0.62 |
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