Direct Speciation of Copper, Lead, Antimony, Zinc and Chromium in Municipal Solid Waste Incinerator Fly Ash by X-ray Absorption Fine Structure Spectroscopy

In Japan, about 50 million tons of municipal solid waste (MSW) are generated every year and more than 75% of MSW is incinerated. MSW incineration is an excellent technology from the viewpoint of the weight and volume reduction of MSW and public sanitation. However, approximately 100 kg of bottom ash and 30 - 50 kg of fly ash are generated when 1 ton of MSW is incinerated. Fly ash contains many toxic substances, various heavy metals and dioxins. It is usually detoxified and disposed in landfills. It is necessary to verify whether the chemical state of heavy metal changes into an insoluble state.

Furthermore, the formation of chlorinated aromatic compounds from an MSW incinerator (MSWI) is known to occur on the surface of fly ash [1]. Some heavy metals act as catalysts. Catalytic activities differ according to the kinds of heavy metal and its species. To evaluate the formation of chlorinated aromatic compounds on fly ash, it is necessary to examine the species of heavy metal in fly ash. Therefore, in this research, direct speciation of copper, lead, antimony and zinc in fly ash taken from the MSWI was conducted using X-ray absorption fine structure spectroscopy (XAFS).

The speciation of fly ash and the content of target elements are presented in Table I. Fly Ash 1 and 3 were sampled from the electrostatic precipitators in different continuous stoker-type MSWIs respectively. Fly Ash 2 was sampled from the bag filter in a continuous stoker-type MSWI. Fly Ash 4 was sampled from the bag filter in an ash melting plant. Fly Ash 2 and 4 contain large quantities of calcium compounds, because calcium hydroxide is injected before the bag filter for acid gas removal. The XAFS measurements were carried out at beamline **BL01B1**. The spectra were collected in fluorescence mode at room temperature with an Si(111) or Si(311) monochromator. The detailed procedure of data reduction has been described elsewhere [2].

Copper is the most active in the formation of dioxin among heavy metal catalysts. Figure 1 shows Cu *K*-edge XANES spectra of four kinds of fly ash and reference materials. According to the position of Cu *K*-edges, Cu(I) the compounds were considered to be contained in MSWI Fly Ash 1 - 3. In the Fly Ash 4 from an ash melting plant, the pre-

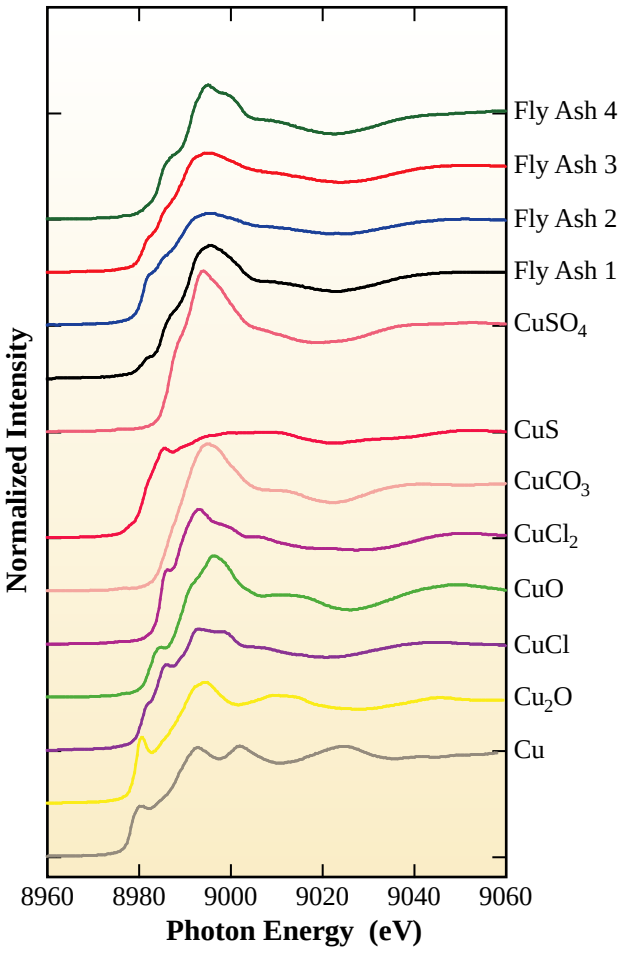

Fig. 1. Cu K-edge XANES spectra in fly ash and reference materials.

edge peak from the 1*s* - 3*d* transition appeared at 8976 eV and the chemical state of copper was estimated to be only Cu(II) compounds. The copper in fly ash was mainly estimated to be a mixture of $CuCl_2$, CuO and Cu(I) compounds by the XANES spectra. Figure 2 shows k^3-weighted EXAFS spectra for four fly ash and reference materials. According to the EXAFS spectra, the fly ash samples were classified into two patterns. As the wave number increased, the EXAFS spectra became ambiguous in Fly Ash 2 and 3 but clear in Fly Ash 1 and 4. The EXAFS spectra indicated that a Cu-Cl bond existed in Fly Ash 2 and 3 in comparison with those of reference materials. On the other hand, the dioxin concentrations in Fly Ash 1 - 4 are 1.5, 6.7, 6.2 and 3.5 ng-TEQ/g, respectively. Dioxins have 210 isomers. Of the various isomers of dioxins, 17 isomers carrying chlorine atoms at the 2-, 3-, 7-, 8-positions are particularly toxic. Therefore, toxicity equivalency conversion is conducted to obtain a total measure of the toxicity of the mixtures of many isomers. The factor called toxic equivalent factor indicates the relative toxicity referring to 2-, 3-, 7-,8-tetrachlorinated dibenzo–p-dioxin as a standard to yield toxic equivalent (TEQ) value [3]. The difference of the EXAFS spectra was considered to have a relationship with the dioxin concentration. Namely the Cu compounds in Fly Ash 1 and 4 were deactivated to give them a lower activity for the formation of dioxin than those in Fly Ash 2 and 3.

As for other heavy metals, lead was mainly estimated to be $PbCl_2$ in MSWI Fly Ash 1 - 3 and PbO in ash melting plant Fly Ash 4 by Pb L_{III}-edge XANES spectra. The same results were also suggested from the EXAFS spectra. According to Zn *K*-edge XANES spectra, the peak shape of Fly Ash 2 was very similar to that of Fly Ash 3. Whereas, that of Fly Ash 4 was different from the others and the peak position shifted to higher photon energy. Zinc was mainly estimated to be $ZnCl_2$ in MSWI Fly Ash 1-3 and the mixture of $ZnCO_3$, ZnO and $ZnCl_2$ in ash melting plant Fly Ash 4. There was no difference in the Sb *K*-edge XANES spectra among the measured fly ash. Antimony in the fly ash was considered to be Sb(V)

Table I. The specification of fly ash and concentrations of target elements.

Sample	Fly Ash 1	Fly Ash 2	Fly Ash 3	Fly Ash 4
Operation	Continuous	Continuous	Continuous	Continuous
Furnace type	Stoker	Stoker	Stoker	Coke bed type ash melting furnace
Dust collector	ESP	BF	ESP	BF
Acid gas removal		$Ca(OH)_2$ injection	Wet scrubber	$Ca(OH)_2$ injection
Cu (mg/kg)	1900	1700	3000	1500
Pb (mg/kg)	8200	11000	13000	15000
Zn (mg/kg)	34000	25000	29000	38000
Sb (mg/kg)	1800	1200	1400	940
Dioxins (ng-TEQ/g)	1.5	6.7	6.2	3.5

ESP: electrostatic precipitator, BF: bag filter, TEQ: toxic equivalent

compounds. The EXAFS spectra indicated that antimony combined not only with oxygen but also with chlorine.

From this research, we were able to obtain the information about the species of heavy metals and suggest the relationship between dioxin concentrations and chemical states of copper compounds in actual Fly Ash [4].

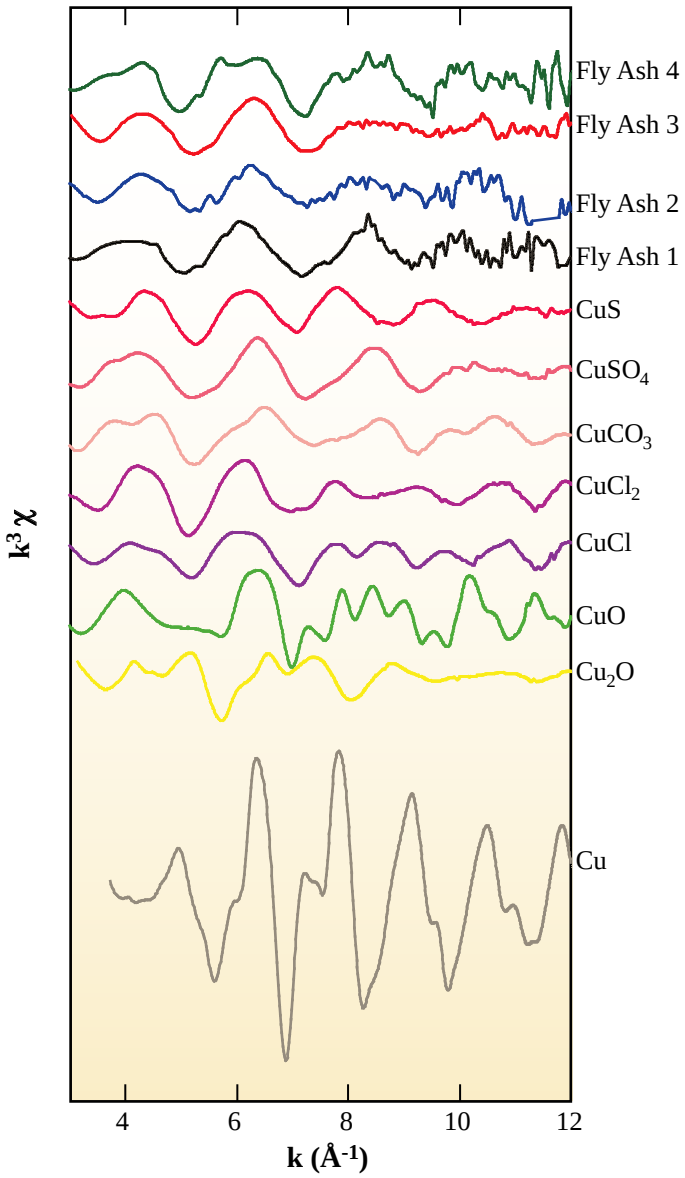

Fig. 2. EXAFS spectra of Cu in fly ash and reference materials.

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