

Leaching characteristics of boron and selenium for various coal fly ashes

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Abstract

The leaching characteristics of B and Se for coal fly ash (CFA) were examined. Twenty-one CFA samples were subjected to a leaching test, in which CFA was shaken with pure water in a liquid to solid ratio (L/S) of 100 for 24 h at room temperature. The correlation between the leaching amount and the concentration of element in CFA was investigated. The leaching amounts of B, Ca, S, and Se were essentially dependent upon their concentrations in CFA. As the degree of % leaching was higher, the leaching amount was more dependent upon the concentration. Also, the leaching test was performed under constant pH conditions. The leaching of Se tended to increase as the pH in the aqueous phase was raised. For CFA samples, which gave large degree of Ca leaching amount, the leaching of B and Se was decreased especially under high alkaline conditions. The effects of pH and the presence of leached Ca ion in the aqueous phase upon the leaching behavior were discussed.

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1. Introduction

Coal contains various hazardous elements in trace amount. When coal is burnt in coal-fired power plants, many of those elements are condensed in coal fly ash (CFA), which is collected by dust collectors, such as electrostatic precipitators. Therefore, CFA contains various hazardous elements in trace but considerable amount [1,2]. Usually, CFA is subjected to disposal or reuse, and the existence of those hazardous elements in CFA will cause environmental problems, mainly due to leaching of those elements into environmental water. Jones has described that As, B, Mo, and Se in CFA are likely to leach out, because those elements tend to form hydrophilic oxides to be dissolved as oxyanion forms [3]. In our previous papers, we studied the leaching of As from two CFA samples and the promotion of

As leaching by the addition of chelating agents was described [4,5].

In Japan, the leaching of B and Se from CFA now becomes one of the great concerns in the disposal of CFA. So far, several studies have been done about the leaching of B and Se from CFA. Cox et al. studied the leaching of B from a CFA and the effect of pH was tested [6]. Halligan and Pagenkopf examined the effect of various factors including liquid to solid ratio (L/S), particle size, and pH upon the leaching of B using five kinds of CFA samples [7]. Also, Hollis et al. investigated the mechanism of B leaching from a CFA [8]. The leaching of As and Se from a CFA was studied by van der Hoek and Comans, and they described that the leaching of those elements was controlled by a sorption mechanism [9,10]. Hassett and co-workers have described that the stabilization of B and Se is attained by the formation of ettringite phase on the surface of CFA [11–13]. There have been several studies about the leaching of B from a CFA, when it is used for a soil amendment [14–18]. Although many works about the leaching of trace elements from CFA have been done

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especially in the United States, still there are not a few things worth being performed. Japan is the world's biggest coal-importing country, and thus many types of coals from various countries are imported and used in a coal-fired power plant. The properties of such coals, including the concentrations of elements, are quite varied, and thus the properties of CFAs produced are also varied. To our knowledge, there have been no systematic studies about the leaching of B and Se by using such Japanese CFAs. It should be important to clarify the essential factor to determine the leaching amount of these elements when the leaching of such CFAs is performed.

The leaching test of CFA samples has been mainly performed with deionized water or acetate buffer solutions [11–13]. Compared to these tests, there have been not many studies about the leaching test under the constant pH conditions. However, considering the effect of acid rain and the clarification of leaching mechanism, the pH-constant leaching is also useful.

In this study, we examined the leaching characteristics of B and Se for 21 kinds of CFA samples, which had been collected from two coal-fired power plants in Japan. The factors affecting the leaching of B and Se are assessed when the kind of CFA is different. The effect of other element leaching as well as that of pH are also discussed, based on the leaching test under constant pH conditions.

2. Experimental

2.1. Coal fly ash

Twenty-one CFA samples (Ashes-1–21) collected from two coal-fired power plants in Japan were tested. The coals

for these CFA samples were bituminous coals from China (Ashes-6, 12, 15, 17, and 20) and Indonesia (Ashes-2, 14, 19, and 21); others were from Australia. The concentrations of elements (except for B and Se) in these CFA samples were analyzed by JIS M 8815 [19] and X-ray fluorescence spectrometry using a Philips PW1404 instrument, and the results are recorded in Table 1.

2.2. Determination of B and Se in CFA

A 0.1 g portion of each CFA sample was weighed and transferred into a pressure-resistant PTFE bottle (volume 100 ml), and the mixture of acids ($\text{HNO}_3 + \text{H}_2\text{O}_2$, 5:3 ml) was added. The bottle was then sealed and placed in a microwave processor (Milestone ETHOS1600), and a digestion program was performed. After cooling and the addition of further $\text{HNO}_3 + \text{H}_2\text{O}_2$ (2:1 ml), microwave processing was performed again. After cooling and filtration, the filtrate was diluted to a fixed volume (50 ml), and the concentration of B in the solution was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin–Elmer Optima 3100RL). For the determination of Se, removal of the acids by evaporation was performed, and then the residue was diluted to a fixed volume (50 ml), and the concentration of Se was measured by graphite furnace atomic absorption spectrometry (GFAAS) using a Thermo Elemental SOLAAR MQZ instrument.

2.3. Leaching test

CFA (0.5 g) was added to 50 ml of pure water, which accounted for a L/S of 100. After being shaken for 24 h in

Table 1
Concentrations of elements in CFA (wt%)

CFA	Al	Ca	Fe	K	Mg	Na	S	Si	B ($\mu\text{g/g}$)	Se ($\mu\text{g/g}$)
Ash-1	19.0	2.08	3.15	0.90	0.57	0.27	0.08	23.8	64	4.2
Ash-2	16.0	2.49	6.04	1.83	1.29	0.67	0.27	23.6	830	5.2
Ash-3	17.1	0.18	1.02	1.16	0.13	0.04	0.09	29.3	32	5.6
Ash-4	12.6	0.54	1.81	1.13	0.45	0.39	0.14	32.1	120	4.0
Ash-5	12.0	4.63	3.68	0.41	0.95	0.17	0.28	28.2	260	16
Ash-6	17.7	3.45	3.40	0.55	1.16	0.59	0.50	23.4	620	95
Ash-7	11.4	0.43	2.08	1.01	0.41	0.33	0.18	33.3	93	8.0
Ash-8	16.6	0.25	1.37	1.20	0.18	0.09	0.18	29.3	52	12
Ash-9	12.5	0.43	2.01	1.14	0.45	0.38	0.23	32.1	110	4.6
Ash-10	11.8	4.49	4.08	0.41	0.92	0.16	0.35	28.1	260	9.4
Ash-11	18.6	2.81	4.09	0.86	0.69	0.37	0.16	22.6	120	22
Ash-12	22.8	4.22	1.44	0.25	0.29	0.05	0.31	20.8	350	19
Ash-13	13.1	0.84	3.00	1.03	0.36	0.42	0.24	30.6	120	8.2
Ash-14	15.3	3.67	3.90	1.02	1.27	0.73	0.71	24.4	1100	35
Ash-15	15.8	4.25	3.90	0.92	1.41	0.70	0.91	23.4	880	70
Ash-16	11.2	0.61	1.94	0.95	0.43	0.51	0.14	33.3	96	5.1
Ash-17	11.9	0.64	3.05	0.91	0.44	0.24	0.19	32.0	96	5.8
Ash-18	11.9	0.66	2.21	0.98	0.47	0.54	0.38	32.4	110	13
Ash-19	18.6	1.81	3.13	0.61	0.51	0.47	0.48	24.6	690	18
Ash-20	14.4	3.20	7.95	0.53	1.50	0.53	0.20	22.2	640	19
Ash-21	18.4	5.17	2.97	1.92	1.17	1.39	0.57	22.4	810	9.4

a stoppered test tube at room temperature (24–25 °C), filtration was performed to separate the CFA. The concentration of Se in the filtrate was measured by hydride generation atomic absorption spectrometry (HGAAS) using a Nippon Jarrel Ash AA890 instrument with a hydride generation system, while those of B and other elements were measured by ICP-AES. The value of ‘leaching amount’ was defined as the amount of element leached per 1 g of CFA. The value of ‘% leaching’ was defined as [(leaching amount)/(element concentration in CFA)] × 100. When the leaching test was performed under a constant pH, a solution of HNO₃ or NaOH was added to the test solution at intervals throughout the test to keep the pH constant.

3. Results and discussion

3.1. Determination of B and Se in CFA

The determinations of B and Se in 21 CFA samples were carried out by use of microwave-assisted acid-digestion followed by ICP-AES analysis and GFAAS analysis, respectively. The results are also recorded in Table 1. The concentrations of B and Se of these 21 CFA samples varied from 32 to 1100 µg/g and from 4.0 to 95 µg/g, respectively. Coals for the 21 CFA samples are from various places, so that the chemical compositions of CFA samples are greatly varied (see Table 1).

The accuracy of the determination of Se was demonstrated by use of a certified reference material, NIST-1633b (National Institute of Standards and Technology, USA; certified, 10.26 ± 0.17 µg/g; measured, 10.8 ± 0.3 µg/g). However, for B, there are no proper certified reference materials possessing the concentration available.

3.2. Leaching of elements from CFA

The 21 kinds of CFA samples listed in Table 1 were subjected to a leaching test, in which CFA was shaken with pure water in L/S = 100 for 24 h. In Table 2, the leaching amounts of B, Ca, Mg, S, and Se as well as the final pH in the leachate are recorded. Fig. 1 presents plots of the leaching amount against the element concentration in CFA for B, Ca, Mg, S, and Se. The correlation between the leaching amount of S and its concentration in CFA was quite high ($R^2=0.96$), and the slope of the correlation was obtained as 0.97, reflecting high degree of %S leaching, i.e. the majority of S in CFA is leached out.

The correlations for B, Ca, and Se were inferior to that for S, and the slopes were rather low (0.22–0.48). The degree of % leaching varied from 13 to 77% for B, while that for Ca, from 12 to 55% and that for Se, from 11 to 51%. However, the leaching amount is essentially dependent upon their concentrations in CFA for these elements (Fig. 1). Consequently, it is found that when CFAs containing high concentrations of B and Se are subjected

Table 2
Leaching of elements from CFA

CFA	Leaching amount (µg/g for B and Se; mg/g for Ca, Mg, and S)					Final pH
	B	Ca	Mg	S	Se	
Ash-1	14	3.1	0.023	0.53	2.1	10.7
Ash-2	380	2.2	0.39	1.9	2.2	9.0
Ash-3	4.0	0.22	0.049	0.48	0.74	4.4
Ash-4	92	1.2	0.16	0.70	1.1	8.5
Ash-5	50	14	<0.005	1.5	5.7	12.0
Ash-6	480	10	0.016	3.6	45	11.3
Ash-7	27	1.1	0.35	1.1	1.4	6.4
Ash-8	8.5	0.46	0.15	1.3	1.3	4.4
Ash-9	31	1.2	0.41	1.8	0.50	4.6
Ash-10	43	12	<0.005	2.2	2.5	11.9
Ash-11	19	3.5	0.068	1.1	6.6	8.7
Ash-12	89	7.4	<0.005	2.7	8.4	11.5
Ash-13	55	2.0	0.23	2.1	1.9	7.8
Ash-14	380	8.1	0.57	5.7	18	10.3
Ash-15	380	10	0.64	9.1	30	10.1
Ash-16	66	1.9	0.16	1.3	1.5	9.0
Ash-17	53	1.6	0.23	1.8	0.70	4.8
Ash-18	62	3.6	0.61	3.7	1.5	4.9
Ash-19	310	2.2	0.52	4.3	1.9	4.6
Ash-20	200	9.0	<0.005	1.8	7.6	12.4
Ash-21	250	5.2	0.64	5.5	1.2	5.8

CFA was shaken with pure water in L/S = 100 for 24 h.

to reuse or disposal, the leaching of these elements should be considered. Almost no correlation was observed when the leaching of Mg was plotted, and the degree of %Mg leaching was quite small (<1–13%). The solubility of MgO, which may be main species of Mg in CFA, is much smaller than that of CaO. Consequently, as the degree of % leaching is higher, the leaching amount tends to be more dependent upon the element concentration in CFA.

To confirm the oxidation state of Se species in the leachate, a reduction procedure (boiling with HCl) was performed before the HGAAS measurement to convert Se(VI) to Se(IV). As shown in Table 3, there were no significant differences between the values obtained with and without the reduction procedure. This result suggests that Se species in the leachate are mainly Se(IV), i.e. selenite ion (SeO_3^{2-}), which has been reported in some literature [3,20,21].

3.3. Dependence of % leaching upon the final pH

In Fig. 2, the final pH in the leachate after the leaching test for 21 CFA samples is plotted against the leaching amount of Ca. When the Ca leaching amount was larger, the pH tended to rise. It appears that the main species of Ca in CFA are alkaline species, such as CaO, and the leaching of CaO will elevate pH in the leachate. The final pH was almost independent of the leaching amount of other alkaline salt elements, such as Mg, Na, and K. This is because the leaching amount of Ca is much greater than those of the elements [22,23]. Also, CFA samples, which gave large leaching amount of S, did not necessarily provide low pH of

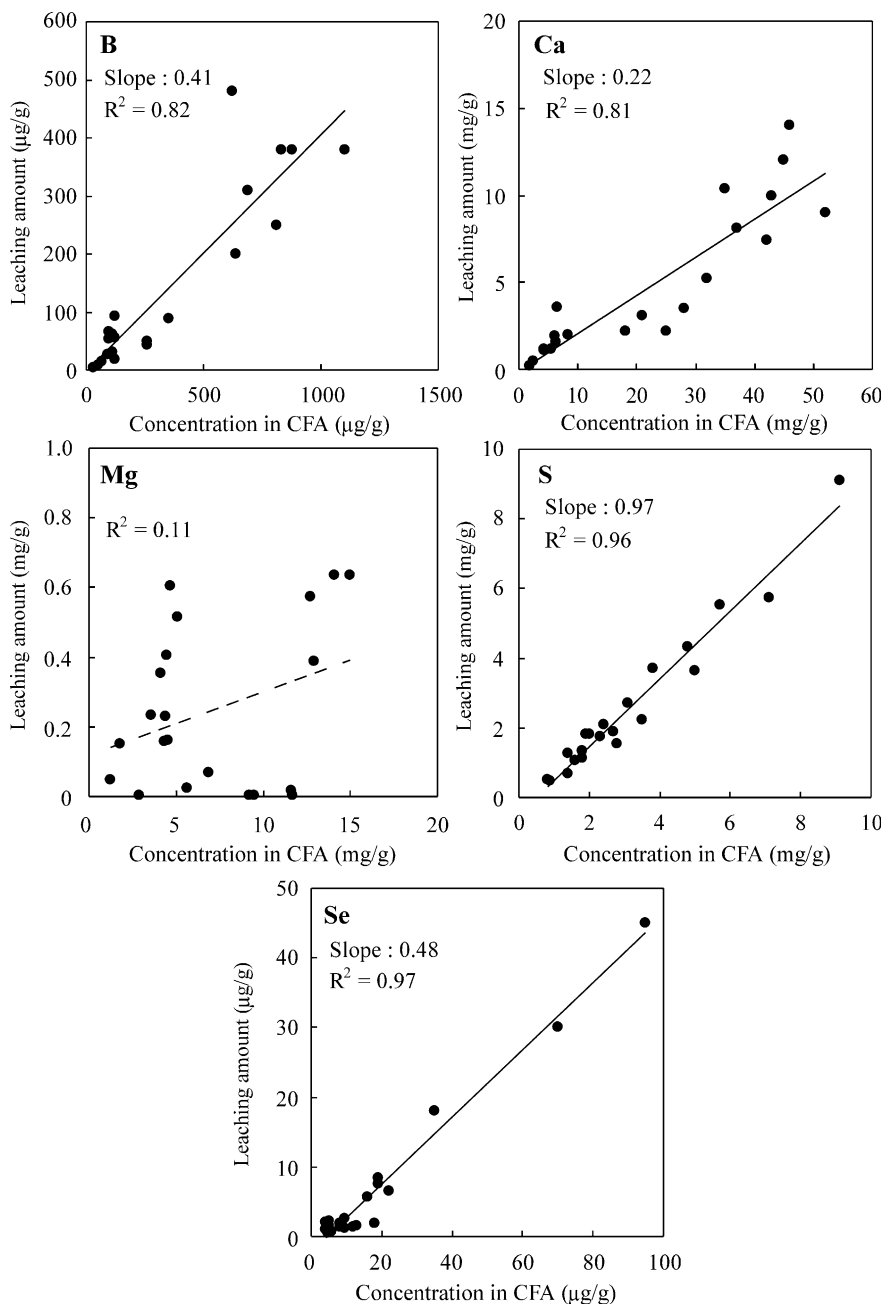


Fig. 1. Correlation between the leaching amount and the concentration of element in CFA.

leachate. It appears that the chemical form of S leached is not acidic sulfates but probably neutral sulfates.

It has been proved that the leaching amount of B and Se is roughly dependent upon the concentration of these elements in CFA (Fig. 1). However, as mentioned above, the degree of % leaching for these elements considerably varied. To clarify the factors affecting the degree of % leaching, its dependence upon the final pH in the leachate was studied, and the results are shown in Fig. 3. Although the degree of % B leaching was almost independent of the final pH, there was some relationship between the %Se leaching and the pH. The leaching of anionic species,

Table 3
Determination of Se in the leachate with and without the reduction procedure

CFA	Se concn. in leachate (mg/l)	
	Without reduction	With reduction ^a
Ash-1	0.021	0.021
Ash-6	0.45	0.47
Ash-15	0.30	0.32
Ash-16	0.015	0.012

Leaching conditions were the same as those in Table 2.

^a The leachate (5 ml) was boiled with 5 ml of concentrated HCl, and then the HGAAS measurement was carried out.

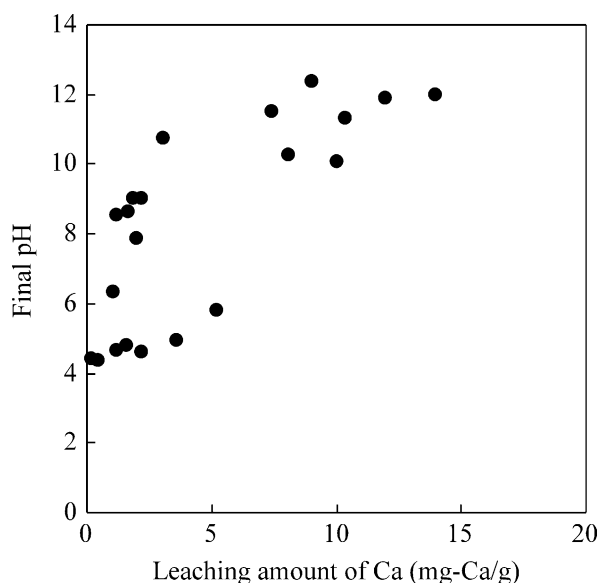


Fig. 2. Plot of final pH vs. the leaching amount of Ca.

such as SeO_3^{2-} , from CFA will increase with an elevation of pH, because the species repel anionic surface of CFA which mainly consists of aluminosilicate and iron oxide phases.

3.4. Leaching of B and Se from CFA under constant pH conditions

To probe the effect of pH upon the leaching behavior of B, the leaching test was carried out under constant pH conditions in the leachate; the pH was controlled by the addition of HNO_3 or NaOH solution at an interval throughout the test. As shown in Fig. 4, the degree of %B leaching for Ashes-5 and 6 tended to decrease with an elevation of pH, whereas that for Ashes-2 and 4 was not so varied. Usually B occurs in oxyanionic forms, such as borate in aqueous media, and the leaching of anionic species from CFA will increase with an elevation of pH due to the electrostatic repulsion between the anionic species and the anionic surface of CFA as mentioned above. However, especially for Ashes-5 and 6, the B leaching displays the opposite feature, in which the leaching decreased when pH was raised.

In Table 4, the leaching amounts of Ca obtained for the leaching test under constant pH conditions are recorded. For all of the four CFA samples, the leaching of Ca showed typical cationic behavior, in which the leaching increases as pH is lowered due to the competitive replacement by H^+ . It is also possible that under high pH conditions the precipitation of CaCO_3 occurs, resulting in the decrease in the Ca leaching; carbonate ion will come from CFA itself and/or atmosphere. The leaching amounts of Ca for Ashes-5 and 6 were much greater than those for Ashes-2 and 4. Therefore, the CFA samples, which provide high Ca leaching amounts, tend to show pH dependence in the leaching of B, whereas those with low Ca leaching amounts have no such a tendency. Thus, it appears that the leaching

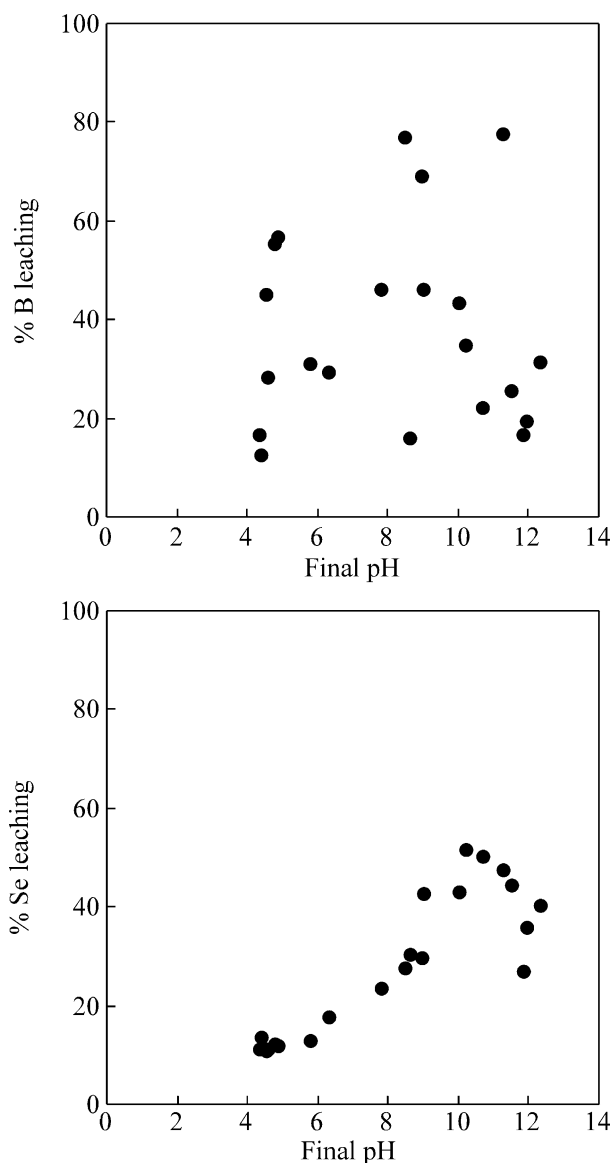


Fig. 3. Plot of % leaching of B and Se vs. final pH.

reaction involves some interaction between B and Ca in the aqueous phase.

It has been reported that hydrated mineral phases, such as ettringite $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$, are formed when CFA is contacted with water under alkaline conditions; ettringite can occur over several hours or can take months depending on the availability of the components [11–13,24,25]. The ettringite phase may trap oxyanionic species, such as borate and selenite. Thus, it is anticipated that the decrease in the B leaching observed for Ashes-5 and 6 is ascribed to the formation of the ettringite phase. Also, some reports have described the possibility of coprecipitation with CaCO_3 in the leaching of B from CFA [8,26]. Consequently, the present leaching reaction of B may involve the mechanisms, (i) trap of B species by the ettringite phase formed, and/or (ii) coprecipitation of B species with CaCO_3 .

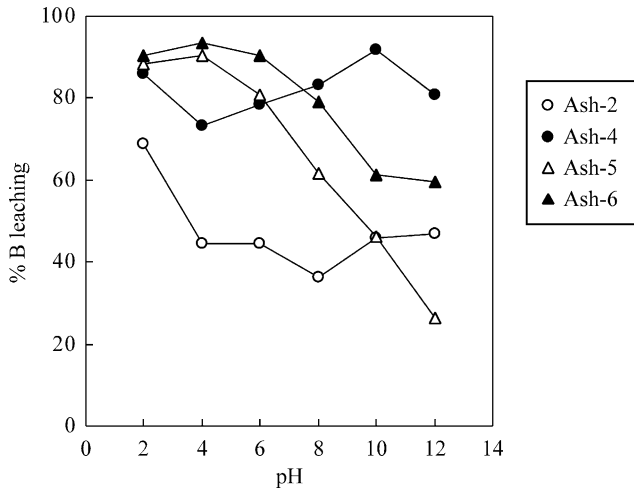


Fig. 4. Plot of % leaching of B vs. pH. Leaching conditions were the same as those in Table 2 except that pH was kept constant.

For Ashes-2 and 4, the B leaching is not so varied by changes in pH, suggesting that normal anionic feature and the opposite feature may compete each other. Actually, as shown in Fig. 5, when CaCl₂ was initially added in the aqueous phase for the leaching test of Ash-4 under alkaline conditions, the B leaching was considerably retarded. This result supports the above idea that some interaction between B and Ca reduces the leaching of B.

Fig. 6 presents the % leaching of Se, when the leaching test was conducted under constant pH conditions. For Ashes-2, 4, and 6, the Se leaching gradually increased up to pH 8, and then the leaching greatly increased above the pH. This fact can be explained as follows. It has been reported that aluminum oxide (activated alumina) and iron oxide have a great adsorption ability for selenite and arsenate, and the adsorption has a pH dependency in which the adsorption is enhanced when monoanionic species (HSeO₃⁻ and HAsO₄⁻) are mainly present [9,10,27,28]. The pK_a values of selenite are 2.53 and 7.3. The pH dependency for Se leaching shown in Fig. 6 apparently reflects the adsorption behavior above mentioned. It is proposed that the aluminosilicate and iron oxide phases on the surface of CFA work as adsorbents and give strong affinities to HSeO₃⁻, and thus the Se leaching is repressed under pH below 8.

Table 4
Leaching amount of Ca from CFA under constant pH conditions

pH	Leaching amount of Ca (mg-Ca/g)			
	Ash-2	Ash-4	Ash-5	Ash-6
2	11.4	2.0	23.5	16.8
4	4.6	2.1	21.1	14.3
6	4.3	1.9	18.8	10.3
8	2.4	1.0	15.0	8.5
10	2.2	1.0	12.3	9.6
12	2.0	0.8	7.1	7.0

Leaching conditions were the same as those in Table 2 except that pH was kept constant.

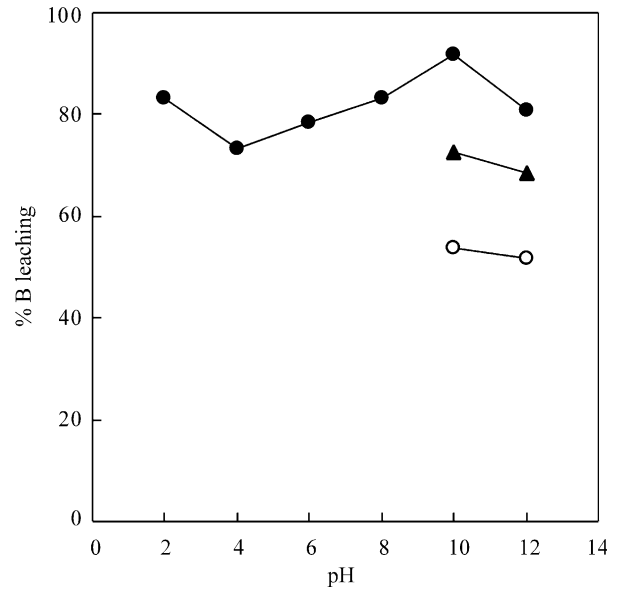


Fig. 5. Effect of adding Ca salt in aqueous phase upon the B leaching for Ash-4. In the aqueous phase, 14 (○), 5 (▲), or 0 mM (●) of CaCl₂ was initially added when the leaching test was carried out under constant pH conditions.

Only Ash-5 exhibited a decrease in the Se leaching under a high pH. As seen in Table 4, Ash-5 gives the largest leaching amount of Ca among the four CFA samples tested. Therefore, it appears that the decrease in the Se leaching is also attributed to the trap of Se species by the ettringite formed.

4. Conclusions

The following conclusions were obtained.

- (1) The leaching amounts of B, Ca, S, and Se were essentially dependent upon their concentrations in CFA.

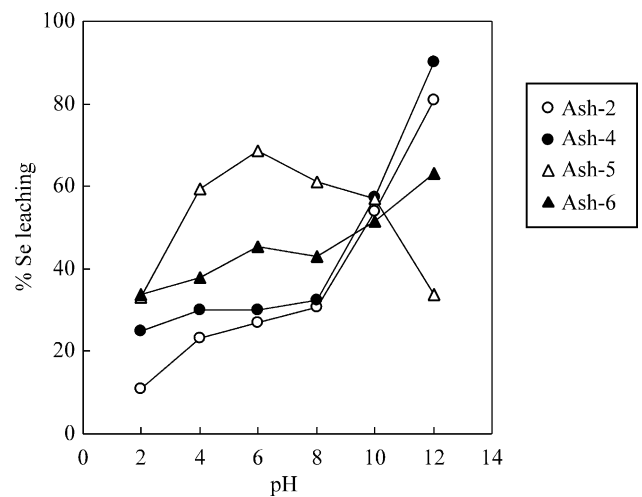


Fig. 6. Plot of % leaching of Se vs. pH. Leaching conditions were the same as those in Table 2 except that pH was kept constant.

As the degree of % leaching in average was higher, the leaching amount tended to be more dependent upon the concentration. Therefore, it is proved that when CFAs containing high concentrations of B and Se are subjected to reuse or disposal, the leaching of these elements should be of special concern.

- (2) Based on the leaching test under constant pH conditions, it was found that the presence of Ca leached in the leachate plays an important role in the leaching behavior of B and Se.
- (3) The leaching of B may involve the trap of B species by the ettringite phase and/or coprecipitation of B species with CaCO_3 , leading to the decrease in the leaching under alkaline conditions.
- (4) The leaching of Se may involve the adsorption of SeO_3^- onto the aluminosilicate and iron oxide phases on the CFA surface. For a CFA, which gives a large Ca leaching amount, the trap of Se species by the ettringite formed is likely to occur.
- (5) The mineralogical composition is also important for the leaching behavior of the elements, and it is hoped that more extended study will be made to clarify the leaching mechanism of the elements.

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