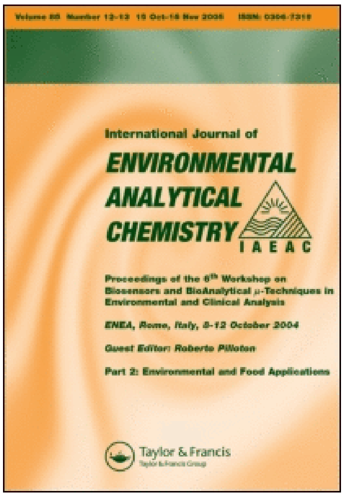

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X-RAY PHOTOELECTRON SPECTROSCOPIC STUDIES OF MUNICIPAL INCINERATOR ASHES*

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Surface predominance of heavy metals such as Pb, Sn, Cu and Zn in the fly and bottom ash particles from a municipal incinerator was demonstrated by X-ray photoelectron spectroscopy (XPS). Their concentrations in the surface layers determined by XPS were apparently higher than their average bulk concentrations whereas those of major elements such as Al, Fe, Mg and Na were lower in the surface than in the bulk. By leaching the ash with water, soluble elements were effectively dissolved from the surface. Lead, once dissolved in the leachate, redeposited on the fly ash particles as sulfate, existence of which was indicated by Pb 4f binding energies, resulting in the surface concentration of Pb higher than that before leaching.

KEY WORDS: Fly ash, municipal incinerator ash, X-ray photoelectron spectroscopy (XPS), heavy metals, surface analysis.

INTRODUCTION

Among surface analytical techniques, X-ray photoelectron spectroscopy (XPS) is suited for the application to environmental samples[1] in that it is not difficult to obtain XP-spectra of reasonable quality of such materials with complicated matrices. The range of its environmental application[1,2] has been limited because it is often not sensitive enough to detect trace elements which are environmentally very important. Once the measurement is successful its elemental informations about the surface layers as well as chemical bonding-state informations are valuable since the surface is where solid environmental matters interact with environment.

It has been shown that, in coal fly ash, volatile heavy metals tend to accumulate at the surface of fly ash particles.[3-7] By XPS, however, direct observation of the surface heavy-metal elements has been difficult because of its limited

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sensitivity.[8-12] In this report, XPS has been applied to municipal incinerator ashes where the higher concentrations of heavy metals have been anticipated.[13-15]

EXPERIMENTAL

Ash samples were obtained from a municipal incinerator. A portion of fly ash which passed through a multicyclone collector was collected by an electrostatic precipitator. Bottom ash was collected after passing through a water tank where the fly ash collected by the multicyclone and the electrostatic precipitator was also added. Thus, the bottom ash in the present study was in fact a mixture of bottom and fly ash treated with water. For analysis the fly ash was passed through a 2 mm-sieve. Coarse residues such as metal and glass debrises were removed from the bottom ash, which was then dehydrated, dried at 30 °C for 48 h, passed through a 2 mm-sieve and crushed to powder.

XP-spectra were recorded on a VG ESCALAB 5 apparatus equipped with Al-Kα and Mg-Kα excitation sources. The measurement procedures were described elsewhere.[2,16] The semi-quantitative analysis by XPS was based on the area intensity of the electron emission line and on the relative atomic sensitivity factor.[2,16] The electron emission lines utilized for the quantification were Si 2s, Al 2s, Fe 2p, Mg-KLL Auger, Na 1s, K 2p, Ca 2p, O 1s, C 1s, S 2p, P 2p, F 1s, Cu $2p_{3/2}$, Zn $2p_{3/2}$, Pb 4f and Sn $3d_{5/2}$. In representing the XPS results in weight percent the contribution of hydrogen and other elements with non-detectable XPS intensities were neglected. The photoelectron binding energies and Auger electron kinetic energies were determined relative to the Au $4f_{7/2}$ binding energy (83.8 eV) of a gold film vacuum evaporated onto the sample.

For the total elemental analysis, the ash samples were digested by HNO_3-$HClO_4$-HF mixed acid. For leaching by water, 1 g of ash was treated by 10 ml of water. The concentrations of elements in the digests and leachates were determined by ICP atomic emission spectrometry (Seiko-JY48PVH) supplemented by atomic absorption spectrometry. Concentrations of anions were determined by ion chromatography after extracting the samples by water under ultrasonification.

RESULTS AND DISCUSSION

Figure 1 shows the survey XP-spectrum of the fly ash using Mg-Kα excitation. It was recorded in 20 min and revealed the characteristic elemental distribution of the surface layers of the fly ash particles probed by XPS. Prominent peaks of Cl and heavy metals such as Zn, Pb, and Sn were easily detected. The results of wet chemical analyses were summarized in Table 1. The 1st and 4th columns are the total elemental composition of the fly ash and bottom ash respectively. The 2nd and 5th columns include the corresponding analytical values for the ashes after leaching by distilled water for 5 min. The 3rd and 6th columns show the percentage portion of each element dissolved by the leaching, calculated as the ratio of the amount leached to the total. For the most elements, amount dissolved

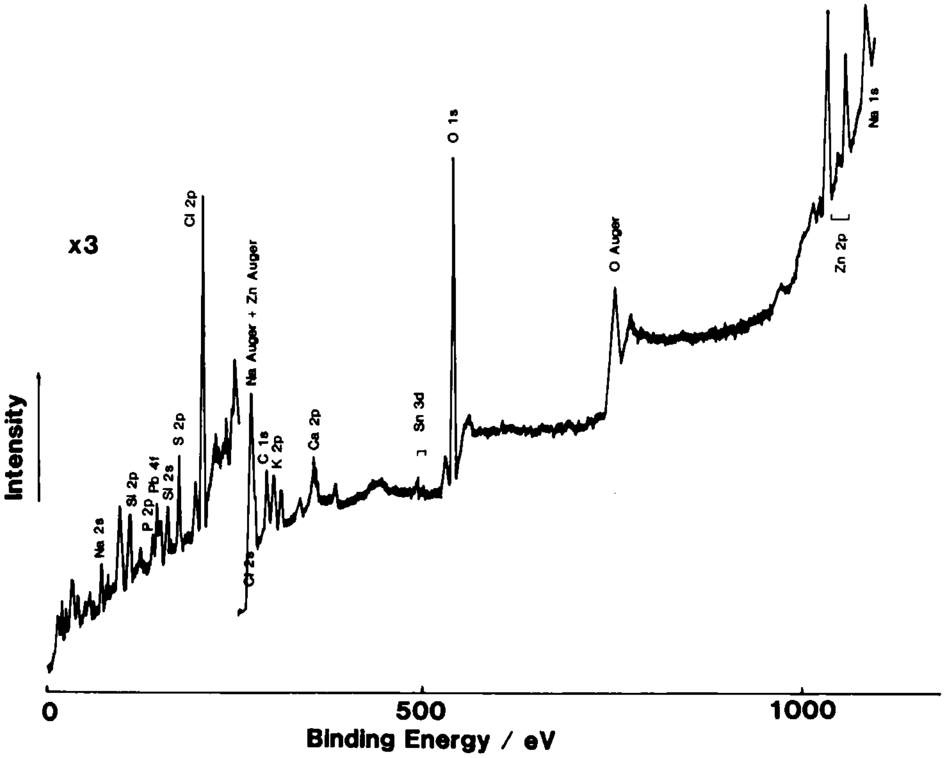

Figure 1 XP spectrum of the municipal incinerator fly ash excited by Mg-Kα.

in the leachates did not change very much after 5 min. As can be seen in the table major constituents of the leachate from fly ash are Na and K as cations and chloride and sulfate anions. The concentrations of sparingly soluble elements such as Al, Fe, Ti and V in the residue of fly ash after the leaching (2nd column) were simply about 1.7 times of those in the original fly ash, that is, 41% (in weight) of the original fly ash was dissolved. Notably, Cd was as easily soluble as alkali ions. The high solubility of Cd in municipal incinerator fly ash was previously reported.[14] Unfortunately, Pb 4d and possibly N 1s lines interfered with the strongest Cd lines in XPS, 3d lines (see below), which made the XPS study of Cd difficult. The solubility of elements in the bottom ash was in general markedly smaller than those in the fly ash. This resulted in the smaller changes in the elemental composition of bottom ash after leaching. One trivial reason for this would be that the bottom ash was already once passed through a cooling water tank.

We compare the XPS and bulk analyses by two figures. Figure 2 depicts the major-elemental composition of the fly ashes. The most remarkable difference between the bulk and surface (XPS) concentration is found for Zn. However, except for Zn, the difference between the bulk and surface compositions and its change after the leaching was not apparent for the other elements in Figure 2. Figure 3 shows the surface to bulk ratio of the concentration of each elements

Table 1 Elemental compositions of the municipal incinerator ashes (mg/kg)

	Fly ash			*Bottom ash*		
	Unleached	*Leached by water for 5 min*	*% leached*	*Unleached*	*Leached by water for 5 min*	*% leached*
Al	51200	90300	<0.1	69200	79800	0.7
Fe	37300	65200	<0.1	38000	32700	<0.1
Mg	35500	59600	4	23600	23100	<0.1
Ca	83600	102000	16	132000	139000	1
Na	76400	15500	78	18600	18100	13
K	94400	19100	68	17700	15900	13
Ti	9410	15700	<0.1	8320	8970	<0.1
Mn	770	1180	5	1000	1050	<0.1
Ba	950	1560	—	850	900	—
Cd	310	100	74	44	45	<1
Cr	400	630	—	270	280	—
Cu	1320	2270	<0.1	650	760	<1
Ni	59	110	—	46	57	—
Pb	5710	9610	2	1030	1020	<1
Sn	1870	2750	—	490	470	—
Sr	210	270	—	250	260	—
V	53	91	<0.1	99	93	<0.1
Zn	19000	27400	14	5050	4990	<0.1
Cl^-	136000	1600		6500	1300	
NO_3^-	590	230		ND	ND	
SO_4^{2-}	122000	36000		9300	5900	

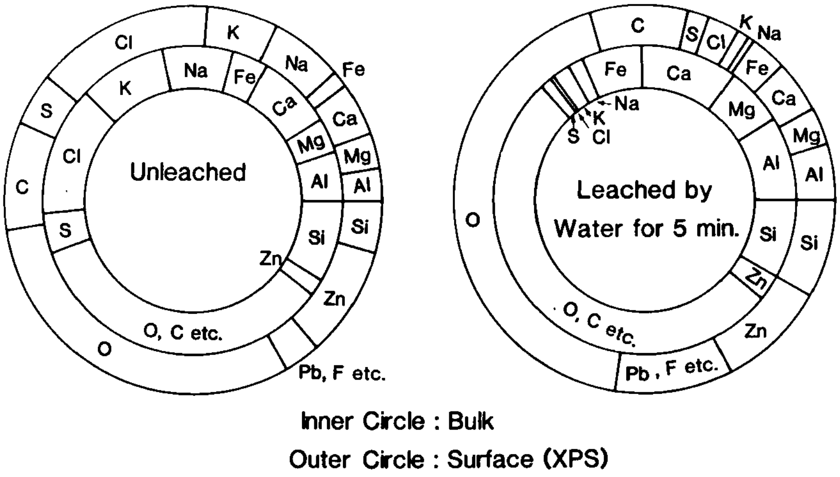

Figure 2 Elemental composition of the municipal incinerator fly ash before and after the leaching by water (in weight %). Inner circles represent the bulk compositions and outer circles the surface composition as determined by XPS.

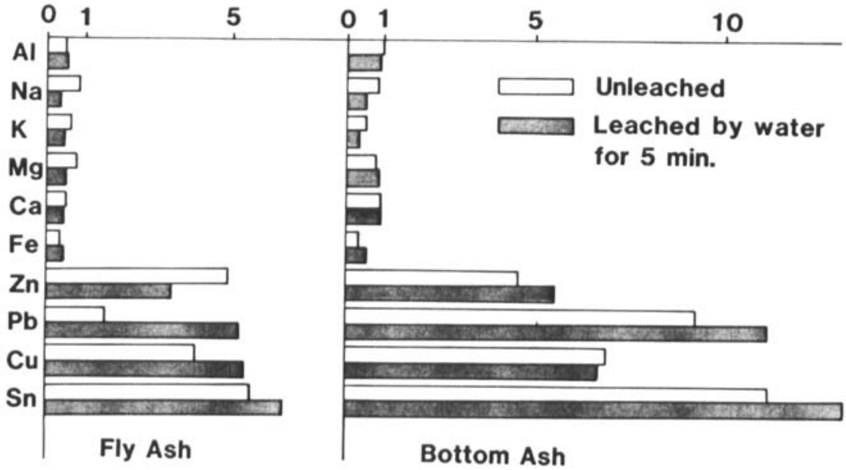

Figure 3 $(\text{Surface})_{XPS}/(\text{Bulk})_{Total}$ ratio of the concentration (in weight) of elements in the municipal incinerator ashes.

before and after the leaching for both the fly ash and bottom ash. The enrichment of heavy metals in the surface of ashes is clearly seen. Similar phenomena were reported for coal fly ashes.[5] Those elements which have the ratio less than unity were regarded to be diluted in the surface layers by the surface enriched elements.

The ratio for soluble major elements in the fly ash such as Na and K decreased after the leaching, suggesting the easier dissolution of those elements from the surface. Correspondingly, the ratio for the sparingly soluble elements such as Fe increased after the leaching. Among heavy metals observed, the ratio for Zn decreased after the leaching showing that Zn in the surface layers was more easily dissolved by water. On the contrary, the surface concentration of Pb significantly increased after the leaching. Pb 4f spectrum (Figure 4) of the fly ash after the leaching demonstrated that the Pb $4f_{7/2}$ binding energy coincided with that of $PbSO_4$ (139.2 eV) within ±0.1 eV. The S 2p binding energy (169.3 eV) showed that sulfate was the surface sulfur species. Accordingly dissolved Pb redeposited onto the surface as $PbSO_4$ giving the higher surface concentration of Pb. The speciation of Pb at the surface of original fly ash by Pb 4f spectrum was difficult because of overlapping Zn 3s line as illustrated in Figure 4. Pb 4d lines are broader than the 4f lines and hence not very suited for the speciation, but the $4d_{5/2}$ line was not seriously disturbed by the lines of other elements. The Pb $4d_{5/2}$ spectra (Figure 5) suggested a positive shift in the binding energy after the leaching. We attribute this to the contribution of $PbCl_2$ in the original fly ash and consider that Pb dissolved as chloro-complexes and precipitated as sulfate. The minor peak around 405 eV in the spectrum of unleached fly ash was attributed mainly to Cd $3d_{5/2}$. The disappearance of this peak after the leaching is consistent with the large solubility of Cd in the fly ash.

2% HCl and 1 M CH_3COONH_4 extracted elements from the ashes more effectively than leaching by water. Preliminary XPS study of those ash particles, as well as the analyses of extracts, revealed the specific changes in the concentrations

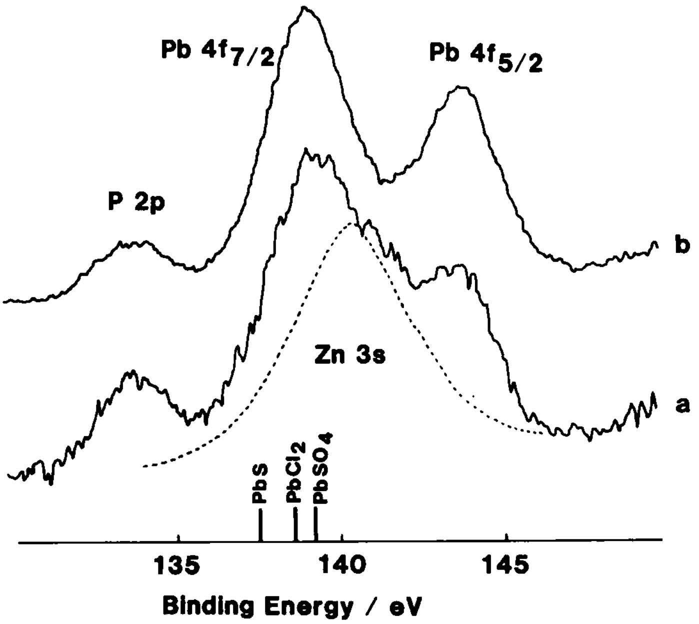

Figure 4 Pb 4f spectra of the municipal incinerator fly ash; a, original unleached sample and b, leached by water for 50 min.

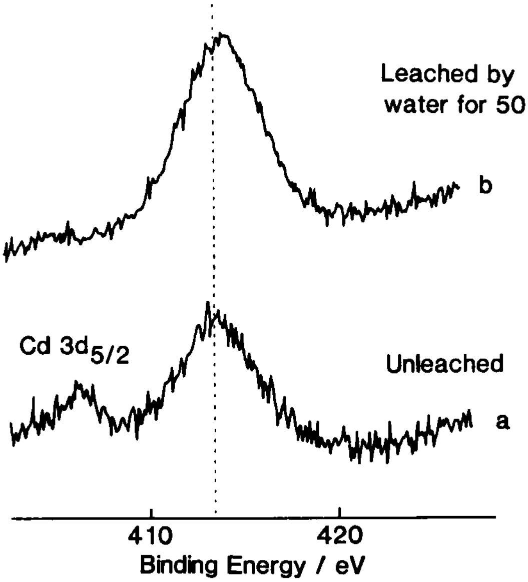

Figure 5 Pb $4d_{5/2}$ spectra of the municipal incinerator fly ash; a, original unleached sample and b, leached by water for 50 min.

of elements in the surface layers along with the behaviors of anions such as Cl^-, PO_4^{3-}, SO_4^{2-} and F^-.

The present study has demonstrated that XPS reveals the distribution of environmentally important elements at the surface layers of municipal incinerator ash particles and its changes by leaching or solvent extraction. Those informations are important in assessing the environmental behavior of ash particles.

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