

Chemical forms of cesium in ashes generated from municipal solid waste incineration

The Fukushima Daiichi Nuclear Power Plant was damaged by a huge earthquake and tsunami in March 2011, resulting in the release of radioactive nuclides, primarily ¹³⁴Cs and ¹³⁷Cs, to the atmosphere. These radioactive nuclides contaminated the disaster waste, municipal solid waste (MSW), and sewage sludge from the surrounding area. According to the IAEA guidelines, incineration is the most commonly used thermal process for reducing the volume of such waste [1]. In Japan, waste that contains ¹³⁴Cs and 137Cs exceeding 8,000 Bq/kg activity is referred to as "specified radioactive waste." Although approximately 80% of the specified radioactive waste consisted of incinerated ash and inorganic soils, the other 20% was combustible waste, i.e., sewage sludge, agricultural waste, and MSW to be treated [2].

Radioactive nuclides in waste can concentrate in the resulting ash (fly ash and bottom ash) formed by incineration and may be in different chemical forms in either ash. The chemical forms of Cs in ash are important for the determination of appropriate treatment and stabilization of the ash, but there is little information about the forms.

Our study attempts to clarify the chemical forms of cesium in ash generated from waste incineration. Specifically, refuse-derived fuel (RDF) with added ¹³³Cs (a stable nuclide) was combusted using a pilot-scale incinerator, and the chemical forms of ¹³³Cs in the bottom ash and fly ash were investigated in relation to the equivalence air ratio (EAR) by X-ray absorption fine structure (XAFS) analysis.

The RDF pellets used in this study were manufactured from MSW from a plant located in west

Japan. An aqueous solution containing nuclides was added to the RDF, and the sample was adjusted to 30% moisture content. The nuclide concentration in the RDF was 5,100 mg/kg for ¹³³Cs added as Cs₂CO₃. A rotary kiln-stoker furnace (processing capacity ~1,000 kg/h, NGK Insulators Ltd.) was used in this study (Fig. 1). The bottom ash was collected from the rotary kiln and stoker. Flue gas was recombusted in the secondary combustor at 900°C. After recombustion, the gas was cooled in the cooling tower, and the fly ash was collected in the ceramic filter. The RDF was incinerated in the rotary kiln at 700°C at a rate of 30 kg/h while being stirred. The EAR was controlled to 2.2, 1.7, and 1.4 by varying the amount of combustion air. MSW ash generally has a high titanium (Ti) content. The energy of the Ti K-edge (4,964 eV) is close to that of the Cs L_3 -edge (5,011 eV). Therefore, the Cs K-edge XAFS spectra of bottom ash and fly ash at beamline BL01B1 were measured [3].

The differential X-ray absorption near edge structure (XANES) spectra of standard Cs substances (CsSO₄, pollucite: the (Cs, Na) (AlSi₂)O₆·nH₂O, Cs₂CO₃, and CsCl), bottom ash, and fly ash samples are shown in Fig. 2. These spectra of the bottom ash and fly ash were different despite the small effect of the EAR, indicating that the EAR has a minimal effect on the Cs in each ash. While the differential XANES spectrum of the bottom ash had a positive peak within the range of 36,032 eV to 36,033 eV and appeared similar to the spectrum for Cs₂CO₃, the spectrum of Cs₂CO₃ in fly ash had a peak in the range of 36,034 eV to 36,035 eV, which was more similar to the spectrum of CsCl.



Fig. 1. Rotary kiln and stoker incineration plant: (a) rotary kiln, (b) secondary combustor, and (c) chamber of ceramic filter.

Most of the potassium (K) in ash exists in the form of KCl gas and $K_2Si_4O_9$ liquid above 780°C, as determined by a theoretical calculation that assumed the thermodynamic equilibrium in a Danish straw incinerator [4]. The same theoretical calculation was performed for ash in a modified MSW incinerator and it was reported that most of the K existed in the form of KCl gas and solid KAlSi₂O₆ above 940°C and 850°C, respectively [5,6]. NIES (2012) investigated ash with K replaced by Cs, and reported CsAlSi₂O₆ and CsCl to be the main forms of Cs in bottom ash and fly ash, respectively [6].

In our XAFS analysis, the main chemical form of Cs in fly ash was CsCl. This finding matched the above results of theoretical calculations. On the other hand, the chemical form of Cs in the bottom ash, Cs_2CO_3 , was different from the calculated results,

which indicated aluminosilicate or silicate, because the combustion temperature in this experiment was approximately 700°C, which is higher than the melting point of Cs₂CO₃ and lower than the temperature of the theoretical calculation. Most of the Cs₂CO₃ remained in the bottom ash without conversion to another chemical form. A part of the Cs₂CO₃ was transferred to the secondary combustor by flue gas, recombusted at 900°C, converted to CsCl, and condensed in fly ash at the ceramic filter. The combustion of MSW contaminated with radioactive Cs in a stoker-type incinerator at higher temperatures of 850°C-900°C, should result in the conversion of Cs to CsCl and aluminosilicate or silicate in the combustion chamber. CsCl should then vaporize and transfer to the fly ash. Therefore, MSW can be separated into a small amount of fly ash with a high concentration of radioactive Cs and bottom ash with a low concentration of radioactive Cs by incinerating at a high temperature.

Kazuyuki Oshita^{a,b,*}, Kenji Shiota^b and Masaki Takaoka^{a,b}

- ^a Dept. Global Ecology, Graduate School of Global
- Environmental Studies, Kyoto University
- ^b Dept. Environmental Engineering, Graduate School of Engineering, Kyoto University

*E-mail: oshita@epsehost.env.kyoto-u.ac.jp

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Fig. 2. Differential XANES spectra of Cs compounds and types of ash.