Characterization of lead, chromium, and cadmium in dust emitted from municipal solid waste incineration plants

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Abstract. The dust is emitted from municipal solid waste incinerators (MSWIs). Volatile toxic heavy metals are abundant in smaller dust particles and influence the toxicity of particulate matter such as fine particles <2.5 µm (PM$_{2.5}$). However, little is known about the properties of these metals in fine dust particles. Therefore, X-ray absorption fine structure (XAFS) spectroscopy was used to investigate the chemical states of lead (Pb), chromium (Cr), and cadmium (Cd) in MSWI dust collected for nine particle size fractions at the inlet of the dust collector and the stacks of two MSWI plants. XAFS spectroscopy of the dust in the inlet of the dust collectors showed that finer dust contained predominantly Pb as PbCl$_2$ with some PbSiO$_3$, coarser dust consisted of Cr forms, including more toxic Cr(VI) species, and all dust contained CdCl$_2$. Although the dust collector removed almost all of the Pb, trace amounts of PbCl$_2$ remained in the stack gas after passing through the dust collector.

1. Introduction
In municipal solid waste incineration (MSWI), volatile toxic heavy metals are abundant in smaller dust particles and influence the toxicity of particulate matter (PM) [1] such as fine particles <2.5 µm (PM$_{2.5}$). Although understanding the behavior and chemical states of heavy metals in the fine particles of MSWI dust is important, few data on such properties are yet available [2]. In this study, we examined the heavy metals lead (Pb), chromium (Cr), and cadmium (Cd) because of their toxicity. This study aimed to investigate the chemical states of Pb, Cr, and Cd in MSWI dust collected in particle size fractions at the inlet of the dust collectors and stacks in MSWI plants by using X-ray absorption fine structure (XAFS) spectroscopy.

2. Materials and Methods
Samples of MSWI flue dust were collected in nine particle size fractions (from submicron to about 10 µm) by an Andersen stack sampler (Tokyo Dylec AS-500), which was inserted into the flue gas ducts at the inlets of the dust collectors in two MSWI plants [plants A and B: two different continuous stoker-type MSWIs with bag filter (BF) dust collectors]. In plant B, samples were also collected from the inlet of the stack (figure 1). In these sampling methods, Japanese Industrial Standards (JIS) Z8808 and K0302 were adopted to collect the dust and to calculate the theoretical particle size of each fraction [3]. The dust samples were leached in deionized water. The residues were dissolved with acid.

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Figure 1 Sampling locations at flue flow in MSWI plants; a. Plant A and plant B have similar flue treatment equipments in flue flow from incinerator to dust collector. Samples were collected at the inlet of BF in Plant A (Case1) and in Plant B (Case2). b. Flue treatment equipments at downstream of BF in plant B is different from that in plant A. Sample was collected at the inlet of stack in Plant B (Case3). CT: Cooling Tower, BF: Bag Filter, WS: Wet Scrubber, SCR: Selective Catalytic Reduction.

Table 1 Property of flue dust samples for Case 1, Case 2, and Case 3; $m^3_N$: Reduced volume of gas in 0 °C, 1 atm, and dried, Gas phase: amounts in cohesive water and H$_2$O$_2$ after removed dust particles.

| Case No. | Particle size ($\mu m$) | Dust weight (mg) | Pb (ng/g) | Cd (ng/g) | Cr (ng/g) | Plant Location | Temperature (°C) | Humidity (%) | Flue gas volume ($m^3_N$) |
|----------|-------------------------|------------------|-----------|-----------|-----------|----------------|-----------------|-------------|------------------------|
| 1-1      | 11.1                    | 48.6             | 360       | 13        | 411       | A, Inlet of BF | 156             | 20.2        | 0.069                  |
| 1-2      | 7.2~11.1                | 31.5             | 550       | 18        | 392       |                |                 |             |                        |
| 1-3      | 4.9~7.2                 | 14.2             | 1100      | 30        | 555       |                |                 |             |                        |
| 1-4      | 3.3~4.9                 | 4.1              | 1800      | 62        | 752       |                |                 |             |                        |
| 1-5      | 2.1~3.3                 | 2.4              | 5640      | 139       | 1230      |                |                 |             |                        |
| 1-6      | 1.0~2.1                 | 7.7              | 10400     | 814       | 838       |                |                 |             |                        |
| 1-7      | 0.5~1.0                 | 9.9              | 11700     | 592       | 541       |                |                 |             |                        |
| 1-8      | <0.42                   | 6.8              | 7000      | 376       | 247       |                |                 |             |                        |
| 1-9      | <0.42                   | 6.9              | 7200      | 314       | 509       |                |                 |             |                        |
| 2-1      | 0.98~2.0                | 16.493           | 7156      | 620       | <17       | B, Inlet of BF | 173             | 17.1        | 0.066                  |
| 2-2      | <0.40                   | 6.714            | 12100     | 750       | <7        |                |                 |             |                        |
| 2-3      | 0.33~0.40               | 2.482            | 10700     | 590       | -         |                |                 |             |                        |
| 3-1      | 6.0~9.0                 | 1.748            | 1756      | 107       | -         | B, Inlet of stack | 163             | 21.3        | 0.08                  |
| 3-2      | 1.7~2.7                 | 1.228            | 6136      | 216       | -         |                |                 |             |                        |
| 3-3      | 0.33~0.40               | 0.482            | 10700     | 590       | -         |                |                 |             |                        |

These solutions for the chemical compositions of the dust were analyzed with ICP-MS (Yokogawa Electric HP4500). Table 1 shows the properties of the flue dust samples and the sampling conditions.

XAFS spectroscopy was carried out in beamline BL01B1 of Super Photon ring-8GeV (SPring-8), in beamline BL-12C of the Photon Factory (PF), and in beamline NW10A of the Photon Factory–Advanced Ring for pulse X-rays (PF–AR). These beamlines have double crystal monochromators of Si(111) in BL01B1 and BL-12C, and Si(311) in NW10A. The dust fractions were prepared by cutting the dust collection filters and setting them into the synchrotron radiation X-ray. XAFS spectra of the dust fractions were collected for Pb-L$_{III}$, Cr-K, and Cd-K in the fluorescence mode using a Ge multielement solid-state detector, and those of reference materials were determined in the transmission mode. The software REX2000 ver. 2.5.5 (Rigaku Co. Ltd.) was used for analyzing the chemical forms of each element in the dust by the linear combination fitting technique (LCF) [4][5]. LCF describes the chemical forms of elements in samples based on ratios to reference materials which for LCF were the
Pb compounds PbCl$_2$, PbSiO$_3$, PbCO$_3$, PbO, PbO$_2$, and PbSO$_4$, the Cd compounds Cd, CdO, and CdCl$_2$, and the Cr compounds Cr metal, CaCr$_2$O$_4$, FeCr$_2$O$_4$, Cr$_2$O$_3$, CrCl$_3$, and CrO$_3$.

3. Results and Discussion

Pb-L$_{III}$ XAFS spectra were collected for 11 dust fractions from the inlets of the dust collectors of plants A and B, three fractions from the stack of Plant B [Figure 2(a)], and the reference materials (Figure S1, Supplementary data). The spectra for each fraction had similar shapes. From plant A (1-1–1-9) The LCF result shows that the dust of each fraction predominantly contained Pb as PbCl$_2$ (15–60 mol%) and PbSiO$_3$ (30–60 mol%), with more PbCl$_2$ tending to occur in finer fractions and more PbSiO$_3$ appearing more often in coarse dust fractions. Each fraction contained other low compounds (10–25 mol%) (Figure 3 and Table S1, Supplementary data).

The spectra of samples collected from the inlet of the stack at plant B (3-1–3-3) were poor because the amount of Pb in those fractions was very small. LCF result indicates that each fraction at the inlet of the BF (2-1, 2-2) predominantly contained Pb as PbCl$_2$ (29–56 mol%) and PbSiO$_3$ (33–34 mol%), with the finer fraction (2-2) containing more PbO and PbSO$_4$ (10–28 mol%). The spectra of the fractions from the inlet of the stack (3-1–3-3) predominantly contained Pb as PbCl$_2$ (about 50 mol%) as shown by LCF, indicating that some Pb compounds, such as PbCl$_2$, remained in the fractions in the stack although the dust collector removed almost all of the Pb contained in dust.

The results of the dust fractions sampled from the inlets of the BF in plants A and B are discussed first. The results for plants A and B were similar. Takaoka et al. [4] and Funatsuki et al. [5] reported the primary Pb chemical forms as PbCl$_2$ or PbSiO$_3$ in unclassified, bulk MSWI fly ash using XAFS and LCF. The results of this paper, showing the primary chemical forms of Pb as PbCl$_2$ and PbSiO$_3$, are similar to those reports. PbCl$_2$ may occur as the result of high concentrations of HCl in the flue gas of MSW1 [4]. The differences in chemical forms among particle sizes may be explained by melting points or species volatility. MSWIs operate at high temperatures of 800–1000°C, at which PbCl$_2$ is volatile, because its melting and boiling points are 501°C and 950°C, respectively. PbCl$_2$ tended to be more abundant in the finer dust fractions because PbCl$_2$ gas is cooled in the flue gas treatment process and may turn into a fine particle solid through aggregation. In fact, Pb occurred in the flue gas phase, which removed dust particles at the inlet of the BF (Table 1). The amounts of Pb leached to deionized water were about 50wt% in some finer fractions, which supports the idea that PbCl$_2$ is a primary compound because of its high solubility. PbSiO$_3$ is not volatile, having a high melting point, and thus could be carried by the flue gas stream and be abundant in coarse dust fractions. Alternatively, PbSiO$_3$
might be composed during the vapor phase [6].

For the dust fractions sampled from the inlet of the stack at plant B, an explanation for the existence of Pb at the inlet of the stack is that Pb compounds, such as PbCl₂ in the flue gas phase, passed the BF and condensed, although the BF removed almost all of the dust. Further research is needed to better understand the other Pb compounds sampled at the inlet of the stack.

Cr-K XAFS spectra were collected for eight dust fractions from the inlets of dust collectors for only plant A [Figure 2(b)] and the reference materials (Figure S1, Supplementary data). The spectra of coarse and fine fractions showed different shapes on the pre-edge and whiteline. A clear pre-edge peak at about 5993 eV, especially in the spectra of some coarse fractions (1-1–1-5), lead to the suggestion of the occurrence of more toxic Cr(VI). LCF results showed that coarse fractions predominantly contained Cr as Cr(III) (57–71 mol%) and some Cr(VI) (13–23 mol%). Cr(III) was present as CaCr₂O₄ (10–47 mol%), FeCr₂O₄ (12–24 mol%), and Cr₂O₃ (17–26 mol%), and Cr(VI) was present as CrO₃. The LCF results also showed that finer fractions contained more Cr metal (13–60 mol%).

Most Cr compounds have high melting points and are not particularly volatile. The particle sizes of the Cr compounds themselves might have caused the differences in the chemical forms observed among dust particle fractions, but this is speculation. Cr compounds at low oxidation states under the high temperatures of the incinerator might have caused some of the Cr(VI) formation.

Cd-K XAFS spectra were collected for eight fractions of dust from the inlets of dust collectors only for plant A [Figure 2(c)] and the reference materials (Figure S1, Supplementary data). Some spectra of coarse fractions (1-1–1-4) were poor because those fractions contained very small amounts of Cd. The spectra of each fraction had similar shapes. The LCF results showed that each fraction predominantly contained Cd as CdCl₂ (40–100 mol%), with some Cd metal (0–60 mol%). This result is similar to that of the Funatsuki et al. on MSWI fly ash [7]. The ratio of CdCl₂ to Cd metal did not show a clear tendency in terms of dust particle size.

Like Pb, CdCl₂ may also occur as the result of high concentrations of HCl in the flue gas of MSWIs [4]. CdCl₂, with its melting and boiling points of 568°C and 960°C, respectively, is easily volatile under the high temperatures of MSWIs. Pinzani et al., using μ-EXAFS, reported primary chemical forms of CdCl₂ and CdSiO₃ in particles of MSWI fly ash [2]. The dust fractions examined in the present study were not well fitted using CdSiO₃ in LCF, indicating that CdSiO₃ was not a primary chemical form in our samples.

4. Conclusion
In summary, XAFS spectroscopy of the dust from the inlets of dust collectors showed that finer dusts predominantly contained Pb as PbCl₂ and some PbSiO₃, coarser dusts contained Cr forms, including more toxic Cr(VI) species, and all dusts contained CdCl₂. Although the dust collector removed almost all of the Pb, some PbCl₂ remained in the stack gas after passing through the dust collector.

Acknowledgements
This study was supported by the research grant from Osaka Bay Regional Offshore Environmental Improvement Center and by the aid for presentation at XAFS15 from Kansai Research Foundation for technology promotion. We thank T. Fujimori (Kyoto University) and beamline staffs for help with the XAFS experiments at SPring-8 (Proposal No.2009B1458) and PF (Proposal No.2009G044).

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