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Short communication

Enhancement of Cs vaporization from simulated granular ash through thermal treatment in N_2 atmosphere with the addition of a mixture of $CaCl_2$ and CaO

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ABSTRACT

This study aims to clarify the vaporization propensity of Cs in simulated granular ash through thermal treatment in N_2 atmosphere at 1100–1500 °C with the addition of a mixture of $CaCl_2$ and CaO. XRD and XPS were employed to specify Cl-bearing species in the treated ash. The results indicated that $CaCl_2$ addition facilitated the vaporization of Cs. The vaporization ratio of Cs as a function of temperature was nonlinear. The ash melt formed at 1400 °C constrained the diffusion of Cs species by blocking the pores and/or decreasing the surface area of the ash particles which, however, was compensated by increasing the temperature to 1500 °C. The addition of the mixture of $CaCl_2$ and CaO highly promoted the vaporization of Cs in the ash compared to that of the addition of $CaCl_2$. Formation of wadalite/igumnovite through chemical reactions among granular ash, $CaCl_2$ and CaO, as well as more liquid produced by additional CaO, were in favor of the reaction of Cs with Cl, thereby synergistically promoting the Cs vaporization. Addition of the mixture of $CaCl_2$ and CaO is highly recommended to remove Cs from Cs-contaminated incineration ash during thermal treatment.

1. Introduction

Incineration is a promising method to treat radiocesium-contaminated solid wastes collected from the area affected by the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident caused by the great earthquake in northeastern Japan on March 11, 2011 [1–4]. After incineration of the solid wastes, the Cs distributed into fly ash and bottom ash; its concentration is several dozen times higher than that in the raw wastes [5,6] and causes potential adverse effects on the surroundings during storage. Therefore, development of a practicable technology to remove Cs from the Cs-contaminated incineration ashes is vital to mitigate the risk in their storage.

CsCl and Cs-aluminosilicate are two major Cs-bearing species in incineration ashes [7,8]. In general, CsCl is concentrated in fly ash, and Cs-aluminosilicate exists in bottom ash. The method of water extraction can remove CsCl in fly ash because of its water-soluble propensity followed by the capture of absorbents [9–11], whereas this process is unavailable for the removal of Cs-aluminosilicate in bottom ash [5]. In our previous studies, the method of thermal treatment with additives addition (such as $CaCl_2$ and $MgCl_2$) has been adopted to vaporize the Cs form a raw ash and a Cs-doped ash [12,13]; this method was widely used to remove heavy metals from incineration ash [14–19]. We have observed that the vaporization behavior of Cs between the raw ash and the Cs-doped ash was very similar. The addition of $CaCl_2$ or $MgCl_2$ during thermal treatment promotes the vaporization of Cs; the addition of $CaCl_2$ is more successful in Cs vaporization than is the addition of $MgCl_2$. The addition of 20% $CaCl_2$ resulted in 95% Cs vaporize at 1200 °C during thermal treatment. These observations were obtained based on the experiments of powder ash, the particle size of which is less than 100 µm. Actual bottom ash collected from an incineration plant has much larger particle size than that used in the previous study. It is unclear whether the results from the powder ash experiments are still in line with that from the granular ash experiments. In addition, utilization of more $CaCl_2$ for the vaporization of Cs could cause corrosion of treatment facilities and environmental issue because a great amount of gaseous Cl was released during thermal treatment. The reduction of the amount of $CaCl_2$ used for obtaining a high Cs vaporization ratio is another issue of focus.

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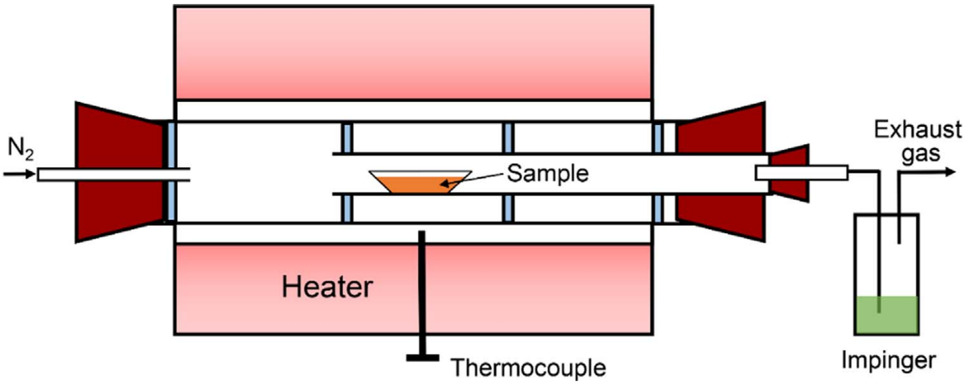

Fig. 1. Schematic of the horizontal furnace.

In this study, we clarify the vaporization of Cs in simulated granular ash (particle size of 0.5–1.4 mm) through thermal treatment in N_2 atmosphere. N_2 atmosphere is employed in this study because it facilitated the vaporization of Cs relative to that in air atmosphere through controlling decomposition of $CaCl_2$ according to our previous study results [13]. Apart from the addition of $CaCl_2$, the addition of mixture of $CaCl_2$ and CaO was also implemented to examine its effects on the vaporization of Cs in terms of a viewpoint that additional CaO addition probably results in ash slagging and/or $CaCl_2$ transformation, thereby affecting the vaporization of Cs. X-ray diffraction analysis (XRD) and X-ray photoelectron spectroscopy (XPS) were conducted to measure the Cl-bearing species in ash during thermal treatment.

2. Experimental section

Thermal treatment experiments of simulated granular ash were conducted in a horizontal electrical-heating furnace, the schematic of which is shown in Fig. 1. Detailed description of the horizontal furnace was given elsewhere [13]. The preparation method of the simulated granular ash is provided in Text S1. The chemical composition of the simulated granular ash and its mixtures with $CaCl_2$ or CaO is shown in Table 1. Si and Al are two dominant elements in the granular ash; the total content exceeds 70%. Cs concentration in the granular ash was 1912 mg/kg. With respect to the chemical species, apart from anorthite ($CaAl_2Si_2O_8$), amorphous phase was primary in the ash sample according to XRD analysis, as shown in Fig. S1. The granular ash of ~2 g (particle size of 0.5–1.4 mm) was mixed with $CaCl_2$ (extra pure reagent, Hayashi Pure Chemical IND., Ltd., Osaka, Japan) and/or CaO (reagent grade, Sigma-Aldrich Co., Germany) and subsequently transferred into a combustion boat (99.6% Al_2O_3). When the temperature reached a desire value, the ash-laden combustion boat was quickly moved into the middle of the furnace. Next, 600 mL/min N_2 was introduced into the reaction tube to continuously remove the vaporized compounds. After a duration of 30 min, the treated ash in the combustion boat was removed from the reactor and later subjected to a natural cooling in air atmosphere. The reaction temperature ranged from 1100 °C to 1500 °C at an interval of 100 °C. The treated ash was pulverized and characterized by a series of analytical instruments. The detailed analysis methods are provided in Text S2. The calculation method of the CaO/$CaCl_2$ content added and the vaporization ratio of Cs and Cl are given in Text S3.

3. Results and discussion

3.1. Effect of the addition of $CaCl_2$ or CaO on the vaporization of Cs

The vaporization of Cs as a function of reaction temperature during thermal treatment with the addition of $CaCl_2$ or CaO is shown in Fig. 2(a). Irrespective of the reaction temperature, an increase in the content of $CaCl_2$ facilitated the vaporization of Cs during thermal treatment, indicating that Cl plays an important role in the Cs vaporization. Cl was very likely to associate with Cs in the ash to form gaseous CsCl [13]. The vaporization ratio of Cs showed a complex trend with increasing temperature; it exhibited an increase from 1100 °C to 1300 °C and from 1400 °C to 1500 °C, whereas a slight decrease was observed when the temperature increased from 1300 °C to 1400 °C, regardless of the content of $CaCl_2$ added. This result could be caused by different melting properties of the treated ash at each temperature. The appearance of the treated ash with the addition of 10% $CaCl_2$ at 1100–1500 °C is shown in Fig. 2(b). As seen, the ash samples treated at 1100–1300 °C begin to partially melt but are still in granular form, whereas plenty of liquid was formed in the ashes treated at 1400 °C and 1500 °C. This observation was consistent with the predicted results based on thermodynamic equilibrium calculation by FactSage 7.0. The method of thermodynamic equilibrium calculation is provided in Text S4. As shown in Fig. 3, the fraction of liquid phase in simulated granular ash and its mixture with 5% $CaCl_2$ and 10% $CaCl_2$ was close at the temperature above 1300 °C. Approximately 70% liquid in the treated ash was formed at 1300 °C; under this condition, the ash particles retained their original shape and can be separated easily with each other

Table 1
Chemical composition of the simulated granular ash sample and its mixtures with $CaCl_2$ or CaO, wt%.

	Simulated granular ash (SGA)	SGA + 5% $CaCl_2$	SGA + 10% $CaCl_2$	SGA + 20% CaO	SGA + 5% $CaCl_2$ + 20% CaO	SGA + 10% $CaCl_2$ + 20% CaO
SiO_2	49.6	44.0	39.9	40.9	37.4	34.4
Al_2O_3	21.5	19.1	17.3	17.7	16.2	14.9
Fe_2O_3	5.32	4.7	4.3	4.4	4.0	3.7
MgO	0.842	0.75	0.67	0.69	0.63	0.58
CaO	19	21.3	23.3	32.1	33.2	33.9
K_2O	1.07	0.95	0.86	0.88	0.81	0.74
Na_2O	0.457	0.40	0.36	0.37	0.34	0.31
TiO_2	1.25	1.10	1.01	1.03	0.94	0.87
P_2O_5	0.29	0.25	0.23	0.23	0.21	0.19
Cl	–	5.68	10.46	–	4.82	9.01
Cs, mg/kg	1912	1697	1539	1577	1442	1326