Distributions and Leaching Behaviors of Toxic Elements in Fly Ash

Quanzhi Tian, Binglin Guo, Shingo Nakama, and Keiko Sasaki

Department of Earth Resources Engineering, Faculty of Engineering, Kyushu University, 744 Motooka, Nishiku, Fukuoka 819-0395, Japan

ABSTRACT: Fly ash usually contains a considerable amount of toxic elements that can be leached into the environment, thereby easily leading to serious contaminations. In this work, the leaching behaviors of poisonous elements including boron (B), phosphorus (P), vanadium (V), chromium (Cr), arsenic (As), selenium (Se), molybdenum (Mo), antimony (Sb), and tungsten (W) from fly ash were explored by sequential extraction. Importantly, the associations of these elements in fly ash were discussed based on their leaching and X-ray absorption near-edge structure (XANES) results. From the XANES results, it was observed that V(IV), Cr(III), As(V), Se(IV), and W(IV) were their main states of existence in fly ash. In terms of leaching results, large amounts of Mo and W were leached into pure water, which indicated their high mobilities. Furthermore, the occurrence of Mo in fly ash was mainly in the form of oxides, and W had complex associations including WX4 (X can be monovalent anions), its reduction state or association with the elements that can be oxidized, and existence in silicates. B was as easily released into the environment as Mo and W. It can have several associations with the other cations, such as Ca2+, Na+, and Mg2+, and occurs in silicates. In contrast, most of the Cr and Sb were locked in silicates, indicating that they were very stable in fly ash. In addition, V, P, and As can exist within the structure of silicates as well. However, a considerable amount of them leached in the reduction step with a low pH. Hence, they can be associated with Ca2+, Na+, Mg2+, or Fe3+. In terms of Se, oxidation processes played an important role in controlling its leaching because of the oxidation of Se(IV) to Se(VI). Calcium selenite should be the predominant form of Se in fly ash.

1. INTRODUCTION

Coal as an energy source for power generation has been used for a long time. Every year, billions of tons of coal are burnt, which, meanwhile, generates large amounts of fly ash that is regarded as an industrial waste.1 If it cannot be disposed off properly, serious environmental problems, such as water and soil contamination and disruption of ecological cycles, would be easily caused. Many aggressive efforts have been carried out toward recycling the fly ash for utilization.2 In addition to being used as an additive in cement, fly ash has been used in many other applications, including road base construction, soil amendment, and zeolite and geopolymor synthesis. However, these applications are not sufficient for the complete utilization of the generated fly ash. There is still a great deal of fly ash disposed in ash ponds, lagoons, or landfills.2 The main harmful aspect of the fly ash during its utilization or disposal is that the toxic elements in the fly ash are likely to be released into the environment when it comes in contact with water. It has been reported that the trace element concentrations in fly ash are generally 4–10 times higher than their original concentrations in coal.3 Among the toxic elements in fly ash, the metalloid elements are usually present in anionic forms in solution. Some metal elements, such as vanadium (V), molybdenum (Mo), and tungsten (W), can also exist in the form of anions in aqueous condition. Because of the negative charge of these ions, they exhibit a higher mobility, which means that they can lead to environmental pollution and human health problems broadly and extensively. Thus, more attention should be paid to the control of anionic pollutants possibly leached from the fly ash; this is imperative for a better understanding of the occurrences of these elements in fly ash.

The possible chemical associations of the trace elements in fly ash have also been noted. Finkelman et al.4 proposed that arsenic (As) was primarily associated with pyrite in coals, which later was decomposed during burning and gave rise to a dominant surface association in fly ash. This was also confirmed by Goodarzi and Huggins.5,6 Being similar to As, boron (B) and Mo are also recognized as surface associations, which means that they can be easily released from fly ash. Sulfur (S) is a major soluble element in fly ash in the form of SO4^{2−} that has a strong relationship with calcium (Ca) leaching. Selenium (Se) is an element that is most strongly enriched in coal with respect to many rocks, and coal fly ash can be viewed as a major source of this element.7,8 A view that the Se species can also be in the structure of calcium sulfide was proposed by Freyrier and Voigt.9 Other elements including chromium (Cr), antimony (Sb), and V are deemed to be associated with the aluminosilicates (primarily in glass phase) in fly ash.5,10,11 However, Hansen’s research implied that V and Sb were associated with the surface materials on the ash
particles. Phosphorus (P) was believed to be extremely insoluble in fly ash, but there are very limited data available in the literature supporting this viewpoint. In terms of W, Vassilev and Vassileva detected soluble scheelite in coal fly ash, and until now, there was no other report on the occurrence of W in fly ash. Therefore, even though the research on chemical associations of trace elements in fly ash has been considerable, the distributions of these elements in fly ash have not been understood comprehensively. There are still contradictions in terms of the existing states of some elements in fly ash. Thus, in this investigation, a modified sequential extraction procedure was adopted to explore the occurrences of elements including B, P, V, Cr, As, Se, Mo, Sb, and W in fly ash. X-ray absorption near-edge structure (XANES) was applied to determine the valences of specific elements by comparing with reference materials. In addition, the properties of fly ash were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), and so forth.

2. RESULTS AND DISCUSSION

2.1. Characterizations of Fly Ash Samples. The particle size distributions of fly ashes are shown in Figure 1. Except for samples YEM and FAR, the yields of 100 μm of other samples exceeded 80%. For YEM and FAR, an approximately 40% proportion of fly ash particles was distributed in the coarse size fraction (+100 μm), especially for YEM. In general, the particle sizes of these samples were mainly under 150 μm, which indicated that fly ash can have a large surface area and may easily release pollutants associated on the surface. Figure 2 presents the XRD patterns of the samples. The main crystalline minerals are quartz (SiO2) and mullite (3Al2O3·2SiO2) in fly ashes. Other minerals, such as annaline, calcium oxide, magnetite, and hematite, were also contained in some fly ashes. At a diffraction angle of approximately 20–30° in the XRD patterns, there were indistinct swell peaks, which implied the existence of amorphous substances in fly ash. Generally, fly ash contained a considerable amount of amorphous substances (generally 50%), mainly consisting of SiO2 and Al2O3, and this had been confirmed by another reference. The compositions and loss on ignition (LOI) values of these samples are shown in Table 1. All the samples used in the study were from class F fly ash [([SiO2 + Al2O3 + Fe2O3] ≥ 70)] according to the ASTM standard (C618). Silica and alumina were the predominant minerals in the fly ashes, and the total content of CaO was approximately 2% except DAT with a CaO proportion of 4.57%. YAN had a higher value of LOI (8.63%) than the other samples, whose LOI values were in the range from 3.60 to 7.03. This suggested that there was more unburned carbon in the sample YAN.

Figure 3 shows the micromorphology images of fly ashes. Generally, fly ash particles are dominantly spherical in shape and mainly consist of solid sphere, cenosphere, irregular debris, and porous unburned carbon. This was in coincidence with the SEM observations of ZHA, YEM, NAY, FAR, DAT, SHU, JAP, and IND. However, spherical particles cannot be found in YAN and PAN, instead, they were mainly composed of irregular-shaped debris. This was because the fly ashes were collected from fluidized bed combustion (FBC) boilers that provided a low combustion temperature of 850–900 °C. Under low temperature, most minerals in coal did not undergo melting but only softened, which led to the morphology of the fly ash particles presented in the SEM images.

2.2. Valences of Toxic Elements in Fly Ash. The elements of P, As, Sb, Cr, Mo, W, B, Se, and V were the focus of this investigation. B and P are generally present in the form of BO3− and PO43− in solution, showing valences of +4 and +5, respectively. Thus, their valences can be easily concluded in the fly ash. However, the other elements can have two or more valences, and their valences in the fly ash can have a significant effect on the leaching behavior. Therefore, a better understanding of their existing states in the fly ash would be very useful for predicting their extent of contamination on the environment. The XANES technology can provide the valence information of the elements in fly ash through comparison with reference materials. The samples YAN (nonspherical particles), FAR, and JAP (spherical particles) were chosen for the XANES tests. Figure 4 shows the XANES spectra of the fly ashes and standard samples. A comparison of the As K-edge XANES spectra (Figure 4c) of the samples to the spectra of reference materials demonstrated that arsenic was predominantly As(V) in fly ash. As in original coal was a mixture of As(III), As(V), or As/pyrite. The high temperature during coal combustion may lead to the oxidation of As(III) or As(0)
It had been reported that calcium played a key role in interacting with arsenic vapor in the slow solid–gas surface reaction mechanism (eqs 1 and 2) that occurs in the post zone. In addition, there was no difference in the valence of As among YAN, FAR, and JAP, and this suggested that the oxidation process of As(III) or As(0) to As(V) can be completed at 850 °C. This was also in coincidence with the previous study.

\[ 3\text{CaO} + \frac{1}{2}\text{As}_2\text{O}_3(g) + \text{O}_2 \rightarrow \text{Ca}_3(\text{AsO}_4)_2 \]  
(1)

\[ 3\text{CaO} - \text{SiO}_2 + \frac{1}{2}\text{As}_2\text{O}_3(g) + \text{O}_2 \rightarrow \text{Ca}_3(\text{AsO}_4)_2 + 3\text{SiO}_2 \]  
(2)

From the Se K-edge XANES spectra (Figure 4d), Se(IV) was found to be the dominant oxidation state in the samples FAR and JAP. For YAN, the spectra showed that it contained a mixture of Se(IV) and Se(VI). Previous studies revealed that selenium in coal was mainly elemental in form (Se⁰) or in an organic association with Se(IV) and Se(VI). Depending on the temperature and flue gas composition, Se can exist in flue gas in thermodynamically stable elemental and oxidized forms. However, elemental Se has the inclination to become the oxidized form. Thus, Se in fly ash is mainly present in the form of Se(IV) (eq 3). At a lower stack temperature, the oxidized forms of Se can be partially reduced in the presence of SO₂. The existence of Se(VI) in the sample YAN can mainly be attributed to the high concentration of Se(VI) in the original coal of YAN.

\[ 3\text{CaO} + \text{SeO}_2(g) \rightarrow \text{CaSeO}_3 \]  
(3)

It can be seen from the Cr K-edge XANES spectra (Figure 4b) of standards that there was a considerable difference between the spectra of Cr(III) and Cr(VI) in the pre-edge region. It has a fairly sensitive fingerprint for the identification of the valence states of chromium. The Cr K-edge spectra showed that Cr(III) was the main state of existence in fly ash. There was no change during the coal combustion process because Cr in the original coal was also present as Cr(III).

### Table 1. Chemical Compositions and LOIs of Fly Ash Samples (% by Weight)

| sample | SiO₂ | Al₂O₃ | Fe₂O₃ | Na₂O | K₂O | CaO | MgO | P₂O₅ | TiO₂ | SO₂ | others | LOI   |
|--------|------|-------|-------|------|-----|-----|-----|------|------|-----|--------|------|
| YAN    | 48.60| 39.90 | 2.79  | 1.69 | 1.02| 2.19| 2.04| 0.09 | 0.67 | 0.93| 0.08   | 8.63 |
| ZHA    | 46.20| 43.70 | 2.20  | n.d. | 0.76| 2.74| 1.81| 0.27 | 0.73 | 1.37| 0.23   | 4.79 |
| YEM    | 49.20| 31.00 | 6.56  | 2.97 | 1.19| 2.05| 2.85| 0.25 | 2.26 | 1.54| 0.13   | 4.38 |
| NAY    | 48.30| 32.00 | 6.57  | 5.17 | 1.33| 1.31| 1.83| 0.22 | 1.97 | 1.09| 0.21   | 6.26 |
| PAN    | 50.20| 32.70 | 3.56  | 3.22 | 1.07| 2.79| 2.58| 0.23 | 2.22 | 1.28| 0.15   | 4.68 |
| FAR    | 49.80| 32.10 | 6.29  | 2.68 | 1.28| 1.97| 2.14| 0.23 | 2.02 | 1.27| 0.22   | 4.79 |
| DAT    | 46.90| 37.50 | 3.10  | 3.33 | 1.08| 4.57| 1.33| 0.24 | 0.65 | 1.04| 0.26   | 3.60 |
| SHU    | 44.60| 46.10 | 1.97  | 1.99 | 0.65| 2.03| 0.77| 0.27 | 0.78 | 0.81| 0.03   | 3.80 |
| JAP    | 51.59| 28.38 | 10.97 | 0.14 | 2.89| 1.70| 0.29| 1.09 | 1.65 | 0.56| 0.74   | 0.65 |
| IND    | 60.30| 22.62 | 6.20  | 0.14 | 2.57| 2.59| 0.53| 0.45 | 2.36 | 1.48| 0.76   | 7.03 |

Figure 3. SEM images of fly ash samples.
Additionally, there was no difference among YAN, FAR, and JAP; so, the combustion temperature had little effect on the valence change of Cr. Compared with the reference materials, the element of V showed V(IV) in fly ash (Figure 4a). However, V is present as V(III) and V(IV) in original coal.25 Thus, the oxidation of V(III) into V(IV) occurred during the burning process. In terms of W, it was determined at the L3-edge and presented as W(IV) in fly ash (Figure 4e). Because the content of W in YAN was too low to be determined on the beamline, its valence in fly ash from the FBC boiler was not included in this work. However, previous research15 showed that soluble scheelite (CaWO₄) was detected in coal fly ash, which was in direct contradiction to the current study.

In this study, the valence of Sb was not determined because of the overlapping energies between the Sb L-edge and Ca K-edge. Because of the limitation of the beamline, the Sb K-edge or Mo L-edge cannot be satisfied by the energy intensity. Thus, the valence information of Sb and Mo was not included in this investigation. From previous studies, it is observed that Sb in fly ash can be present in both Sb(III) and Sb(V) states.26,27 To a large extent, this depends upon the sources of the original coal. Mo(0) can be easily oxidized into Mo(VI) above 600 °C and Mo may be present as Mo(VI) in coal fly ash, which needs further confirmation. Through XANES analysis, the chemical states of some elements in fly ash have been known, and this can provide new insights into the possibility of these trace elements released into the aqueous environment. However, it is not enough to make predictions on the leaching behaviors of pollutants from fly ash in aqueous conditions judged only by the valence. Therefore, a sequential extraction experiment was conducted to explore the leaching behaviors and distributions of trace elements in the fly ashes.

2.3. Sequential Extraction Results. The environmental behavior of potential toxic elements mainly depends upon the forms in which they occur. Sequential chemical extraction is an effective way to explore the fate of heavy metals in wastes and assess their mobility and bioavailability. As can be known, F1 is the most readily mobile and has the potential for environmental contamination. F2 would be easily released under weak acidic conditions, and it can also be regarded as having good mobility in the environment. F5 is expected to be the most stable for a long time in the natural environment, mainly associated with silicates. Figures 5 and 6 present the sequential leaching results of major elements including Ca, Mg, Al, Fe, S, and P and trace elements including B, V, Cr, As, Se, Mo, Sb, and W.

Ca, Mg, Al, Fe, and S are usually present in significant amounts in fly ash. They (mainly Ca and S) play a key role in the pH of fly ash leachate and promote the precipitation of metalloid-bearing phases such as ettringite, which can incorporate environmentally sensitive elements. Generally, Ca controls the leachate composition for the most part and the leachability of trace contaminants to a large extent.28 From Figure 5a, it can be seen that most of the Ca content in the examined samples was released in F1, F2, and F3, and there were still small amounts of Ca in F4 and F5. This is mainly because some Ca can occur as silicates.14 S (Figure 5e) was similar to Ca, except that F1 accounted for a higher percentage, especially for YEM, NAY, and FAR. However, the total content of Ca was 1 order of magnitude higher than that of S, which
indicated that all of these samples were alkaline fly ashes. Mg mainly distributed in F2, F3, and F4, and the proportion varied from sample to sample (Figure 5c). For YAN and ZHA, more than 60% of Mg was released in F2 compared with other samples whose F2 fractions were lower than 45%. This suggested that Mg in fly ash was almost insoluble in alkaline conditions and appeared to be easily soluble in acidic pH, which had been confirmed by previous studies.14 Al (Figure 5b) is usually abundant in fly ash. Although the content of Al in fly ash was much higher than that of Ca and Mg, the magnitude of the total amount of leached Al was the same. In the last step, HF was used to dissolve the silicates, and the minerals of AlF3 and KAlF4 were formed. In these fly ashes, most of the Al content was leached from F3 and F4, and this implied that Al in fly ash had a higher solubility at low pH. Fe is also a very common element in fly ash. From XRD patterns, it has been found that it is related to iron minerals such as hematite and magnetite. Generally, this element is not easily released from fly ash under the conditions of pH > 1.5.29 The leaching results (Figure 5d) showed that most of the Fe content was released in F5, and a small proportion was leached in F3 and F4, which implied that Fe in the fly ash stayed in a very stable state. These major elements usually control the leaching behaviors of harmful elements such as As, Se, and Cr by adsorption or precipitation; so, the possible associations with the major elements will be discussed as follows. P is usually insoluble under natural water conditions. From the results (Figure 5f), it has been observed that there was a high concentration of P in fly ashes ranging from approximately 150 to 1200 mg/kg. In terms of the occurrence of P in fly ash, Jones30 suggested its association with highly insoluble Ca phosphates. In this study, low proportions of P were present in F1 and F2, which indicated that P in fly ash was difficult to be released under natural or slightly acidic conditions. However, once in a lower pH (F3: 1.5, F4: 2), the amount of leached P increased dramatically. This may be due to the dissolution of Ca phosphate, which was soluble in the presence of HNO3. On the other hand, for YEM, FAR, JAP, and IND, a considerable amount of P leached in F5, and this verified the point that P could be associated with the silicate minerals, which was proposed by Dudas.31 Therefore, the occurrence of P in fly ash would mainly be in the form of phosphate and exist in the structure of silicates. Compared with P, the total concentration of As in fly ash was lesser than 100 mg/kg (Figure 6d). However, it has attracted considerable attention because of its toxicity and mobility through a wide pH range.14 In all samples, F3, F4, and F5 accounted for most of the As leached from fly ash, and this meant that As stayed in a stable phase. Specifically, a larger amount of As (around 30–40%) leached in F3 than that in F4. This may be because As in fly ash had a valence of 5, and As(V) was reduced in the reduction process (F3) and then easily leached into the

Figure 5. Sequential extraction results of (a) Ca, (b) Al, (c) Mg, (d) Fe, (e) S, and (f) P from different fly ashes.
solution. In addition, a considerable fraction of As was released in F5, which was similar to that of Fe to some extent. From previous studies, it is observed that As is primarily associated with As-bearing pyrite in the original coal. After combustion, it condenses on the surface of fly ash particles as sparingly soluble species. Therefore, Fe controls its leaching behavior, as As has a high affinity with iron minerals. For samples JAP and IND, in addition to the characteristics described above, approximately 20% of As was leached in F1 as well. This may be because As was in a soluble form, such as Na arsenate or K arsenate. Therefore, As in fly ash can have associations including soluble and sparingly soluble arsenates and existence in silicates. Being in the same group with P and As, Sb (Figure 6g) is an element that is not fully understood in fly ash. Almost all of the Sb content in fly ash leached in F5, which indicated that Sb was in a major association with the silicates. Only a minor fraction of Sb was in a nonsilicate association, which could be observed from the leaching results of YAN, DAT, IND, and JAP in F1. Therefore, Sb in fly ash existed in a very stable phase, and the total concentration was in the range from approximately 10 to 70 mg/kg, which indicated that it had little potential hazard to the environment. On the other hand, as for the same elemental group elements, P, As, and Sb, the possibility of leaching followed the sequence: P > As > Sb. They are difficult to be released from fly ash with the increase in time.

Comparing the same B-subgroup elements, Cr, Mo, and W, there was no similar rule in their sequential leaching results because Cr under acidic conditions is present in cationic form. The situations considering the elements Mo and W also

Figure 6. Sequential extraction results of (a) B, (b) V, (c) Cr, (d) As, (e) Se, (f) Mo, (g) Sb, and (h) W from different types of fly ashes.
presented the trends similar to that of P, As, and Sb. Specifically, the leaching behavior of Cr (Figure 6c) was, to some extent, similar to that of Sb. The total concentration of Cr in fly ash was approximately 100 mg/kg on average, and at least 70% of Cr stayed in F5, which suggested that Cr was also associated with silicates, which could be illite or spinel minerals, as proposed by previous studies.11,33,34 There was a small proportion of Cr leached in F1 to F4. As described above, Cr appeared in the form of CrO3. Therefore, it behaved like some cations discussed in other studies,14,35 as the solution acidity became stronger, the leaching possibility increased. For Mo, its concentration in fly ash was less than that of Cr. The leaching behavior of Mo (Figure 6f) was opposite to that of Cr. A large amount of Mo was leached in F1, which indicated that Mo had good mobility in deionized water. Generally, the associations of Mo in the original coal are mostly in the forms of sulfide (MoS2) and organic compounds.36 During coal combustion, they are then oxidized into MoO3, SO2, and other compounds. Therefore, it is known that Mo in fly ash is mainly present in the form of MoO2, which is easily soluble in alkaline conditions. This provides an explanation for the above phenomenon, as all the leachates of the fly ash in the first step are alkaline. However, the leaching behavior of Mo in acidic fly ash would be different. Under acidic conditions, Mo compounds generally cannot be dissolved, but can be adsorbed on Fe oxyhydroxides (maximum at pH 3–4) and Al oxyhydroxides (pH range 4–5).37 Thus, the occurrence of Mo in fly ash was mainly in the form of oxides, condensing on the surface of fly ash particles. For all samples except YEM, there were also small parts released in F2, F3, and F4. Only in YAN, JAP, and IND, approximately 12%, 5%, and 6% of Mo, respectively, leached in F5, which suggested that Mo was able to be associated with the silicates. W (Figure 6h), another group member with Cr and Mo, showed leaching trends similar to that of Mo. The concentration of W in fly ash was mostly in the range of 2–13 mg/kg. However, for JAP and IND, there were higher concentrations possessing approximately 160 and 100 mg/kg, respectively. A considerable amount of W was released in F1, and this implied that the association of W in fly ash may be similar to that of Mo. From the XANES results, it is observed that W is present as W(VI) in the fly ashes selected for the XANES tests. Therefore, it can be deduced that the association of W during coal combustion goes through both oxidation and reduction processes because of the existing oxidative and reductive substances. In the case of W(VI), it cannot be in the form of scheelite (CaWO4) as proposed by Vassilev and Vassileva.38 Additionally, the oxidative form (WO3) is a less soluble mineral in alkaline solution. Therefore, the association of W in fly ash may be mainly in the form of WX4 (X can be monovalent anions). In addition, a part of W also leached in weak acidic conditions (F2), especially for NAY and PAN. This is contradictory to the view that W is immobile below pH 5 as proposed by Ward et al.39 Obviously, the other fractions including F3, F4, and F5 accounted for a respectable amount of W. W can be associated with silicates due to the less than 10% of W leached in F5. Step 3 and step 4 are the reduction and oxidation processes at pH 1.5 and 2, respectively. After leaching in step 3, there was still a proportion of W released in F4, which indicated that the oxidation process may play a role in this element’s leaching. Thus, W in fly ash has complex associations that include WX4 (X can be monovalent anions), reduction state, or associations with elements that can be oxidized and exist in silicates.

B (Figure 6a), the same main group element with Al, with a content of 100–500 mg/kg, is also present in an anionic form in solution. To some extent, its leaching behavior has similar trends to Al. The main difference was that the element of Al was leached to a considerable amount in F3 and F4, with low contents in F1 and F2; however, B was released in a considerable amount in F1, F2, and F3 with a very small content in F4. This suggested that, compared with Al, B was more easily leached from fly ash in the natural environment. There are many researchers who underline B as one of the most mobile trace elements in coal fly ash.36 B generally shows the form of BO3−2 in nature, and then, in fly ash, it can have several associations with other cations, such as Ca2+, Na+, and Mg2+. Obviously, compounds that consist of BO3−2 and different cations have variant deliquescent properties, thereby leading to different leaching behaviors under different aqueous conditions. These compounds mainly present surface association in fly ash; a similar conclusion has also been put forward by Querol.36 There was always a part of B leached in F5. Particularly, approximately 40% of B was released in F5 for JAP and IND, and this can be best explained by its cohesion with silicates. In some coals, B occurred in illite or in the highly refractory tourmaline, as Boyd58 noted that the aforementioned silicate structures can lock B up at high temperatures. Therefore, the main associations of B in fly ash could be with cations, such as Ca2+, Na+, and Mg2+ and cohesion with silicates.

In terms of Se (Figure 6e), which belongs to the same main family as that of sulfur, the concentration in fly ashes studied in this research was approximately 30 mg/kg. There was no Se leached in F5 except for JAP. JAP had an extremely small amount of Se in the last step, which contributed to the detection that Se might be associated with easily soluble compounds such as CaSeO3 under acidic conditions,41 condensing on the surface of fly ash particles. In all samples, approximately 20% of Se leached in F1 and F2, except that Se leached more than approximately 30% in JAP and IDO. This can be attributed to the occurrence of selenite in fly ash, which is relatively mobile. Furthermore, there may be Na selenite (soluble in water) existing in fly ash, in addition to Ca selenite (insoluble in water). Less than 10% of Se leached in F3; however, more than 40% leached in F4. Under the Se leaching process, the oxidation process (F4) played an important role in controlling its leaching, as Se(IV) appeared to be the dominant species in fly ash based on the XANES results, and it can be oxidized into Se(VI). Compared with Se(IV), Se(VI) rarely associates with other cations for precipitation and then exhibits higher mobility.8 Even though the XANES spectra showed that Se in FAN was in the form of Se(IV) and Se(VI), there was no obvious difference in terms of their leaching behaviors, which implied that the amount of Se(VI) in FAN may be very small. From the comparison of the leaching behaviors of Se and S, it is observed that Se is more difficult to be released than S from fly ash, which is the same trend as that with B, Al, P, As, and Sb. Therefore, it can be deduced that for the same group elements, the element with a higher atomic number is more stable in fly ash.

The total concentration of V (Figure 6b) was in the range of 40–200 mg/kg, and it was an element that was not easily leached from fly ash because there was only a small amount released in F1 and F2. From the XANES results, it is observed
that the main state of existence was V(IV), which possessed both reducing and oxidizing abilities. A substantial amount of V was leached in F3, except for JAP and IND in which F5 accounted for more than 60%. In step 3, there may be two reaction processes including direct dissolution or reduction of V compounds. These V compounds such as VO$_2$ can easily dissolve in acidic or basic solution. On the other hand, V(IV) in fly ash can be reduced into a lower valence state [V(III)] and then released into the solution. Thus, the reduction/oxidation process of steps 3 and 4 may control the leaching behavior of V. A previous study revealed that V had complex associations in fly ash including surface association, constrained in the magnetite or glass phase. From the leaching results, it was observed that there was always a part of V leached in F5 in all samples, especially JAP and IND. This confirmed the above views that V could also be associated with silicates. Thus, V in fly ash is mainly in the form of oxides and silicates.

3. CONCLUSIONS

The distributions of toxic elements including B, P, V, Cr, As, Se, Mo, Sb, and W in fly ash were explored using a modified sequential extraction procedure and XANES. From the XANES results, it has been observed that V(IV), Cr(III), As(V), Se(IV), and W(IV) are the main existing states in fly ash. In terms of leaching results, Mo and W were leached in large amounts in pure water, exhibiting high motilities. The association of Mo was mainly in the form of oxides, condensing on the surface of fly ash particles. W had complex associations including WX$_4$ (X can be monovalent anions), a reduction state or association with the elements that can be oxidized, and existed in silicates. B, being similar with Mo and W, was easily released into the environment under acidic conditions. It can have several associations with other cations, such as Ca$^{2+}$, Na$^+$, and Mg$^{2+}$, and occur in silicates. In contrast, most of the Cr and Sb were locked in silicates. In addition, P, V, and As can also participate in the structure of silicates in a moderate amount, and a considerable amount of them leached in the reduction step with a low pH. They could possibly be associated with calcium, sodium, potassium, or iron. In terms of Se, oxidation processes played an important role in controlling its leaching because of the oxidation of Se(IV) to Se(VI), and it was mainly in the form of CaSeO$_3$ in fly ash. On the other hand, through comparing the leaching behaviors of the same elemental group elements, the rule that an element would become increasingly difficult to be released from fly ash with the increase in the atomic number was confirmed.

4. EXPERIMENTAL SECTION

4.1. Materials. Coal fly ash samples including eight samples collected from China, one from Japan, and one from Indonesia were used in this study and were named YAN, ZHA, YEM, NAY, PAN, FAR, DAT, SHU, JAP, and IND, based on their sources. Their original coals vary from sample to sample. The fly ash YAN, ZHA, YEM, and SHU were from the combustion of bituminous coal, and DAT, JAP, and IND were from subbituminous coal burning. For NAY and FAR, anthracite was the source of the original coal. There was also one sample (PAN) collected from a power plant that used coal gangue as an energy supply. On the other hand, most of them were produced at a high temperature (>1000 °C), although YAN and PAN were produced at 850–900 °C, which led to different morphologies (Figure 3). All samples were collected through a scientific procedure, mixed homogeneously, and then stored in a dry cabinet.

4.2. Sequential Extraction Procedure. A five-step extraction procedure used in the research was modified from the extraction procedure proposed by the Commission of the European Communities (BCR), as shown in Table 2. This procedure differentiated elements into several behavioral fractions including the water-soluble fraction (F1), acid-soluble fraction (F2), reducible fraction (F3), oxidizable fraction (F4), and silicate fraction (F5). At the fifth step, to decompose the silicate minerals in fly ash, HF (46%, Wako) was used with HNO$_3$ (60%, Kanto industry) and H$_2$O$_2$ (46%, Wako) under microwave conditions (Milestone ETHOS). In addition, CH$_3$COOH (99%) and NH$_2$OH-HCl (95%) were also purchased from Wako industry (Osaka, Japan). The specific experimental procedure was as follows: 1 g of each fly ash was separately taken and placed in 50 mL polypropylene bottles, and no delay occurred between the addition of extractant solution and the beginning of the shaking. At the same time, five parallel tests were done to collect the solid residues from every step. All the leaching tests were conducted with a shaker (MM-10) at a speed of 100 rpm at 25 °C. The extracts were separated from the solid residues by centrifugation at 3000 rpm for 20 min, and the supernatant liquid was decanted into Teflon containers for 20 min at 220 °C in a microwave oven. This procedure differed from the previous one, which used a drying oven to remove the water.

4.3. Instrumentation. A laser particle analyzer (Horiba LA950) was used to determine the particle size distribution of fly ash. XRF spectroscopy (Rigaku ZSX Primus II) and TG-DTA (2000 SA thermal balance, Bruker, Germany) were adopted to analyze the composition and LOI of the fly ash. The heating rate and airflow were 10 °C/min and 100 mL/min, respectively. The element concentrations in the extracts were measured by an inductively coupled plasma optical emission spectrometer (PerkinElmer, Optima 8300, US). The solid phases in the fly ash and leaching residues were...
characterized by a Rigaku Ultima IV XRD (Akishima, Japan): Cu Ka (40 kV, 40 mA) with a Ni filter at a scanning speed of 2° min⁻¹ and a scanning step of 0.02°. The SEM observations were carried out by a VE-9800 scanning electron microscope (Keyence, Osaka, Japan) with an acceleration voltage of 20 kV.

The XANES spectra of fly ashes including YAN, FAR, and JAP were collected at room temperature on a BL-06 beamline at the SAGA Light Source (Tosu, Japan). The electron storage ring operated with an energy of 1.4 GeV, and a silicon (111) double-crystal monochromator was used to obtain the incident X-ray beam. The energy range of this light source is 2.1–23 keV. The typical photon flux is 10¹⁰ photons/s. The intensities of the fluorescence X-rays were monitored with a silicon drift detector and an ionization chamber. Specifically, the XANES region extending from approximately −50 to +50 electron volts (eV) was collected in the fluorescence mode, which can provide information about the valences of the target elements in fly ash through comparison with the reference materials. In this test, the elements including Cr, As, Se, W, and V were explored for their valences occurring in the fly ash. Accordingly, the XANES spectra of known reference materials including CrCl₃, Na₂CrO₄, NaAsO₂, KH₂AsO₄, Se, Na₂SeO₃, Na₂SeO₄, WC, Na₂WO₄, V₂O₅, VOSO₄, H₂O, and V₂O₅ were measured on the beamline. The data processing was carried out on the ATHENA, which is an independent package of IFEFFIT.²²

■ AUTHOR INFORMATION

Corresponding Author
E-mail: keikos@mine.kyushu-u.ac.jp. Phone/Fax: +81-92-802-3338 (K.S.)

ORCID
Quanzhi Tian: 0000-0001-7729-253X
Keiko Sasaki: 0000-0002-2882-0700

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the JSPS (Japan Society for the Promotion of Science) Kaken Kiban A project (no. JP16H02435) and the China Scholarship Council (no. 201706420068).

■ REFERENCES

(1) Yao, Z. T.; Ji, X. S.; Sarker, P. K.; Tang, J. H.; Ge, L. Q.; Xia, M. S.; Xi, Y. Q. A comprehensive review on the applications of coal fly ash. Earth-Sci. Rev. 2015, 141, 105–121.

(2) Almaraz, M. A review on the utilization of fly ash. Prog. Energy Combust. Sci. 2010, 36, 327–363.

(3) Akar, G.; Polat, M.; Galecki, G.; Ipekoglu, U. Leaching behavior of selected trace elements in coal fly ash samples from Yenikoy coal-fired power plants. Fuel Process. Technol. 2012, 104, 50–56.

(4) Finkelman, R. B. Modes of occurrence of environmentally-sensitive trace elements in coal. In Environmental aspects of trace elements in coal; Swaine, D. J., Goodarzi, F., Eds.; Springer, 1995; pp 24–50.

(5) Goodarzi, F.; Huggins, F. E.; Sanei, H. Assessment of elements, specification of As, Cr, Ni and emitted Hg for a Canadian power plant burning bituminous coal. Int. J. Coal Geol. 2008, 74, 1–12.

(6) Huggins, F. E.; Shah, N.; Huffman, G. P.; Robertson, J. D. XAFS spectroscopic characterization of elements in combustion ash and fine particulate matter. Fuel Process. Technol. 2000, 65, 203–218.

(7) Lebly, A. D. Aquatic selenium pollution is a global environmental safety issue. Ecotoxicol. Environ. Saf. 2004, 59, 44–56.

(8) Komonweeraket, K.; Cetin, B.; Benson, C. H.; Aydilek, A. H.; Edil, T. B. Leaching characteristics of toxic constituents from coal fly ash mixed soils under the influence of pH. Waste Manag. 2015, 38, 174–184.

(9) Freyer, D.; Voigt, W. Crystallization and phase stability of CaSO₄ and CaSO₄·2H₂O—based salts. Monatsh. Chem./Chem. Mon. 2003, 134, 693–719.

(10) Kim, A. G.; Kazonich, G. The silicate/non-silicate distribution of metals in fly ash and its effect on solubility. Fuel 2004, 83, 2285–2292.

(11) Spears, D. A.; Martinez-Tarrazona, M. R. Trace elements in combustion residues from a UK power station. Fuel 2004, 83, 2265–2270.

(12) Hansen, L. D.; Fisher, G. L. Elemental distribution in coal fly ash particles. Environ. Sci. Technol. 1980, 14, 1111–1117.

(13) Moreno, N.; Querol, X; Andrés, J.; Stanton, K.; Towler, M.; Nugteren, H.; Janssen-Jurkovicová, M.; Jones, R. Physico-chemical characteristics of European pulverized coal combustion fly ashes. Fuel 2005, 84, 1351–1363.

(14) Izquierdo, M.; Querol, X. Leaching behaviour of elements from coal combustion fly ash: an overview. Int. J. Coal Geol. 2012, 94, 54–66.

(15) Vassilev, S. V.; Vassileva, C. G. Mineralogy of combustion wastes from coal-fired power stations. Fuel Process. Technol. 1996, 47, 261–280.

(16) Liu, S. C.; Jiang, C. S.; Hoo, Q. J.; Li, Q. L.; Shi, Y. The Particle Size Distribution, Gross Contents of Heavy Metals and its Leaching Behavior of Fly Ash from Municipal Solid Wastes Incineration of Chongqing. Advanced Materials Research; Trans Tech Publ, 2012; pp 166–171.

(17) Sarkar, A.; Rano, R.; Udaybhanu, G.; Basu, A. A comprehensive characterisation of fly ash from a thermal power plant in Eastern India. Fuel Process. Technol. 2006, 87, 259–277.

(18) Huggins, F. E.; Senior, C. L.; Chu, P.; Ladwig, K.; Huffman, G. P. Selenium and arsenic speciation in fly ash from full-scale coal-burning utility plants. Environ. Sci. Technol. 2007, 41, 3284–3289.

(19) Sterling, R. O.; Helble, J. J. Reaction of arsenic vapor species with fly ash compounds: kinetics and speciation of the reaction with calcium silicates. Chemosphere 2003, 51, 1111–1119.

(20) Zielinski, R. A.; Foster, A. L.; Meeker, G. P.; Brownfield, I. K. Mode of occurrence of arsenic in feed coal and its derivative fly ash, Black Warrior Basin, Alabama. Fuel 2007, 86, 560–572.

(21) Shah, P.; Strelov, V.; Prince, K.; Nelson, P. F. Speciation of As, Cr, Se and Hg under coal fired power station conditions. Fuel 2008, 87, 1859–1869.

(22) Shah, P.; Strelov, V.; Stevanov, C.; Nelson, P. F. Speciation of arsenic and selenium in coal combustion products. Energy Fuels 2007, 21, 506–512.

(23) Rivera, N.; Hesterberg, D.; Kaur, N.; Duckworth, O. W. Chemical Speciation of Potentially Toxic Trace Metals in Coal Fly Ash Associated with the Kingston Fly Ash Spill. Energy Fuels 2017, 31, 9652–9659.

(24) Huffman, G. P.; Huggins, F. E.; Shah, N.; Zhao, J. Speciation of arsenic and chromium in coal and combustion ash by XAFS spectroscopy. Fuel Process. Technol. 1994, 39, 47–62.

(25) Huggins, F. E.; Huffman, G. P. Modes of occurrence of trace elements in coal from XAFS spectroscopy. Int. J. Coal Geol. 1996, 32, 31–53.

(26) Miravet, R.; López-Sánchez, J. F.; Rubio, R. Leachability and analytical specification of antimony in coal fly ash. Anal. Chim. Acta 2006, 576, 200–206.

(27) Narukawa, T.; Takatsu, A.; Chiba, K.; Riley, K. W.; French, D. H. Investigation on chemical species of arsenic, selenium and antimony in fly ash from coal fuel thermal power stations. J. Environ. Monit. 2005, 7, 1342–1348.

(28) Wang, T.; Wang, J.; Tang, Y.; Shi, H.; Ladwig, K. Leaching characteristics of arsenic and selenium from coal fly ash: role of calcium. Energy Fuels 2009, 23, 2959–2966.
(29) Seidel, A.; Zimmels, Y. Mechanism and kinetics of aluminum and iron leaching from coal fly ash by sulfuric acid. *Chem. Eng. Sci.* 1998, 53, 3835–3852.

(30) Jones, D. The leaching of major and trace elements from coal ash. In *Environmental Aspects of Trace Elements in Coal*; Swaine, D. J., Goodarzi, F., Eds.; Springer, 1995; pp 221–262.

(31) Dudas, M. J. Long-term leachability of selected elements from fly ash. *Environ. Sci. Technol.* 1981, 15, 840–843.

(32) Zhao, S.; Duan, Y.; Chen, L.; Li, Y.; Yao, T.; Liu, S.; Liu, M.; Lu, J. Study on emission of hazardous trace elements in a 350 MW coal-fired power plant. Part 2. arsenic, chromium, barium, manganese, lead. *Environ. Pollut.* 2017, 226, 404–411.

(33) Spears, D. A. The use of laser ablation inductively coupled plasma-mass spectrometry (LA ICP-MS) for the analysis of fly ash. *Fuel* 2004, 83, 1765–1770.

(34) Zhang, Y.; Cetin, B.; Likos, W. J.; Edil, T. B. Impacts of pH on leaching potential of elements from MSW incineration fly ash. *Fuel* 2016, 184, 815–825.

(35) Zhao, S.; Duan, Y.; Lu, J.; Guptasahai, D.; Liu, S.; Liu, M.; Lu, J. Chemical speciation and leaching characteristics of hazardous trace elements in coal and fly ash from coal-fired power plants. *Fuel* 2018, 232, 463–469.

(36) Querol, X.; Fernández-Turiel, J.; López-Soler, A. Trace elements in coal and their behaviour during combustion in a large power station. *Fuel* 1995, 74, 331–343.

(37) Ward, C.; French, D.; Jankowski, J. *Comparative Evaluation of Leachability Test Methods and Element Mobility for Selected Australian Fly Ash Samples*; Pittsburgh Coal Conference: Pittsburgh, Pa, 2004.

(38) Boyd, R. J. The partitioning behaviour of boron from tourmaline during ashing of coal. *Int. J. Coal Geol.* 2002, 53, 43–54.

(39) Wan, X.; Wang, W.; Ye, T.; Guo, Y.; Gao, X. A study on the chemical and mineralogical characterization of MSWI fly ash using a sequential extraction procedure. *J. Hazard. Mater.* 2006, 134, 197–201.

(40) Yoo, K.; Sasaki, K.; Hirajima, T.; Tsunekawa, M. Analysis of heavy metals in a tailing impoundment of abandoned Mn mine by using two sequential extractions. *Mater. Trans.* 2002, 43, 3189–3194.

(41) Zhang, Y.; Wang, P.; Wang, J.; Norris, P.; Romero, C. E.; Pan, W.-p. Trace element (Hg, As, Cr, Cd, Pb) distribution and speciation in coal-fired power plants. *Fuel* 2017, 208, 647–654.

(42) Ravel, B.; Newville, M. ATHENA and ARTEMIS: interactive graphical data analysis using IFEFFIT. *Phys. Scr.* 2005, 2005, 1007.