Analysis of arsenic and some other elements in coal fly ash by X-ray photoelectron spectroscopy

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Abstract

Surface characterization of coal fly ash (CFA) was carried out by use of X-ray photoelectron spectroscopy (XPS), especially focusing on the occurrence of As. A peak in the XPS spectrum of CFA was assigned to oxide forms of As(3d). The molar ratios of Al, As, Ca, Fe, and S normalized to Si were obtained from XPS analysis (MR-X). Also, the molar ratios of those elements were calculated from bulk analysis (total element concentration in CFA) (MR-B). The MR-X/MR-B ratio of As was much higher than those of other elements, suggesting that As is highly enriched on the surface of CFA. When eight CFA samples were analyzed, there was an approximate relationship between the MR-X values and MR-B values for As. The leaching of elements from CFA was examined by XPS analysis and by bulk analysis. The leaching tests using EDTA and HNO_3 resulted in a great decrease in the As(3d) peak area; the %leaching of As obtained by XPS analysis was almost equal to that by bulk analysis.
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1. Introduction

In coal, many kinds of elements including hazardous heavy metals, such as As, Hg, Pb, and Se, are present [1–3]. A portion of highly volatile metals, Hg and Se, in coal is discharged into the air in the process of coal combustion. On the other hand, moderately volatile metals, such as As and Pb, are said to be concentrated in coal fly ash (CFA), although those metals are little released into the air. Such CFAs will cause trouble when they are reused and/or disposed of, because these metals are probably enriched on the surface.

X-ray photoelectron spectroscopy (XPS) is a nondestructive surface analysis method for solid materials, and it provides the information of chemical composition on very surface (0.2–0.5 nm). Several studies about the XPS analysis of CFA have been hitherto done. Hirokawa and Danzaki [4] and Hirokawa [5] have reported the surface characterization of CFA by XPS for Ca, Fe, P, and S, and leaching behavior of these elements was assessed by XPS. The leaching behavior of some elements from CFA has been also examined using XPS by several researchers [6,7]. Takaoka et al. [8] analyzed the municipal waste fly ash by XPS, and the chemical mode and surface enrichment of some heavy metals, such as Cu, Pb, and Zn, were investigated.

However, to our knowledge, detailed studies about the analysis of heavy metals in CFA by use of XPS have scarcely been done. In this study, we conducted the XPS analysis of CFA, especially focusing on the occurrence of As; its surface enrichment was evaluated by the comparison between the XPS surface analysis and bulk analysis (total element concentration in CFA). Also, the leaching tests for CFA were performed by use of various leachants, and the leaching behavior

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of elements was studied by XPS analysis as well as by bulk analysis.

2. Materials and methods

2.1. Coal fly ash, determination of elements, and chemicals

Two certified reference materials of CFA samples from the National Institute of Standard and Technology, USA (NIST; 1633b and 2689) were used. Also, other six CFA samples, which had been collected in some coal-fired power plants in Japan, were examined. The concentrations of elements in CFA samples used are listed in Table 1. The concentrations of elements (except for As) were measured according to Japanese Industrial Standards (JIS M 8815), in which after an acid-digestion or an alkaline fusion of CFA, the concentrations of metals in the resulting solution were determined by volumetric or calorimetric analysis. All chemicals used including HNO_3 and ethylenediaminetetraacetic acid disodium salt (EDTA·2Na) were of reagent grade and purchased from Wako Pure Chemical Industries (Osaka, Japan).

2.2. Determination of As 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 a mixture of acids ($HNO_3 + HF + H_2O_2$, 5:1:2 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 $HNO_3 + H_2O_2$ (2:1 ml), microwave processing was performed again. After cooling, removal of the acids by evaporation was done. The residue was rinsed with 5 M HCl (5 ml) and then diluted to a fixed volume (50 ml), and the concentration of As was measured by graphite furnace atomic absorption spectrometry (GFAAS, Thermo Elemental SOLAAR MQZ). The determination of As as well as other elements were done at least twice and the deviation was less than 10% of the average value.

The concentrations of As in six CFA samples (CFA-1 to CFA-6) are recorded in Table 1 together with the data for NIST CFA samples. The As concentrations of these eight CFA samples varied from 7.5 to 200 μg/g for which NIST-2689 has the highest value while CFA-2 had the lowest. For NIST-1633b, which has the certified reference value of As, the accuracy of the determination of As was demonstrated (measured value, 130.6 ± 1.2 μg/g; certified value, 136.2 ± 2.6 μg/g).

2.3. XPS analysis

The metal concentration on the surface of CFA was determined by XPS. A CFA sample (0.1 g) was mixed with powdery graphite in an agate mortar, and the mixture was molded into a disc. The procedure was done in a glove box in which pure nitrogen gas was made to flow. Then the disc was allowed to stand in a vacuum (10^{-6} Pa) for one day. The sample was analyzed by use of a Shimadzu ESCA-1000 with a Mg Kα radiation for which an X-ray source power of 300 W, a sampling time of 298 ms, and a measurement area of 3 mm × 10 mm were used. To compensate for sample charging, all binding energies were referenced to C(1s) at 285 eV. The XPS peaks obtained were processed by use of software GRAMS/386 (Galactic Industries Co.), and the peak area for each element was obtained. The measurement was done at least twice, and it was confirmed that the deviation was less than 10%.

2.4. Leaching test

A CFA sample (0.3 g) was added to 25 ml of pure water or an aqueous solution containing an agent, which accounted for a liquid to solid ratio (L/S) of 80. After being shaken for 24 h in a stoppered centrifuge tube at room temperature (24–25 °C), the filtration was performed to separate the CFA. The resulting CFA was subjected to XPS analysis in a similar manner to that mentioned above. Also, the concentration of As in the filtrate was measured by GFAAS, while those of other elements were done by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Perkin-Elmer Optima 3100RL instrument.

Table 1
Concentrations of elements in CFA (wt.%)

CFA	Al	Ca	Fe	K	Mg	Na	S	Si	As[a]
NIST-1633b[b]	15.1	1.5	7.8	2.0	0.48	0.20	0.21	23.0	136
NIST-2689[c]	12.9	2.2	9.3	2.2	0.61	0.25	–	24.1	200
CFA-1	14.9	2.3	5.3	1.3	0.71	0.83	0.20	22.7	16.6
CFA-2	12.3	0.78	3.0	0.80	0.32	0.41	0.10	29.5	7.5
CFA-3	16.0	5.3	3.6	0.65	1.4	0.20	0.20	23.8	28.8
CFA-4	14.8	3.0	3.4	0.55	0.80	1.5	0.18	25.8	21.9
CFA-5	16.6	0.25	1.4	1.2	0.18	0.09	0.18	29.3	26.4
CFA-6	11.4	0.43	2.1	1.0	0.41	0.33	0.18	33.3	37.5

[a] μg/g.
[b] Certified values.
[c] Certified values except for As (reference value).

3. Results and discussion

3.1. XPS spectrum of CFA

For NIST-1633b, narrow scan spectra of Al(2p), Ca(2p$_{3/2}$), Fe(2p$_{3/2}$), S(2p), and Si(2p) were obtained; the peaks of these elements appeared at 78.4, 352.0, 715.0, 171.2, and 106.6 eV, respectively. The peak positions were almost independent of the kind of CFA. As shown in Fig. 1, an XPS narrow scan spectrum of NIST-1633b gave a peak at 48.5 eV. When the CFA sample was molded with graphite into a disc, 1 mg of Na$_2$HAsO$_4$·7H$_2$O or Ca$_3$(AsO$_4$)$_2$·3H$_2$O was further added; the XPS spectrum is also seen in Fig. 1. The addition of these arsenic oxide compounds resulted in an enlargement in the peak at 48.5 eV. This result suggests that the peak is assigned to As(3d) for arsenic oxide species. The peak at 50.5 eV seen in the XPS spectrum (Fig. 1) should be assigned to Mg(2p); the peak was not essentially changed in the addition of arsenic oxide compounds.

3.2. Comparison between XPS surface analysis and bulk analysis

For NIST-1633b, the molar ratios of Al, As, Ca, Fe, and S normalized to Si were calculated from the XPS spectral peak of each element mentioned above, and the molar ratios (MR-X) are recorded in Table 2; MR-X for each element E
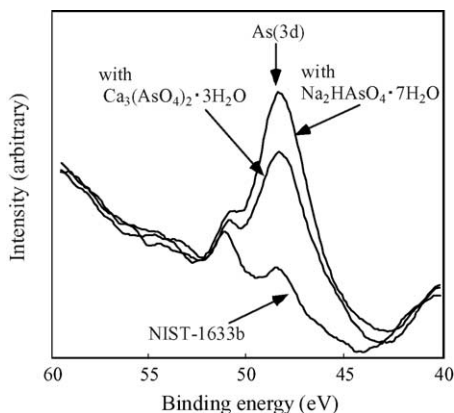

Fig. 1. XPS spectra for As(3d).

Table 2
Comparison between molar ratio for XPS analysis (MR-X) and that for bulk analysis (MR-B) (NIST-1633b)

Element (E)	Molar ratio E/Si × 10^2 (mol/mol)		MR-X/MR-B
	MR-X	MR-B	
Al	62	68	0.91
As	2.0	0.022	91
Ca	13	4.6	2.8
Fe	5.2	17	0.31
S	4.5	0.79	5.6

Table 3
Comparison between molar ratio for XPS analysis (MR-X) and that for bulk analysis (MR-B) (CFA-6)

Element (E)	Molar ratio E/Si × 10^2 (mol/mol)		MR-X/MR-B
	MR-X	MR-B	
Al	32	36	0.89
As	1.2	0.0042	270
Ca	1.7	0.90	1.9
Fe	2.1	3.1	0.69
S	8.7	0.053	170

is defined as follows.

$$\text{MR-X} = \left(\frac{\text{PA}_E/\text{PCS}_E}{\text{PA}_{Si}/\text{PCS}_{Si}} \right) \ (\text{mol/mol})$$

where PA and PCS denote XPS peak area and photoionization cross section, respectively. XPS is a semiquantitative analysis, so that the molar ratio of each element to Si is used for the comparison between XPS surface analysis and bulk analysis (total element concentration in CFA); this method has been used in the literatures [4,5,7].

In Table 2, the normalized molar ratios for the bulk analysis (MR-B), which were calculated from the certified data in Table 1, are also presented. MR-B for each element E is also defined as follows.

$$\text{MR-B} = \frac{\text{MF}_E}{\text{MF}_{Si}} \ (\text{mol/mol})$$

where MF represents the molar fraction of each element obtained from bulk analysis.

For Al, the degree of MR-X was almost similar to that of MR-B, i.e., the MR-X/MR-B ratio was obtained as 0.91, suggesting that Al equally distributes both in bulk and on surface in CFA. This result is consistent with the fact that Al and Si are matrix phase elements in CFA. The MR-X/MR-B ratios for Ca and S were 2.8 and 5.6, respectively, reflecting surface enrichment of those elements in CFA. Interestingly, As provided a quite high MR-X/MR-B ratio of 91. As described above, XPS is a semiquantitative analysis, so that this value does not necessarily represent the precise surface enrichment ratio. However, it is apparent that As is highly enriched on the surface of CFA. For Fe, the MR-X/MR-B ratio was lower than 1, which means that Fe is present in core part of CFA rather than on surface.

The high surface enrichment of As is explained as follows. As is a considerably volatile element, and thus, the element is easily vaporized in a boiler followed by condensation onto the surface of CFA in an electrostatic precipitator. When the condensation of As occurs, the CFA matrix is already completed, and therefore, the high surface enrichment will take place.

In Table 3, the results of the comparison between XPS analysis (MR-X) and bulk analysis (MR-B) for another CFA sample, CFA-6, is presented. The situation of surface enrichment of each element is generally similar to that for NIST-1633b. Al gave the MR-X/MR-B ratio of 0.89. The ratios
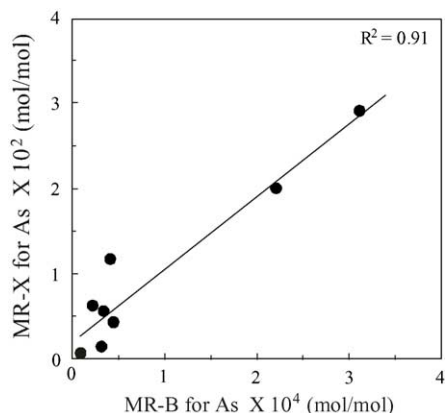
Fig. 2. Comparison between MR-X and MR-B for As in eight CFA samples.

for Ca and Fe were a little higher than 1 and lower than 1, respectively, while As provided a high MR-X/MR-B ratio. However, the MR-X/MR-B ratio of S for CFA-6 was much higher than that for NIST-1633b.

As shown in Fig. 2, there was an approximate relationship between the MR-X values and MR-B values for As, when eight CFA samples listed in Table 1 were tested; the MR-X values were 44–270 times larger than the MR-B values. Consequently, the situation of As surface enrichment is common for various CFA samples. In Fig. 3, the same plot (MR-X versus MR-B) for Al was presented, and a linear relationship was also observed. The slope of this plot was 0.97, suggesting that Al distributes in whole body of CFA.

3.3. Leaching of elements from CFA

Leaching tests of NIST-1633b were conducted under three leachant conditions: (i) pure water, (ii) 0.1 M EDTA·2Na, and (iii) 0.1 M HNO₃. The main purpose of leaching test in this study was the confirmation of surface enrichment of As in CFA. Therefore, powerful leachant conditions, such as adding EDTA and HNO₃, were used [9,10]. Fig. 4 shows an XPS spectrum of As(3d) for the raw CFA as well as those for the resulting CFA samples after the leaching test. When
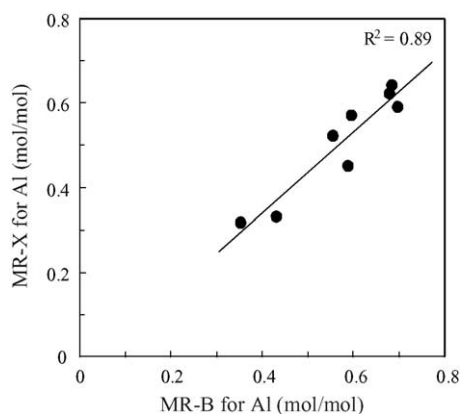

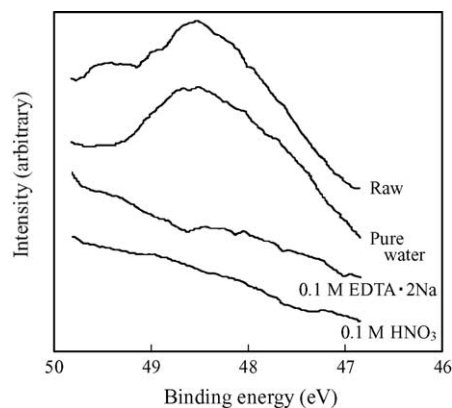Fig. 3. Comparison between MR-X and MR-B for Al in eight CFA samples.

Fig. 4. XPS spectra for As(3d) before and after the leaching (NIST-1633b).

the CFA was leached with pure water, a little decrease in the peak area was observed. The leaching tests using EDTA and HNO₃ resulted in a great decrease in the peak area.

The %leaching for XPS analysis (%L-X) was obtained from the change in the MR-X for each element before and after the leaching test. Also, the %leaching for bulk analysis (%L-B) was derived from the amount of element leached from CFA into the aqueous phase.

$$\%\text{L-X} = \left[1 - \frac{(\text{MR-X after leaching})}{(\text{MR-X before leaching})}\right] \times 100$$

$$\%\text{L-B} = \left[1 - \frac{(\text{MR-B after leaching})}{(\text{MR-B before leaching})}\right] \times 100$$

The two kinds of %leaching, %L-X and %L-B, for Al, As, Ca, and Fe are recorded in Table 4. The degree of %L-B for Si was quite small even compared to Al, so that the leaching of Si was neglected when %L-X was obtained.

For As, the degree of %L-X was similar to that of %L-B in all leachant conditions shown in Table 4. This result clearly indicates that As is almost exclusively present on the surface of CFA. It has been reported that As in CFA usually occurs in $Ca_3(AsO_4)_2$, which is hardly soluble in water [11,12]. However, as seen in Table 4, a measurable degree of %L-B is observed when even pure water is used as a leachant. It appears that the surface enrichment of As greatly contributes the susceptibility of leaching, although the element is present in hardly soluble forms. For another CFA, CFA-1, the degree

Table 4
Comparison between %leaching for XPS analysis (%L-X) and that for bulk analysis (%L-B) (NIST-1633b)

Element	Leachant					
	Water		0.1 M EDTA·2Na		0.1 M HNO₃	
	%L-X	%L-B	%L-X	%L-B	%L-X	%L-B
Al	[a]	[a]	28	[a]	41	5
As	12	9	70	67	90	92
Ca	22	14	67	22	86	47
Fe	[a]	[a]	33	1	56	4

[a] <1%.

of %L-X for As was also similar to that of %L-B (ca. 80%), when the leaching test with HNO_3 was performed.

For Ca, the degree of %L-X was higher than that of %L-B in all leachant conditions. It is reasonable that the leaching from surface is larger than that from bulk. The leaching of Al and Fe from bulk was quite small, however a measurable degree of %L-X was observed, when EDTA and HNO_3 were used as leachants.

4. Conclusions

The surface analysis of CFA by XPS was conducted, especially focusing on the occurrence of As. An XPS spectrum of CFA at 48.5 eV was assigned to oxide forms of As(3d). A high surface enrichment of As was proved by the fact that the MR-X value for As was much higher than MR-B. The leaching of elements from CFA was examined by XPS analysis and by bulk analysis. When the leaching test was performed by use of EDTA and HNO_3, the degree of %L-X for As was almost equal to that of %L-B. This result strongly supports the surface enrichment of As in CFA.

Acknowledgements

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