

## Comparison of cesium retention ability in cesium silicates at high temperatures

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### 1. Introduction

The tragic Fukushima accident put emphasis on the nuclear fuel safety giving rise to an accident-tolerant fuel (ATF) concept. The ATF has attracted interest from many researchers [1-3]. The Korea Atomic Energy Research Institute is developing microcell  $\text{UO}_2$  pellets on the desired purpose [4, 5]. As a way of it, a ceramic microcell is now under development. It is intended to capture the fission gases by chemical reactions.

Cesium has been considered as one of fission products that should be captured due to large amount and high radioactivity [6]. Trapping the cesium improves fuel safety by reducing the rod internal pressure and suppressing any other problems resulting from its release [5]. The benefits from the capture can be extended to an accident depending on the operation temperature. It is determined by retention ability of trapping agent. In other words, a trapping agent that can retain cesium up to high temperature range should be adopted. However, a high sintering temperature during the fabrication of  $\text{UO}_2$  fuel pellet often deteriorate the chemical affinity of the cell wall materials. This strictly limit the possible candidates for the cell wall material to several silicates.

Zr-Si-O [7] and Al-Si-O [8, 9] compounds have been reported as promising materials in terms of high temperature cesium retention ability. Especially, the Zr-Si-O is reported to form a Cs-Zr-Si-O compound that retain more than 40 % of cesium even at 2000 °C. A similar excellence cesium retention-ability of Al-Si-O was reported [8, 9]. It forms a Cs-Al-Si-O compound that more than 90 % of cesium up to 1400 °C [9]. However, in the previous studies published so far, any experimental evidence was not sufficiently provided to distinguish superior one: a lack of experimental data or limited to specific temperature range that covers normal operation temperature of nuclear fuel. Therefore, there should be a comparative study on the cesium retention ability at high temperatures.

In this study, the high temperature stability of Cs-Al-Si-O and Cs-Zr-Si-O was compared by cumulative weight loss behaviors up to 1750 °C. Considering that its application as a cesium trapping agent in an ATF that mitigates FGR, a beneficial candidate was distinguished in a practical viewpoint.

### 2. Experimental

Cesium compounds were prepared from commercial powders of kalolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})$ , Sigma-Aldrich,

USA),  $\text{ZrSiO}_4$  (Alfa Aesar, USA), and  $\text{Cs}_2\text{CO}_3$  (99.9 wt. % purity, Sigma-Aldrich, USA). Both powders were separately mixed with a sufficient amount of  $\text{Cs}_2\text{CO}_3$  powder in a turbula mixer for 30 min. The powder mixtures were heat-treated to obtain relevant cesium compounds. Based on previous studies [7, 9], the heat treatment was established as progressive three steps: reaction, crystallization, and homogenization. Firstly, the reaction heat treatment was carried out at 630 °C for 5 h in a dry air atmosphere. The reacted Cs-Al-Si-O (hereafter, CASO) and Cs-Zr-Si-O (hereafter, CZSO) samples were heat treated for further crystallization at 800 °C for 3 days. Then the samples were homogenized by heat treatment at 1050 °C for 18 h in air for the CASO sample while at 900 °C for 5 h, 1200 °C for 5 h, and 1600 °C for 5 h for the CZSO sample. The experimental flow chart is shown in Fig. 1. According to the thermal history, reacted samples were denoted by (R) and homogenized samples were denoted by (H), respectively.

The crystal structure of the powder samples was examined by X-ray diffraction (XRD) analysis (Rigaku Mini-Flex, Japan). The diffraction patterns of the samples were identified by using a MDI Jade 6 (Materials Data, Inc.). The cumulative weight loss values were calculated from TG analysis (TG-92, SETARAM, France). During the measurement, an Ar atmosphere was maintained with a flow rate of 20 mL/min and a heating rate of 15 °C/min. To quantify the volatile behavior, the cumulative weight loss of the samples was calculated from the TGA data, assuming that weight loss occurs only due to the volatilization of  $\text{Cs}_2\text{O}_3$  [9].

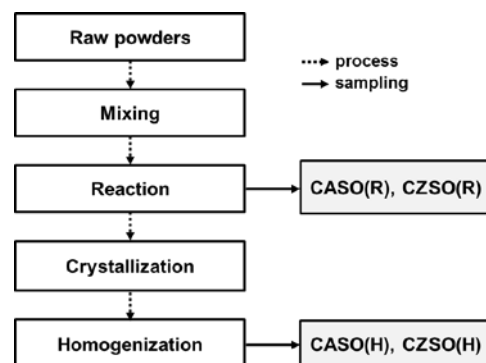


Fig. 1. Flow chart showing experimental procedures and related material variations.

### 3. Results and Discussion

Figure 2 shows the XRD patterns of the CASO, CZSO samples prepared by heat treatments. The heat treatments for the CASO and CZSO samples include: reaction, crystallization, and homogenization (denoted by R, C, and H in Fig. 2). In the case of CASO samples, similar XRD patterns were observed from samples obtained after different heat treatment, as shown in Fig. 2(a). Although the unknown peaks at  $\sim 21$  and  $34^\circ$  (denoted by downward arrows) were observed in the reacted sample, most of the diffraction peaks matched well with  $\text{CsAlSiO}_4$ . This elucidates a temperature range at which the cesium compound is stable. The temperature range lies between 630 (reaction) and 1200  $^\circ\text{C}$  (homogenization), which is similar with the LWR fuel temperature during normal operation (500–1200  $^\circ\text{C}$  [10]).

In contrast, in the CZSO samples, different XRD patterns were obtained as heat treatment proceeded, as shown in Fig. 2(b). The inset in Fig. 2(b) reveals the tendency more clearly with enlarged XRD patterns. It is plausible that a cesium-trapping reaction occurs, however, the chemical form of the resultant material would not be  $\text{CsZrSi}_3\text{O}_{8.5}$ , which is known to have excellent high-temperature stability [7]. Considering the XRD behaviors, only the homogenized CZSO sample seemed to be in the form of  $\text{CsZrSi}_3\text{O}_{8.5}$ . Unfortunately, the  $\text{CsZrSi}_3\text{O}_{8.5}$  phase cannot be identified by XRD [7]. Despite the lack of identification, it is evident that the  $\text{CsZrSi}_3\text{O}_{8.5}$  compound forms at higher temperature than in the CASO. It should be noted that the homogenization temperature for the CZSO sample (1600  $^\circ\text{C}$ ) exceeds the temperature range in the LWR fuel. Therefore, the  $\text{CsZrSi}_3\text{O}_{8.5}$  phase is hardly formed during normal operation. Nonetheless, the reacted and crystallized CZSO samples need to be examined because they are still feasible in the real fuel environment.

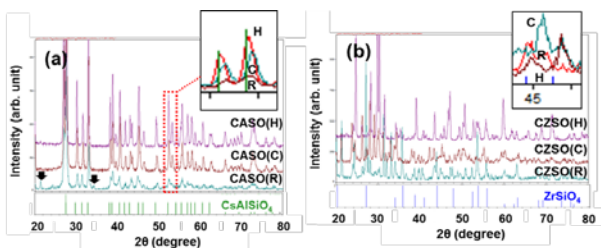


Fig. 2. XRD patterns of the CASO and CZSO samples after each step of heat treatment.

Figure 3 shows. In addition, the wide range of measuring temperature covered abnormal accident conditions in which the temperature rises to 1750  $^\circ\text{C}$ . Both the CASO and CZSO samples exhibited much lower weight loss in the homogenized samples than in the reacted samples. The homogenized CASO and CZSO samples hardly release volatile cesium up to

1200  $^\circ\text{C}$ , whereas the reacted samples lost significant amounts of volatile cesium  $\sim 12\%$  in the CASO sample and  $\sim 23\%$  in the CZSO sample at 1200  $^\circ\text{C}$ . In the CASO sample, the enhancement may be related to the stabilization of the crystal structure, which is shown in Fig. 2(a). The CZSO samples showed relatively poor cesium retention ability in both the homogenized and reacted cases. Moreover, the CZSO sample lost volatile cesium at a lower starting in comparison to the CASO sample. Consequently, the cumulative weight loss range of the CZSO samples lies beyond that of the CASO samples:  $\sim 8.07\%$  to  $\sim 87.72\%$  for the CZSO samples and 2.36% to 34.75% for the CASO sample. From the reacted CZSO sample, most of the captured  $\text{Cs}_2\text{O}$  was released at 1750  $^\circ\text{C}$ . The weight loss behavior clarifies that the retention of cesium in the form of CASO is more favorable than in other forms from a practical viewpoint for ATF.

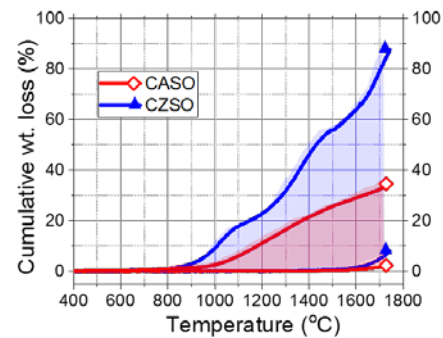


Fig. 3. Weight loss behaviors of the CASO and CZSO samples with respect to temperature.

### 4. Conclusions

The cesium retention ability of Cs–Al–Si–O, Cs–Zr–Si–O was compared by their weight loss behaviors over a wide temperature region up to 1750 $^\circ\text{C}$ . To reflect the real fuel environment having a severe temperature gradient, the Cs–Al–Si–O and Cs–Zr–Si–O compounds were prepared at different temperatures. This concept allows to compare the two samples as ranges. The highest fraction of cesium was maintained in the Cs–Al–Si–O phase: only 2.36% of cesium was released at 1750 $^\circ\text{C}$ . The results demonstrate that Al–Si–O has benefits, thus, suitable for the application in accident-tolerant fuel as a cesium-trapping agent.

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