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Journal of Hazardous Materials B119 (2005) 213–217

Journal of Hazardous Materials

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

Akira Ohki*, Tsunenori Nakajima, Yuka Sakaguchi, Akira Iwashita, Hirokazu Takanashi

Department of Bioengineering, Faculty of Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

Received 21 December 2003; received in revised form 8 November 2004; accepted 15 December 2004
Available online 26 January 2005

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.

Keywords: Coal fly ash; X-ray photoelectron spectroscopy; Surface analysis; Arsenic; Leaching behavior

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

* Corresponding author. Tel.: +81 99 285 8335; fax: +81 99 285 8339.
E-mail address: ohki@be.kagoshima-u.ac.jp (A. Ohki).

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doi:10.1016/j.jhazmat.2004.12.016

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).