In situ analysis of Cs species in an alkali-activated solid waste incineration fly ash and pyrophyllite-based system

Alkali-activated materials (AAMs) synthesized from aluminosilicates under highly alkaline conditions, such as geopolymers and zeolites, have been researched as alternatives to cement, concrete, and ceramics [1]. One of the alternative uses is as a solidification agent in the treatment of various wastes. Recently, there has been much interest in the use of AAMs obtained from aluminosilicates for the treatment of radionuclide-contaminated waste from the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident. In particular, radioactive cesium (^{134}Cs and ^{137}Cs) in radionuclide-contaminated solid waste incineration fly ash (SWIFA), a residue from thermal treatment of the waste, is soluble and cannot be stabilized sufficiently by general solidification using ordinary Portland cement [2].

The solidification process of an AAM obtained from aluminosilicates may involve the dissolution of aluminosilicates in a highly alkaline solution, gelation, reorganization, polymerization/crystallization, and hardening (Fig. 1(a)) [1]. Kinetic analysis of the process is essential for the design of curing conditions and important for understanding the reaction mechanism for the effective stabilization of hazardous substances. Although kinetic analyses have been reported, almost all of them focused on changing the AAM matrix such as the environment around Si and Al, which form a Si–O–Al chain or an amorphous phase. In the stabilization of Cs, Cs species before and after the stabilization are also important for understanding the mechanism. However, little research is available on kinetic analysis focusing on Cs and its species in AAMs obtained from aluminosilicates.

In this study, we focused on the Cs species during the reaction in an alkali-activated SWIFA and pyrophyllite-based system, which simulated the treatment of radionuclide-contaminated SWIFA from the FDNPP accident. We investigated the chemical kinetics of the Cs species during the reaction by performing an *in situ* X-ray absorption fine structure (*in situ* XAFS) experiment. Pyrophyllite was used in this system because there is little knowledge of its application to AAMs as an aluminosilicate source.

SWIFA that had not been treated with any flue gas control agents (e.g., slaked lime, activated carbon) was collected from a baghouse at an SWI plant in Japan. We added CsCl to the SWIFA so that the concentration of CsCl in the SWIFA was 5 wt% to simplify the identification of changes in the Cs species. Pyrophyllite was dehydrated for 12 h at 900°C. Pastes of the AMM system in this study were prepared by mixing the same weight of each of the municipal solid waste incineration fly ash (MSWIFA) with 5 wt% CsCl, dehydrated pyrophyllite, sodium silicate solution, and 14 mol/L aqueous NaOH solution. To evaluate the stabilization of Cs in the system, the Japanese leaching test (JLT-46) for solid products obtained from 30 g of the pastes was performed at intervals of 0 to 24 h during 48 h curing at four different temperatures (room temperature, 60°C, 80°C, and 105°C) in batch experiments. The *in situ* XAFS experiments for the system were conducted at SPring-8 **BL01B1** (Fig. 1(b)). Approximately 200 g of each paste was

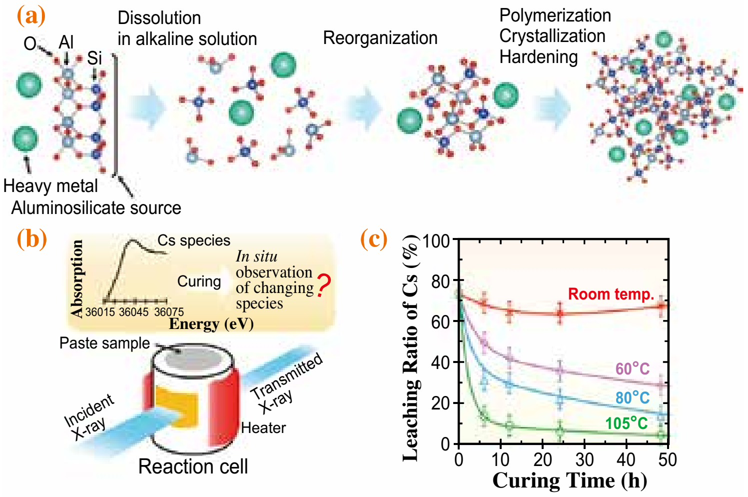

Fig. 1. **(a)** Scheme of a reaction process of an AAM obtained from aluminosilicates [1]. **(b)** Schematic illustration of *in situ* X-ray absorption fine structure (*in situ* XAFS) experiment. **(c)** Leaching ratio of Cs from products in an alkali-activated municipal solid waste incineration fly ash and pyrophyllite-based system obtained from Japanese leaching test (JLT-46). 'Leaching ratio' means the weight percentage of Cs in the leachate to the total Cs in a product.

placed in four custom-built reaction cells, which were cured under the four curing conditions. The *in situ* XAFS spectra at the Cs-*K* edge were collected in transmission mode at intervals of approximately 1 to 10 h (6 runs for 34 h) for each curing condition [3].

The leaching ratio of Cs from the product under room temperature curing decreased very little during JLT-46, by contrast, that of the product cured at 105°C decreased the most to less than 10% of its initial value after 12 h (Fig. 1(c)). These results showed that the AAM system in this study can be stabilized to a greater extend and faster by employing a higher curing temperature and longer curing time.

The results of *in situ* XAFS experiments on samples subjected to 60°C and 105°C curing are shown in Figs. 2(a) and 2(b). The spectra for both curing conditions markedly changed and became increasingly similar to that of pollucite with increasing curing time. The changes in the spectra were greater and the similarity to pollucite was observed earlier for curing at 105°C than for curing at 60°C. We estimated changes in the pollucite content in this system from all the spectra obtained from the *in situ* experiments using factor analysis and linear combination fitting technique using the spectra of reference materials (Fig. 2(c)). The pollucite content in the case of room temperature curing was below the detection limit. By contrast, that in the case of 105°C curing increased fastest to approximately 60 mol% of the total Cs species after 12 h. These results and further analyses of the reaction rate using a simple reaction model (not shown, see Ref. 3) showed that the pollucite formation rate was faster under a higher curing temperature. In addition, the pollucite content had a negative correlation with the Cs leaching ratio, which suggested that the formation of pollucite during the change in the Cs species played an important role in its stabilization using the system. By calculating the rate constants of pollucite and the slope of its Arrhenius plot [3], the activation energy of pollucite formation in the system was estimated to be 31.5 kJ/mol, which is similar to the values for geopolymers or zeolite materials in some alkali-activated systems [4,5]. This result indicates that pollucite can form as a result of the reaction energy in the alkali-activated system in this study.

As shown above, we demonstrated the chemical kinetics of Cs species in an alkali-activated MSWIFA and pyrophyllite-based system and revealed a quantitative relationship between the stabilization of Cs and the formation of pollucite.

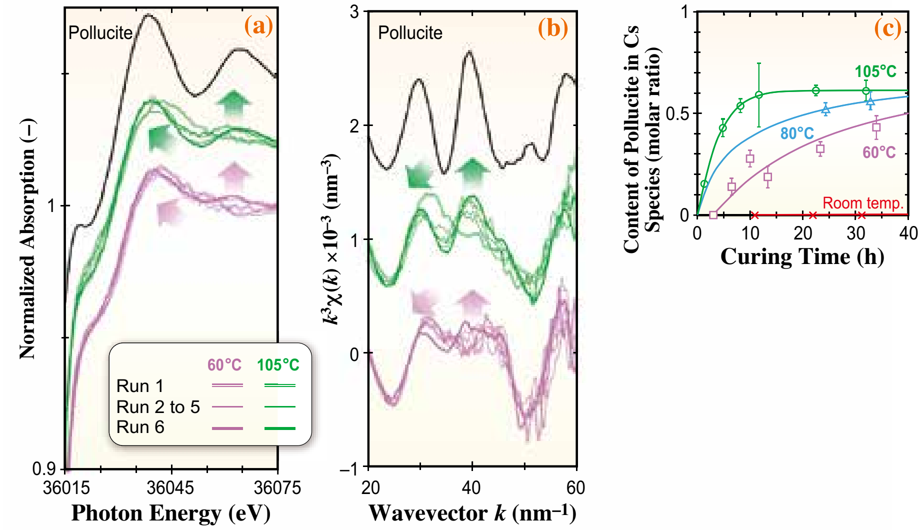

Fig. 2. **(a)** Cs *K*-edge X-ray absorption near edge structure (XANES) of pollucite and result of *in situ* experiments (60°C and 105°C). **(b)** Cs *K*-edge $k^3\chi(k)$ extended X-ray absorption fine structure (EXAFS) of pollucite and result of *in situ* experiments (60°C and 105°C). **(c)** Estimated content of pollucite during *in situ* experiments. Arrows indicate changes in spectral features during the *in situ* experiments.

Kenji Shiota[a,*] and Masaki Takaoka[a,b]

[a] Department of Environmental Engineering,
Kyoto University
[b] Graduate School of Global Environmental Studies,
Kyoto University

*Email: shiota.kenji.4x@kyoto-u.ac.jp

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