

## 〈論文〉

## Changes in the Chemical Form of Heavy Metals During Acid Extraction of Melting Furnace Fly Ash

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### Abstract

Melting furnace fly ash (MFA) produced by solid waste thermal treatment facilities is a regulated hazardous material and a precious resource. Recent studies have focused on recovering heavy metals from MFA. Aqueous acids are often used to dissolve metals in MFA, but limited data are available to understand the processes occurring during acid extraction. We used three conventional acids [sulfuric, hydrochloric, and nitric ( $H_2SO_4$ ,  $HCl$ , and  $HNO_3$ , respectively)] and water to investigate changes in the chemical form of heavy metals during acid extraction. The extraction characteristics produced different results depending on the type of acid used and the metal tested. According to X-ray absorption near-edge structure analysis, lead (II) sulfate ( $PbSO_4$ ) was the predominant species, and the high proportions identified in the residue after adding all acids suggested that the chemical state of lead in the residue was not dependent on the acid type used.

**Keyword** : Heavy metal, Acid extraction, Melting furnace fly ash, X-ray absorption near edge structure

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## 1. INTRODUCTION

Incineration of municipal solid waste (MSW) reduces the weight and volume of waste for public sanitation. However, incineration generates by-products such as bottom ash and fly ash. Fly ash must be pretreated before landfilling to immobilize the hazardous materials and to decompose toxic organics such as dioxins and furans. Melting is a suitable technology for stabilizing fly and bottom ash from MSW incineration (MSWI). The melting process heats the fly and/or bottom ash to a fusion temperature, normally  $>1,200^\circ C$ , and transforms the ash into a more stable molten slag<sup>1)</sup>. Organic pollutants decompose during the melting process, and the volume of fly ash and bottom ash is reduced by 70%. The molten slag can be used as a construction material because heavy metals are stabilized in the slag. However, the melting process also produces melting furnace fly ash (MFA), with a higher concentration of heavy metals than that in the original MSWI fly ash; therefore, the product is more hazardous<sup>1)</sup>. Immobilizing heavy metals in the

MFA is necessary prior to landfilling to prevent environmental pollution. In that case, a large amount of chemical agents (such as chelators) is usually required. MFA contains many valuable metals from a resource recovery perspective, such as zinc (Zn) and lead (Pb). The amount of Zn and Pb in MFA is equivalent to more than 5% of the annual demand for each metal in Japan<sup>2,3)</sup>. In our previous study, environmental loads and costs for treating MFA were determined, and findings indicated that MFA could be supplied to mining industries as a raw material to recover valuable metals after hydrometallurgy pretreatment<sup>4,5)</sup>. Thus, the recovery of these metals is beneficial from both economic and environmental perspectives. Recovery of heavy metals from MFA, which can solve problems associated with waste treatment and resource recovery, is an important research topic. Most metals obtained by hydrometallurgical processes are recovered using an extraction process. Aqueous acids are often used to dissolve the metals present in MFA<sup>6)</sup>. Previous studies have investigated the leaching characteristics of heavy metals in wastes using various

acid agents<sup>7-11</sup>). However, the characteristics of acid extraction depend on various conditions, such as the hydrogen ion and counter ion concentrations in solution and waste properties. Acid should be used in accordance with the waste characteristics to improve extraction efficiency and minimize the residue volume after the extraction. Therefore, understanding exactly what is happening during acid extraction is important to obtain the highest extraction efficiency. However, few studies have been reported on the processes occurring during acid extraction. In this study, we used three conventional acids [sulfuric, hydrochloric, and nitric ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , and  $\text{HNO}_3$ , respectively)] and water to investigate the basic extraction performance of Zn, Pb, and copper (Cu) and investigated changes in the chemical forms of the heavy metals in MFA during acid extraction. In particular, we used synchrotron X-ray absorption near-edge structure (XANES) spectroscopy to analyze the extraction characteristics of the heavy metals in MFA.

## 2. MATERIALS AND METHODS

### 2.1 Materials

MFA from a surface melting furnace at an ash melting plant in Japan was obtained for use in this study. This facility melts both bottom ash and fly ash from incinerators. Calcium hydroxide was not injected because the flue gas after the bag filter in the melting furnace is sent to an incinerator flue gas treatment system. The original samples were thoroughly mixed during sample preparation. The average particle size of MFA was  $20.4 \mu\text{m}$ , but it was divided into a fine fraction ( $<1 \text{ mm}$ ) by sieving to remove some lumps and obvious impurities such as rust. The MFA was placed in a pan and dried in a vacuum dryer at  $105^\circ\text{C}$  for 24 h. The MFA had a moisture content of 0.4%.

### 2.2 Methods

#### (1) Basic chemical properties of MFA

The basic chemical properties of the MFA were determined using X-ray fluorescence (XRF; XRF-1700, Shimadzu Corp.), X-ray diffraction (XRD; D/Max 2200 PC Ultima III, Rigaku Corp.), and total dissolution. The MFA was completely dissolved using aqua regia (A. R.;  $\text{HCl}:\text{HNO}_3=3:1$ , v/v). A. R. digestion is generally used in Japan to prepare samples for metal concentration analysis. However, A. R. does

not total dissolve metals in silicate matrices when incineration residues are digested; hence, a hydrofluoric acid (HF) digestion step was added. Total dissolution experiments were conducted using a published extraction method<sup>12</sup>. Metal concentrations [sodium (Na), potassium (K), Zn, Pb, aluminum (Al), Cu, iron (Fe), magnesium (Mg), titanium (Ti), chromium (Cr), and manganese (Mn)] were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; IRIS Intrepid Duo, Thermo Electron Corp.).

#### (2) Removal of salts by water-washing

A water-washing step was performed before the acid extraction phase to concentrate the heavy metals in the water-washed residue by removing the high contents of salts, such as Na and K, in the MFA<sup>5,8</sup>. Water washing was performed by determining a suitable liquid/solid (L/S) ratio and washing time for a mechanical shaker (SA300, Yamato Scientific Co., Ltd.) at room temperature, followed by filtration using a glass fiber filter. **Table 1** provides the basic experimental conditions adopted for the water-washing procedure in this study. Elements in the washing solution were analyzed by ICP-AES. The washed MFA was dried in a vacuum dryer at  $105^\circ\text{C}$  for 24 h.

**Table 1** Experimental conditions for water-washing

Factor	Level
L/S ratio (–)	5/1, 10/1, 15/1, 20/1
Washing time (min)	30, 60, 180, 300

#### (3) Extraction of heavy metals with acid agents

The water-washed MFA was extracted using  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , and  $\text{HNO}_3$ . These acids are all representative strong acids that have been commonly used to extract heavy metals in previous studies<sup>13-15</sup>, and each has different extraction characteristics according to the different heavy metals in the wastes<sup>16-18</sup>.

This step was controlled by the acid concentration, L/S ratio, temperature, and extraction time. Although the acid concentration was set as volume concentration in advance, the value was converted to molar concentration (M). Standard values (std) for each of these experimental factors were determined before commencing work. Once these standard values were established for each of the experimental factors, the effect of varying the experimental conditions was investigated to determine their influence on heavy metal extraction efficiency. The acid extraction step

used various acid concentrations (std: 1.8 M H<sub>2</sub>SO<sub>4</sub>, 1.2 M HCl, and 3.2 M HNO<sub>3</sub>) depending on how the acid characteristics influenced the L/S ratio (std: 10/1) and temperature (std: 50°C). Extraction time was varied between a minimum of 30 min and a maximum of 180 min based on the point when pH equilibrium was reached, compared to the standard of 1 h according to a Korean leaching test of incinerated fly ash and bottom ash<sup>18)</sup>. **Table 2** shows the tested experimental conditions for extracting heavy metals using the different acids. Extraction was conducted using a hot plate magnetic stirrer, and the acid-extracted samples were chemically analyzed by ICP-AES. Extraction efficiency was defined as follows.

$$\text{Extraction efficiency (\%)} = \frac{\text{the amount extracted in the step}}{\text{the amount in original MFA}} \times 100 \quad (1)$$

**Table 2** Experimental conditions for the extraction of heavy metals using the different acids

Factor	Level
Acid	H <sub>2</sub> SO <sub>4</sub> , HCl, HNO <sub>3</sub>
Conc. of acids (M)	0.58-4.0
L/S ratio (-)	5/1, 10/1, 15/1
Extraction time (min)	30, 60, 180
Temperature (°C)	30, 50, 70

\*Standard condition : H<sub>2</sub>SO<sub>4</sub>, 1.8 M, 10/1, 60 min, 50°C

#### (4) Analysis of heavy metals in the residue after extraction using XANES spectroscopy

XANES spectroscopy was performed for various elements on all solid residues at Beamline BL14B2 and BL01B1 (SPring-8; Hyogo, Japan) to clarify the changes in the chemical form of the heavy metals during acid extraction. The detailed data reduction procedure has been described previously<sup>19)</sup>. MFA and reference samples were analyzed using XANES to determine the atomic species in neighboring metals within the respective samples. XANES is an elemental speciation technique that uses the X-ray absorbance measurement in the vicinity of an absorption edge of the element of interest. XANES spectra reflect the local structure around the absorbing atom. Because of limited beam time, the XANES spectra were recorded in selected samples. Data reduction was performed using REX2000 ver. 2.3.3. software (Rigaku Corp.).

In addition, chemical species were distinguished

using the linear combination fit (LCF) technique. The LCF of XANES spectra have been used to identify and quantify major species in particulate matter<sup>20, 21)</sup>. One free running parameter (partial concentration) was refined for each reference spectrum in the LCF of XANES. The residual value (R), calculated using Eq. 2, was used to evaluate the LCF for the experimental spectra<sup>22)</sup>:

$$R = \frac{\sum (XANES_{measd} - XANES_{calcd})^2}{\sum (XANES_{measd})^2} \quad (2)$$

where R is the goodness-of-fit parameter. A lower R indicates a small divergence between the measured and the synthesized (calculated) spectra using those of various reference materials.

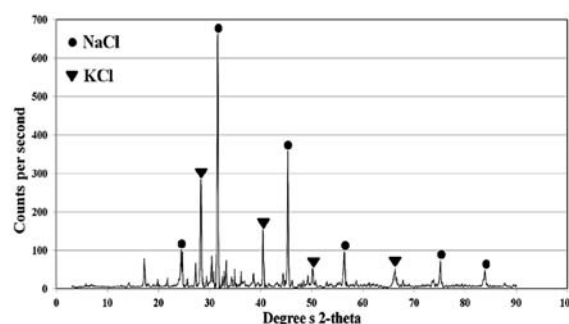
### 3. RESULTS AND DISCUSSION

#### 3.1 Basic characteristics

As a preliminary test, elemental and crystal structure analyses of the materials were conducted. The analyses were performed on raw MFA samples. **Table 3** shows the chemical composition of MFA determined using ICP-AES and XRF. As shown in **Figure 1**, the main mineral constituents of the MFA included halite (NaCl) and sylvite (KCl). The crystalline phases of the heavy metals were not observed by XRD.

**Table 3** Chemical composition of MFA

Element	Content (wt%)	Method	Element	Content (mg/kg)	Method
O	33	XRF	Zn	82,700	ICP
Cl	26	XRF	Pb	50,200	ICP
Na	13	ICP	Cu	29,500	ICP
K	13	ICP	Fe	7,000	ICP
Si	2.8	XRF	Mg	1,740	ICP
Ca	0.4	XRF	Ti	438	ICP
Al	0.2	ICP	Cr	200	ICP



**Fig. 1** XRD spectrum of melting furnace fly ash (MFA)

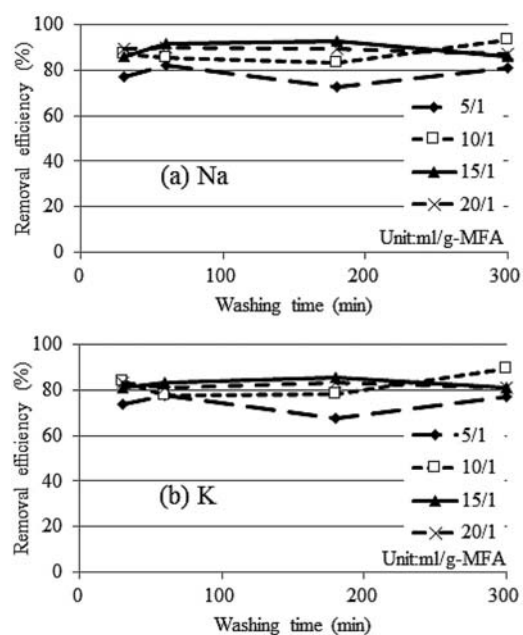


Fig. 2 Salt removal efficiency with water

### 3.2 Removal of salts by water-washing

Water washing the MFA to remove NaCl and KCl was performed prior to extracting the heavy metals. The removal efficiency of the water-soluble salts by water washing is shown in **Figure 2** and did not change despite increased the washing time. The determination was made that 30 min of washing with 10 mL/g-MFA was sufficient to remove water-soluble salts. Most of the other metals were barely leached from samples during water washing, except K and Na. However, about 25% of the Zn was leached compared to the other heavy metals. pH was 5.5. XANES spectra were collected to clarify the processes occurring during water washing. The effect of the water-washing stage on acid extraction was investigated. **Figure 3** shows the heavy metal extraction efficiencies in wastes following treatment with various acids, both with and without the water-washing stage. The results indicate that water washing was necessary to improve Cu extraction efficiency, but results for Zn and Pb were slightly different. Pb had a particularly high extraction efficiency in  $\text{HNO}_3^{15}$ .

### 3.3 Extraction of heavy metals with different acids

The effect of the acid concentration was examined by conducting a series of experiments in which concentrations were varied from 0.58 to 4.0 M. As shown in **Figure 4**, increasing the acid concentration did not improve heavy metal solubility. Heavy metal dissolution was independent of acid concentration,

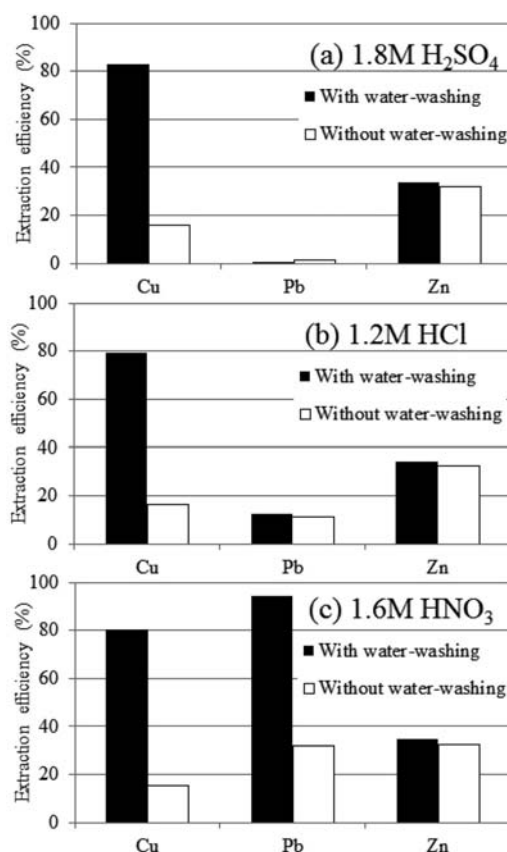


Fig. 3 Extraction efficiency of heavy metals with and without water-washing using various acids (Time=60 min, L/S ratio=10/1, Temp.=50°C)

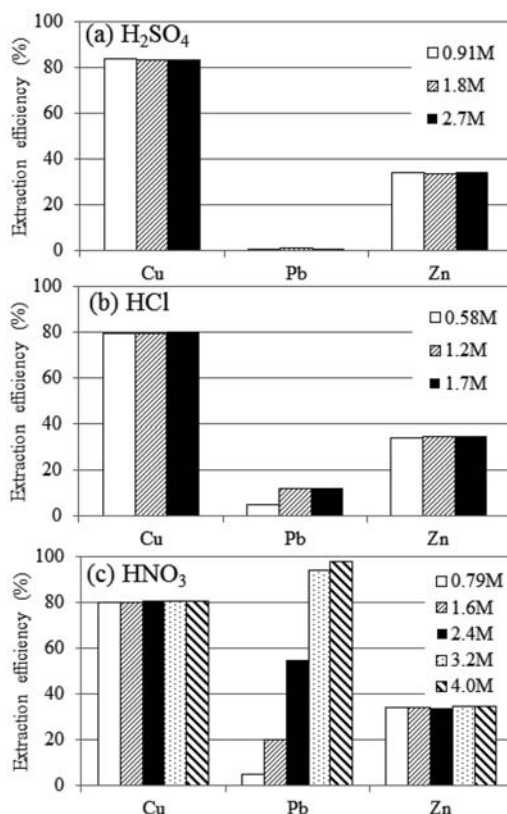
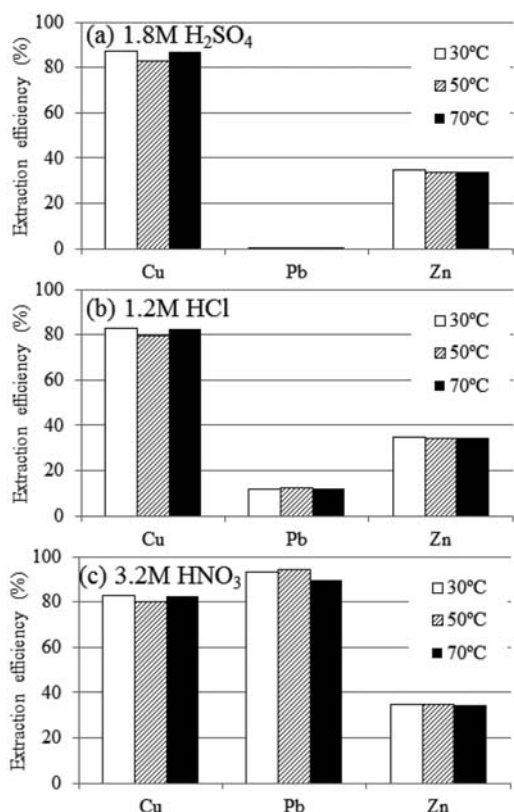


Fig. 4 Effect of acid concentration on extraction efficiency (Time=60 min, L/S ratio=10/1, Temp.=50°C)

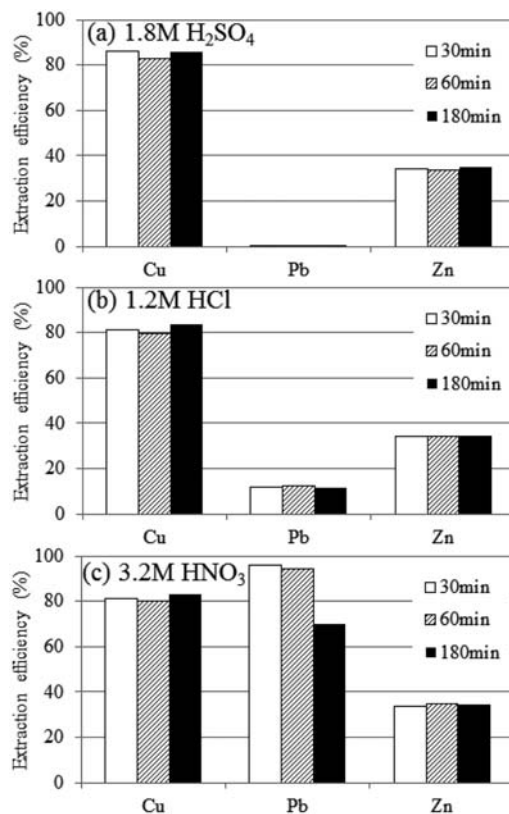
except for Pb in HNO<sub>3</sub>. This result suggests that a certain fraction of the Cu and Zn was not easily leached by even strong acids or that Cu and Zn were leached once and reprecipitated under solubility control. Less than 1.0 M of acid concentration was sufficient to extract Cu from MFA. Pb in the MFA was dissolved significantly by >3.2 M HNO<sub>3</sub>. Previous studies have reported that HNO<sub>3</sub> results in significantly higher Pb extraction efficiency compared to other acids<sup>14</sup>.

The effect of temperature on extraction efficiency was investigated because temperature influences the equilibrium (solubility) and mass transfer rate, as shown in **Figure 5**. Some researchers have reported that an increase in temperature increases the extraction yield because some metals might degrade at high temperatures, and that temperature effects are different for different metals<sup>23, 24</sup>. However, in this study, only a slight effect of temperature on metal dissolution was observed for Cu and Zn, and Pb was not affected by temperature. A temperature of 30°C was determined to be suitable for heavy metal extraction, considering the energy savings.

The effect of extraction time was examined by conducting a series of experiments in which time



**Fig. 5** Effect of temperature on extraction efficiency (Time=60 min, L/S ratio=10/1)



**Fig. 6** Effect of extraction time on extraction efficiency (L/S ratio=10/1, Temp.=50°C)

intervals were varied from 30 min to 180 min. As shown in **Figure 6**, extraction time had only a slight effect on metal dissolution. Extraction efficiency did not increase with longer extraction times, and Pb extraction efficiency tended to decrease (**Figure 6c**). Therefore, a 30 min extraction time was better in terms of energy efficiency of the extraction process.

The effect of the L/S ratio was examined by conducting a series of experiments in which the L/S ratio was varied from 5/1 to 15/1. As shown in **Figure 7**, the L/S ratio had only a slight effect on Cu extraction efficiency using all of the acid reagents. However, Zn and Pb extraction efficiencies increased with increasing L/S ratio for all acids. A large difference between an L/S ratio of 5/1 and 10/1 was observed for Pb in HNO<sub>3</sub>. Therefore, an L/S ratio of 10/1 was suitable for extracting the greatest amount of heavy metals and providing energy-efficient recovery of heavy metals from MFA.

### 3.4 XANES spectroscopy analysis of heavy metals in the residue after extraction

#### (1) Zinc

The changes in the chemical forms of Zn in MFA using different acids and the spectra of the reference

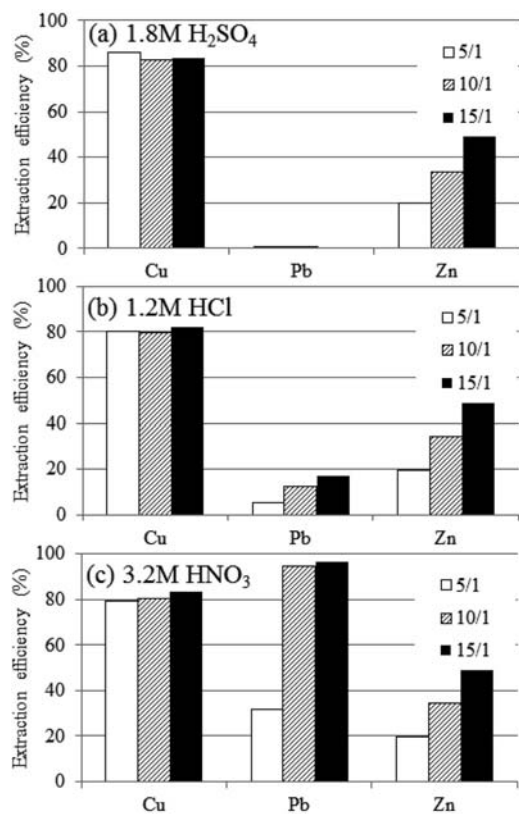


Fig. 7 Effect of L/S ratio on extraction efficiency (Time=60 min, Temp.=50°C)

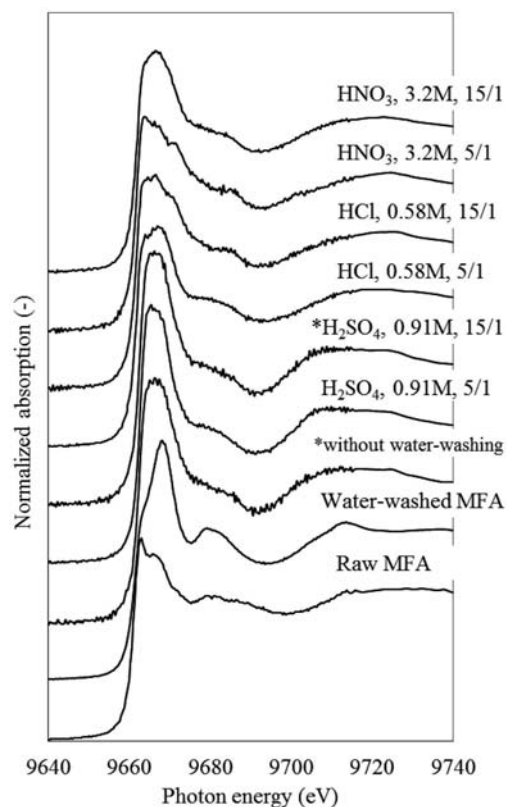


Fig. 8 Zn K-edge XANES spectra in MFA using different acids with different concentrations and L/S ratios

samples are shown in **Figures 8** and **9**, respectively. The XANES spectra were different before and after acid extraction, confirming that reactions occurred and depended on the acid used. **Table 4** shows the percentages relative to the total Zn obtained by the LCF for the XANES spectra of MFA. The residual values in most cases were relatively high; hence, the species and ratios include some ambiguity. One of the reasons might be the “lack of reference materials.”

Zn compounds in the raw MFA were mainly composed of zinc sulfide (ZnS; 52%), zinc chloride (ZnCl<sub>2</sub>; 26%), and zinc oxide (ZnO) or zinc hydroxide [Zn(OH)<sub>2</sub>; 22%]. These species have been observed in municipal solid waste incinerator fly ash<sup>19</sup>. Because the residual value was relatively high, the calculated spectrum was not in complete agreement with the measured spectrum. However, the above mentioned leach ratio (25%) during the water-washing treatment matched the ratio of the easily soluble Zn compound ZnCl<sub>2</sub>. When acid extraction was conducted following water washing, the spectrum changed substantially, and ZnO or Zn(OH)<sub>2</sub> was predominant. The ratio of ZnO or Zn(OH)<sub>2</sub> increased to 52% of the total Zn in the water-washed MFA, whereas ZnS in the raw MFA may have been

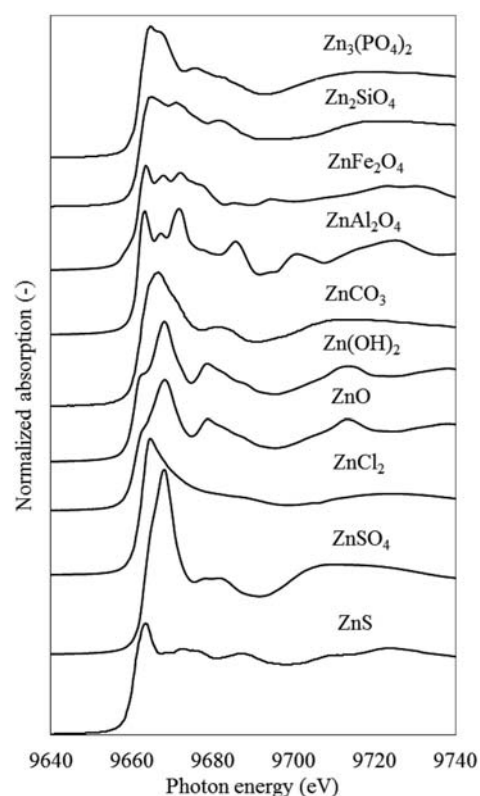


Fig. 9 Zn K-edge XANES spectra in reference materials

converted to other Zn compounds.

Although large differences were observed in the spectra of water-washed MFA and the MFA after H<sub>2</sub>

**Table 4** Linear combination fittings (LCF) of Zn K-edge XANES spectra indicating the relative proportions of Zn species in the samples

Sample condition	ZnS	ZnSO <sub>4</sub>	ZnCl <sub>2</sub>	ZnO or Zn(OH) <sub>2</sub> **	ZnCO <sub>3</sub>	ZnAl <sub>2</sub> O <sub>4</sub>	ZnFe <sub>2</sub> O <sub>4</sub>	Zn <sub>2</sub> SiO <sub>4</sub>	Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	R
Raw MFA*	52	—	26	22	—	—	—	—	—	0.036
Water-washed MFA	—	23	—	52	—	—	—	25	—	0.021
H <sub>2</sub> SO <sub>4</sub> , 1.8 M, 15/1	—	31	—	—	42	—	—	—	27	0.032
H <sub>2</sub> SO <sub>4</sub> , 1.8 M, 5/1	—	42	—	—	21	—	—	—	37	0.039
H <sub>2</sub> SO <sub>4</sub> , 0.91 M, 15/1 without water-washing	—	23	—	—	53	—	—	—	24	0.033
HCl, 0.58M, 15/1	—	—	18	—	48	—	34	—	—	0.018
HCl, 0.58M, 5/1	18	26	17	—	—	—	—	39	—	0.019
HNO <sub>3</sub> , 3.2M, 15/1	—	—	—	—	75	—	25	—	—	0.021
HNO <sub>3</sub> , 3.2 M, 5/1	—	—	23	—	32	16	29	—	—	0.013

\* X-ray fluorescence detected by a 19-element solid-state detector

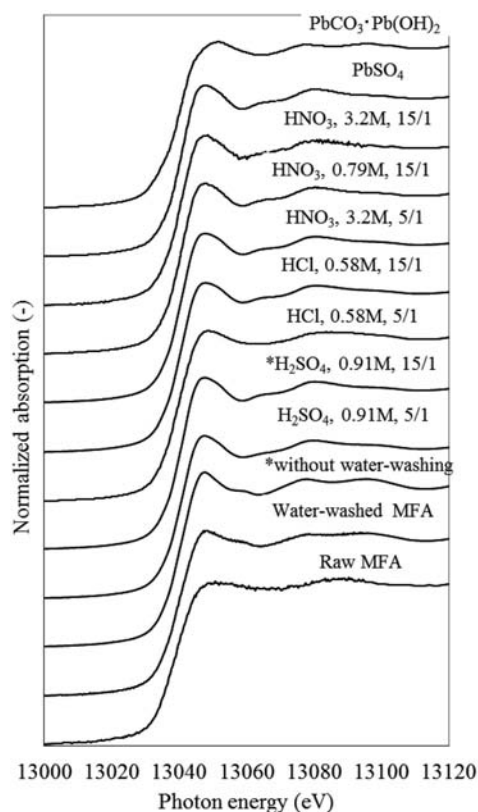
\*\*Close similarity to XANES spectrum shape, LCF of Zn (9650–9730 eV) by using 12 Zn reference compounds ≥ 15%

SO<sub>4</sub> extraction, the chemical forms of Zn present with and without water washing prior to H<sub>2</sub>SO<sub>4</sub> extraction were similar in both samples (\*H<sub>2</sub>SO<sub>4</sub>, 0.91 M, 15/1 and \*without water washing). The XANES results corresponded to the extraction efficiency results shown in **Figure 3**. The LCF for the XANES spectra of Zn in the MFA after H<sub>2</sub>SO<sub>4</sub> extraction determined the combination of zinc sulfate (ZnSO<sub>4</sub>), zinc carbonate (ZnCO<sub>3</sub>), and zinc phosphate [Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>]. None of the peak shapes in any of the spectra were sharp after acid extraction, suggesting that some Zn compounds were included in the residues.

Higher extraction efficiencies were obtained for all acid reagents with a larger L/S ratio. Although increasing the L/S ratio improved the extraction efficiency, as shown in **Figure 7**, the Zn K-edge XANES spectra showed a similar pattern for 0.91 M H<sub>2</sub>SO<sub>4</sub> at different L/S ratios. However, the Zn K-edge XAFS spectra produced different patterns for different L/S ratios when using HCl and HNO<sub>3</sub>. **Table 4** gives the XANES results of the relative proportions of Zn species in the samples treated with different acids and at different L/S ratios. Although the proportion of ZnCO<sub>3</sub> increased with increasing L/S ratio for all acids, ZnCO<sub>3</sub> did not appear in the water-washed MFA. Because clear results were not obtained for Zn speciation, other experimental methods or types of fly ash should be employed in future research.

**(2) Lead**

Pb extraction was significantly different depending on whether H<sub>2</sub>SO<sub>4</sub> or HNO<sub>3</sub> was used. This result suggests that extraction of Pb was negatively affected by H<sub>2</sub>SO<sub>4</sub>, whereas HNO<sub>3</sub> had little impact on Pb extraction<sup>20</sup>. The Pb LIII-edge XANES spectra for the reference materials and MFA samples are shown



**Fig. 10** Pb LIII-edge XANES spectra in reference materials and MFA using different acids with different concentrations and L/S ratios

in **Figure 10**. The predominant chemical form of Pb was PbCO<sub>3</sub>·Pb(II) hydroxide [Pb(OH)<sub>2</sub>] in the raw MFA and water-washed MFA, but it was PbSO<sub>4</sub> in acid-treated MFA, except for the 0.58 M HCl extracted sample. Although the Pb LIII-edge XANES spectra of samples with all acid reagents indicated the presence of chemical forms of Pb similar to those in the reference materials, the extraction efficiency was only high when HNO<sub>3</sub> was used.

The LCF analyses investigated the differences in Pb LIII-edge XANES spectra more quantitatively and computed the proportions of the different Pb species in

the samples. As shown as **Table 5**, the proportion of  $\text{PbSO}_4$  was  $>76\%$  except for the 0.58 M HCl extraction using the lower L/S ratio, suggesting that Pb existed mainly as  $\text{PbSO}_4$ . Pb precipitates with sulfuric ions when sulfuric ions are leached into solution.  $\text{PbSO}_4$  is less soluble in dilute  $\text{H}_2\text{SO}_4$  but is more soluble in dilute  $\text{HNO}_3$  and in concentrated  $\text{H}_2\text{SO}_4$  than in pure water<sup>25)</sup>. Therefore,  $\text{PbSO}_4$  formed in dilute  $\text{H}_2\text{SO}_4$  is insoluble<sup>13, 26)</sup>, whereas  $\text{PbSO}_4$  formed in dilute  $\text{HNO}_3$  is soluble<sup>25, 26)</sup>. The residual values in most cases were relatively low; hence, the species and ratios are considered reasonable.

### (3) Copper

Extraction of Cu was not significantly different under any of the conditions, except with and without the water-washing stage. Therefore, a XANES analysis was conducted for selected samples. Changes in the chemical forms of Cu in MFA are shown in **Figure 11**.

**Table 6** presents percentages relative to total Cu obtained by the LCF for the XANES spectra of MFA. Cu compounds were mainly composed of atacamite [ $\text{Cu}_2(\text{OH})_3\text{Cl}$ ; 37%], Cu(II) oxide (CuO; 37%), and cuprous chloride (CuCl; 26%) in raw MFA. These species have been observed in municipal solid waste

**Table 5** Linear combination fittings of Pb LIII-edge XANES spectra indicating the relative proportions of Pb species in the samples

Sample condition	$\text{PbCO}_3$	$\text{Pb}(\text{OH})_2$	$\text{PbSO}_4$	R
Raw MFA*	76	24	0.011	
Water-washed MFA	61	39	0.009	
$\text{H}_2\text{SO}_4$ , 0.91 M, 15/1	—	100	0.004	
$\text{H}_2\text{SO}_4$ , 0.91 M, 5/1	—	100	0.005	
$\text{H}_2\text{SO}_4$ , 0.91 M, 15/1 without water-washing	24	76	0.012	
HCl, 0.58 M, 15/1	15	85	0.004	
HCl, 0.58 M, 5/1	61	39	0.007	
$\text{HNO}_3$ , 3.2 M, 15/1	—	100	0.008	
$\text{HNO}_3$ , 0.79 M, 15/1	—	100	0.004	
$\text{HNO}_3$ , 3.2 M, 5/1	—	100	0.004	

\*X-ray fluorescence detected by a 19-element solid-state detector LCF of Pb (13000~13120 eV) using 19 Pb reference compounds  $\geq 10\%$

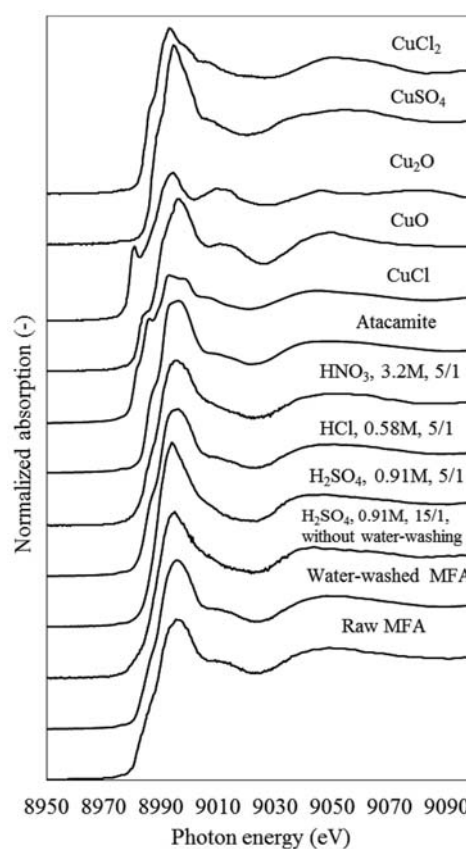
**Table 6** Linear combination fittings of Cu K-edge XANES spectra indicating the relative proportions of Cu species in the samples

Sample condition	Atacamite	CuCl	CuO	$\text{Cu}_2\text{O}$	$\text{CuSO}_4$	$\text{CuCl}_2$	R
Raw MFA*	37	26	37	—	—	—	0.009
Water-washed MFA	61	—	39	—	—	—	0.010
$\text{H}_2\text{SO}_4$ , 0.91 M, 15/1 without water-washing	46	—	—	22	32	—	0.022
$\text{H}_2\text{SO}_4$ , 0.91 M, 5/1	—	—	—	—	72	28	0.028
HCl, 0.58 M, 5/1	65	—	16	—	—	18	0.010
$\text{HNO}_3$ , 3.2 M, 5/1	55	—	30	—	—	15	0.014

\*X-ray fluorescence detected by a 19-element solid-state detector, LCF of Cu (8960~9130 eV) using 12 Cu reference compounds  $\geq 10\%$

incinerator fly ash<sup>22, 27)</sup>. CuCl forms a complex with chloride ions in aqueous solution, but the Cu leach ratio was low during water washing. Therefore, the CuCl fraction was converted to  $\text{Cu}_2(\text{OH})_3\text{Cl}$  and precipitated.

The extraction efficiencies of Cu improved during  $\text{H}_2\text{SO}_4$  extraction following water washing, compared to that without water washing (**Figure 3**). In addition, the L/S ratio did not significantly affect the extraction. The  $\text{Cu}_2(\text{OH})_3\text{Cl}$  fraction disappeared in the residue after  $\text{H}_2\text{SO}_4$  extraction with water washing, and  $\text{CuSO}_4$  and  $\text{CuCl}_2$  were predominant, suggesting that new products were precipitated in  $\text{H}_2\text{SO}_4$  solution after the Cu compounds dissolved.  $\text{CuCl}_2$  was



**Fig. 11** Cu K-edge XANES spectra in reference materials and MFA using different acids with different concentrations and L/S ratios



also produced during the HCl extraction. However, the spectra for both the HCl and HNO<sub>3</sub> extractions were similar. The linear combination fitting result might be artificial for the HNO<sub>3</sub> extraction because we could not measure the Cu (II) nitrate [Cu (NO<sub>3</sub>)<sub>2</sub>] XANES spectrum.

#### 4. CONCLUSIONS

Recovery of heavy metals from MFA using different acids was compared and the appropriate experimental conditions were determined for a variety of experimental variables.

Water washing was necessary to improve Cu extraction efficiency from MFA. Less than 1.0 M concentrated acid, an L/S ratio of 10/1, and a 30 min reaction time were suitable for dissolving the heavy metals in MFA.

The extraction characteristics of Zn, Pb, and Cu were established by XAFS measurements. The Zn and Cu extraction characteristics produced different results depending on the type of acid used. However, the chemical state of Pb in the residue was not dependent on the acid used. Pb extraction efficiency using H<sub>2</sub>SO<sub>4</sub> was significantly different from that using HNO<sub>3</sub>. The Pb LIII-edge spectra suggested that PbSO<sub>4</sub> was the predominant chemical species and that it was present in high proportions following extraction with all acids, although the extraction efficiency was likely determined by the type of acid. The PbSO<sub>4</sub> that formed in dilute H<sub>2</sub>SO<sub>4</sub> was insoluble, whereas the PbSO<sub>4</sub> that formed in dilute HNO<sub>3</sub> was soluble. Because clear results were not obtained for Zn speciation, other experimental methods or types of fly ash should be employed in future research.

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#### REFERENCES

- 1) N. Takeda, W. Wang, M. Takaoka : Solid Waste Management, Urban Environment 3, Kyoto University Press (2014)
- 2) M. Takaoka : Remove toxic metals from waste incineration fly ash, *Kagaku*, Vol. 76, No. 1, pp. 91-94 (2006)
- 3) JOGMEC : Mineral Resource Information, <http://mric.jogmec.go.jp/index.html> (2014)
- 4) T. Fujiwara, N. Takeda, K. Nakahara, T. Akashi, M. Tsurui, H. Nagasaki : Feasibility study on heavy metals recovery from fly ash of ash melting furnace by utilizing existing production facilities as social resources, *Energy and resources*, Vol. 23, No. 1, pp. 55-60 (2002)
- 5) M. Takaoka, T. Kawai, N. Takeda, K. Oshita : Recovery of heavy metals in fly ash from ash melting furnace by solvent extraction, *Environ, Eng, Res.*, Vol. 39, pp. 403-412 (2002)
- 6) G. C. Tian, J. Li, Y. X. Hua : Application of ionic liquids in hydrometallurgy of nonferrous metals, *Transactions of Nonferrous Metals Society of China*, Vol. 20, No. 3, pp. 513-520 (2010)
- 7) F. S. Zhang, H. Itoh : Extraction of metals from municipal solid waste incinerator fly ash by hydrothermal process, *J. Hazardous Materials B136*, 663-670 (2006)
- 8) S. Nagib, K. Inoue : Recovery of lead and zinc from fly ash generated from municipal incineration plants by means of acid and/or alkaline leaching, *Hydrometallurgy*, Vol. 56, pp. 269-292 (2000)
- 9) S. Anand, K. S. Rao, P. K. Jena : Pressure leaching of copper converter slag using dilute sulphuric acid for the extraction of cobalt, nickel and copper values, *Hydrometallurgy*, Vol. 10, pp. 303-312 (1983)
- 10) A. Aydogan, M. Canbazoglu, U. Akdemir : Processing of Hafik-Madentepper slag using conventional leaching methods, *Mineral Proc. on the 21st Century*. Balkema, Rotterdam, pp. 529-533 (2000)
- 11) F. E. Huggins, N. Shah, G. P. Huffman, J. D. Robertson : XAFS spectroscopic characterization of elements in combustion ash and fine particulate matter, *Fuel Proc. Technol.*, Vol. 65-66, 203-218 (2000)
- 12) C. Y. Chan, D. W. Kirk : Behaviour of metals under the conditions of roasting MSW incinerator fly ash with chlorination agents, *Journal of Hazardous Materials*, Vol. 64, No. 1, pp. 75-89 (1999)
- 13) M. Fujita, N. Tanaka, T. Matsuto : Recovery of zinc, lead and copper from melting furnace fly ash by means of acid leaching, *Proc. of the 13th Annual Conf. of The Japan Society of Waste Manage. Experts*, pp. 522-524 (2002)
- 14) G. Van Weert, M. Boering : Selective pressure leaching of zinc and management from natural and man-made spinels using nitric acid, *Hydrometallurgy* Vol. 39, pp. 201-213, 1995.
- 15) D. A. Wynn : A complete dissolution procedure for Sn-Pb solders using nitric and hydrochloric acids with simultaneous determination of major and trace elements by ICP/OES, *Talanta*, Vol. 40, No. 8, pp. 1207-1211 (1993)
- 16) K. H. Kim, C. K. Shin, I. R. Jung, J. J. Jeon, S. H. Song : Study on pH-Dependent Leaching Characteristics of Metals in Ash at MSW incinerator, Korean Society of Waste Management, *The conference of KWMS 2004* autumn, pp. 1-17 (2004)
- 17) S. V. Plokhov, I. G. Matasova, V. A. Utkin, V. Yu. Vodzinskii : Specific Features of Ion-Exchange Zinc(II) Extraction from Washing Water of Zinc Plating, *Russian Journal of Applied Chemistry*, Vol. 75, No. 6, pp. 950-953 (2002)
- 18) Y. K. Kim, J. L. Kim, W. K. Lee : Comparison of Leaching Characteristics of Copper and Zinc from MSWI Fly Ash by Oxidation-acid Leaching Method, *Journal of Korean Society of Waste Management*, Vol. 23, No. 6, pp. 534-541 (2006)
- 19) M. Takaoka, T. Yamamoto, T. Tanaka, N. Takeda, K. Oshita, T. Uruga : Direct Speciation of Lead, Zinc and Antimony in fly Ash from Waste Treatment Facilities by XAFS spectroscopy,

- Physica Scripta*, Vol. T115, pp. 943-945 (2005)
- 20) D. Roberts, A. C. Scheinost, D. L. Sparks: Zinc Speciation in Contaminated Soils Combining Direct and Indirect Characterization Methods. In *Geochemical and Hydrological Reactivity of Heavy Metals in Soils*; H. M. Selim, W. L. Kingery, Eds.; Lewis Publishers: Boca Raton, FL, pp. 188-227 (2003)
- 21) T. Ressler, J. Wong, J. Roos, I. L. Smith: Quantitative speciation of Mn-bearing particulates emitted from autos burning (methylcyclopentadienyl) manganese tricarbonyl-added gasolines using XANES spectroscopy. *Environ. Sci. Technol.* Vol. 34, pp. 950-958 (2000)
- 22) M. Takaoka, A. Shiono, K. Nishimura, T. Yamamoto, T. Uruga, N. Takeda, T. Tanaka, K. Oshita, T. Matsumoto, H. Harada: Dynamic Change of Copper in Fly Ash during de Novo Synthesis of Dioxins, *Environ. Sci. Technol.* Vol. 39, pp. 5878-5884 (2005)
- 23) G. Spigno, L. Tamelli, D. M. de faveri: Effects of extraction time, temperature and solvent on concentration and antioxidant activity of grape marc phenolics. *J. Food Eng.*, Vol. 81, pp. 200-208 (2007).
- 24) A. N. Banza, E. Gock, K. Kongolo: Base metals recovery from copper smelter slag by oxidizing leaching and solvent extraction, *Hydrometallurgy* 67 (2002) 63-69.
- 25) H. Sakurai, J. Noro, A. Kawase, M. Fujinami, K. Oguma: Digestion of Plastic Materials for the Determination of Toxic Metals with a Microwave Oven for Household Use, *Analytical Sciences*, Vol. 22, pp. 225-228 (2006)
- 26) H. P. Cady: *Inorganic Chemistry: International Chemical Series (Classic Reprint)*, Forgotten Books, pp. 521 (2000)
- 27) M. Takaoka, T. Yamamoto, A. Shiono, N. Takeda, K. Oshita, T. Matsumoto, T. Tanaka: The effect of copper speciation on the formation of chlorinated aromatics on real municipal solid waste incinerator fly ash, *Chemosphere*, Vol. 59, pp. 1497-1505 (2005)

## 溶融飛灰中重金属の酸抽出時の化学形態変化に関する基礎的検討

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### 概 要

都市ごみ溶融飛灰は重金属等を含む有害物質であるとともに、金属資源として貴重な資源でもある。溶融飛灰からの重金属回収にはしばしば酸溶液が使用されるが、酸抽出中に生じているプロセスを理解するための文献は限られている。本研究では、3つの一般的な酸（硫酸、塩酸、硝酸）を使用して酸抽出中の重金属の化学形態の変化を調査した。酸抽出の結果は対象とする金属及び酸の種類により異なる結果となった。X線吸収端近傍構造分析により、抽出後残さ中鉛は酸の種類によらず、硫酸鉛の形態で主に存在することがわかった。

キーワード：重金属，酸抽出，溶融飛灰，X線吸収端近傍構造