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TECHNICAL REPORT

Simultaneous immobilization of cesium and strontium by crystalline zirconium phosphate

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In the present study, simultaneous gross immobilization of radioactive Cs and Sr in zirconium phosphate was investigated by two methods. In the "dry method," a mixture of $HZr_2(PO_4)_3$ with varying amounts of $CsNO_3$ and $Sr(NO_3)_2$ was heat-treated at 700 °C for 5 h to prepare Cs + Sr immobilized samples. At Cs + Sr immobilization of 0.3 + 0.15, the leaching amounts of Cs and Sr in 1 mol·dm^{-3} of HCl solution treated at 160 °C for 24 h were 2.9 × 10^{-4} g·m^{-2} and 3.9 × 10^{-4} g·m^{-2}, respectively. In the "autoclave method," aqueous solutions containing 0.5 and 0.25 mol of $CsNO_3$ and $Sr(NO_3)_2$, respectively, against 1 mol of $(H_3O)Zr_2(PO_4)_3$ were thermal-treated at 150–250 °C for 24 h to prepare Cs + Sr immobilized samples; immobilization of Cs and Sr was observed at 150 °C. The immobilized amount of Cs and Sr increased as the treated temperature increased, while the leaching amounts of Cs and Sr in 1 mol·dm^{-3} of HCl solution treated at 160 °C for 24 h decreased. The amount of immobilized Cs and Sr on $(H_3O)Zr_2(PO_4)_3$ at 250 °C were 0.30 and 0.20, and leaching amounts of Cs and Sr were 1.0 × 10^{-3} g·m^{-2} and 1.4 × 10^{-3} g·m^{-2}, respectively.

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1. Introduction

Cs137 and Sr90 are radioactive elements with long half-life, which are present in high-level radioactive waste generated from nuclear power plants.[1)–3)] Previously, we studied the immobilization of Cs and Sr using zirconium phosphate ($HZr_2(PO_4)_3$) as an immobilizer for the permanent immobilization of Cs137 and Sr90. We established that mixing $HZr_2(PO_4)_3$ with $CsNO_3$ or $Sr(NO_3)_2$ followed by heat-treatment at 700 °C could easily immobilize Cs or Sr; this immobilization method is hereafter described as the "dry method."[4),5)] The immobilized Cs and Sr exhibited heat and chemical resistance. In addition, the leaching resistance of Cs and Sr to various solvents was 100 to 1000 times better than that of the borosilicate glass immobilized materials.[6)] Furthermore, the amount of Cs and Sr immobilized by this method was several times higher. However, only nitrates can be used as the target metallic elements for immobilization in the "dry method," while metallic elements that decompose into oxides without melting cannot be used. Therefore, to overcome this disadvantage, we developed an autoclave technique to immobilize metallic elements at a high temperature and high pressure. This immobilization method is hereafter referred to as the "autoclave method."[7)–10)] In the "autoclave method," $(H_3O)Zr_2(PO_4)_3$ obtained by treating $HZr_2(PO_4)_3$ in an aqueous solution at 150 °C in advance was used as the immobilizing agent. Cs and Sr can be easily immobilized by ionic substitution of H_3O^+ in $(H_3O)Zr_2(PO_4)_3$ and Cs^+ or Sr^{2+} under an aqueous solution using an autoclave at 150 °C or higher. To date, immobilization was investigated for each Cs and Sr. However, simultaneous immobilization of Cs and Sr was attempted in this study using $(H_3O)Zr_2(PO_4)_3$, and various properties of the obtained immobilized materials were investigated.

2. Experimental procedure

In the "dry method," aqueous solutions of $CsNO_3$ and $Sr(NO_3)_2$ were added to 1 mol of $HZr_2(PO_4)_3$ at a concentration of 0.1–0.5 mol of Cs and 0.05–0.25 mol of Sr, mixed in a mortar, and dried at 100 °C. The mixture was placed in an alumina crucible (Nikkato Co., SSA-S), heat-treated at 700 °C for 5 h in air, and subsequently washed in deionized water for 10 min. The Cs + Sr immobilized sample was then filtered and dried at 100 °C. In the "autoclave method," solutions of $CsNO_3$ and $Sr(NO_3)_2$ and were placed in an autoclave container along with $(H_3O)Zr_2(PO_4)_3$ at concentration of 0.5 mol of Cs and 0.25 moles of Sr for 1 mol of $(H_3O)Zr_2(PO_4)_3$. The sample was then thermal-treated from 150 °C to 250 °C for 24 h, and the Cs + Sr immobilized sample was prepared.

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The immobilized samples were subjected to X-ray diffraction measurements (Rigaku, MiniFlex) in the range of $2\theta = 10°–40°$ using $CuK_{\alpha 1}$ radiation. An energy dispersive X-ray fluorescence spectrometer (Shimadzu, EDX-700) was used to determine the amount of Cs and Sr in each immobilized sample. The leaching resistance test was performed as follows: 2 g of each immobilized sample was placed in an autoclave container with 16 cm^3 of 1 $mol \cdot dm^{-3}$ of HCl solution. The mixture was then left in a drier for 24 h at 160 °C. After cooling to room temperature, the solids and the solution were separated by filtration, and the amount of Cs and Sr leached into the solution was determined using an atomic absorption spectrophotometer (Shimadzu, AA-6200).

3. Results and discussion

3.1 Cs + Sr immobilized sample prepared by "dry method"

The XRD patterns of Cs + Sr immobilized samples and the immobilizer $HZr_2(PO_4)_3$ are shown in **Fig. 1**. The composition of Cs + Sr immobilized samples after heat-treatment at 700 °C was $H_{1-x-2y}Cs_xSr_yZr(PO_4)_3$, $(x, y) =$ (0.1, 0.05), (0.2, 0.1), (0.3, 0.15), (0.4, 0.2), and (0.5, 0.25). These results are in good agreement with the previously reported XRD patterns of $CsZr_2(PO_4)_3$ and $SrZr_4(PO_4)_6$ in the hexagonal system with NASICON-type structure (space group: R3c); no peaks attributed to $CsNO_3$, Cs_3PO_4, CsO_2, Cs_2CO_3, $Sr(NO_3)_2$, $Sr_3(PO_4)_2$, SrO, and $SrCO_3$. The relationship between the amount of Cs + Sr immobilized and the lattice constant of the Cs + Sr immobilized sample is illustrated in **Fig. 2**, along with the lattice constant of the immobilizer $HZr_2(PO_4)_3$.[4),5)] The *a*-axis decreased, while *c*-axis increased with the increasing amount of immobilized Cs + Sr. This trend was consistent with the ICDD card lattice parameter data, wherein the *a*-axis of $CsZr_2(PO_4)_3$ ($a = 0.8581$ nm, $c = 2.4965$ nm, ICDD No. 34-196) and $SrZr_4(PO_4)_6$ ($a = 0.8693$ nm, $c = 2.3389$ nm, ICDD No. 34-1360) was smaller than that of $HZr_2(PO_4)_3$ ($a = 0.8803$ nm, $c = 2.3230$ nm, ICDD No. 38-4), while the *c*-axis was larger.

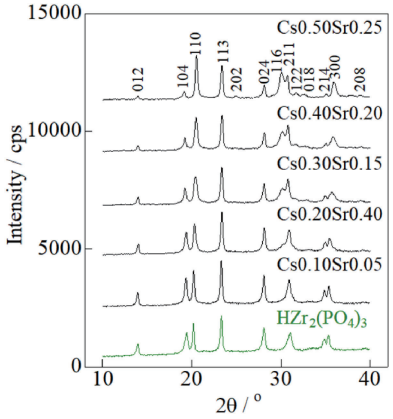


Fig. 1. X-ray diffraction patterns of $HZr_2(PO_4)_3$ and the (Cs + Sr) immobilized sample prepared by the "dry method" at various molar ratio $[CsNO_3 + Sr(NO_3)_2]/HZr_2(PO_4)_3 = [(0.1–0.5) + (0.05–0.25)]/1$. The number of each peak in the figure indicates the Miller index with reference to ICDD No. 34-1360 [$SrZr_4(PO_4)_6$].

Figure 3 demonstrates the relationship between the immobilized amount of Cs + Sr and the amount of Cs and Sr leached into 1 $mol \cdot dm^{-3}$ of HCl solution at 160 °C for 24 h. When the immobilized amount of Cs + Sr was 0.2 + 0.1, the leaching amount and weight ratio of the leaching amount to the immobilized amount of Cs and Sr (R) were 2.2×10^{-4} $g \cdot m^{-2}$ and 1.7 wt % (R_{Cs}) for Cs, and 3.5×10^{-4} $g \cdot m^{-2}$ and 8.1 wt % (R_{Sr}) for Sr. In addition, the leaching amount of Cs and Sr increased with an increase in the immobilized amount of Cs + Sr. The leaching amount of Cs and Sr were 2.9×10^{-4} $g \cdot m^{-2}$ (R_{Cs}: 1.5 wt %) and 3.9×10^{-4} $g \cdot m^{-2}$ (R_{Sr}: 6.2 wt %), respectively, when the immobilized amount of Cs + Sr was 0.3 + 0.15. When the Cs + Sr immobilization amount was 0.2 + 0.1 and 0.3 + 0.15, the leaching ratio R was approximately equal. For the individual immobilized samples of Cs and Sr, the leaching amounts of Cs and Sr were 6.6×10^{-5} $g \cdot m^{-2}$ (R_{Cs}: 0.3 wt %) and 2.0×10^{-3} $g \cdot m^{-2}$ (R_{Sr}: 22.2 wt %) at the Cs and Sr immobilization levels of 0.4 and 0.2, respectively.[4),5)] The Cs leaching amount increased by a factor of 4.3, while the Sr leaching amount decreased by a factor of 1/5. This observation was attributed to the easy leaching

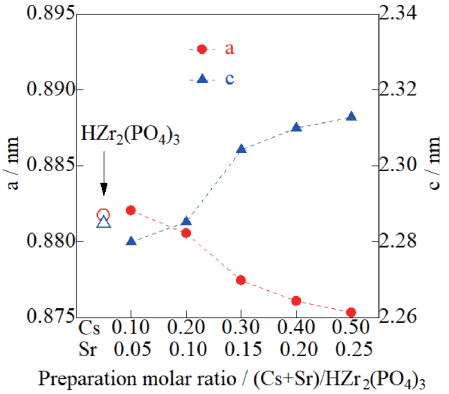


Fig. 2. Relationship between the lattice parameters and the preparation molar ratio of (Cs + Sr) immobilized samples prepared by the "dry method."

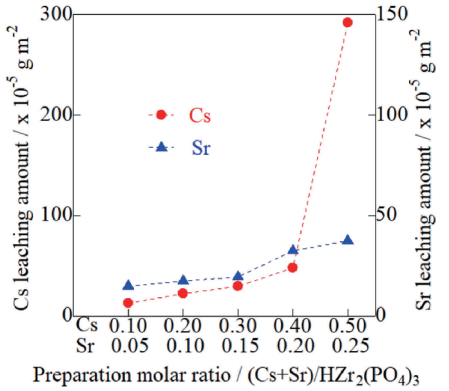


Fig. 3. Relationship between the preparation molar ratio and the leaching amount of Cs and Sr in 1 $mol \cdot dm^{-3}$ of HCl after heating at 160 °C for 24 h per 1 m^2 of surface area of the (Cs + Sr) immobilized samples prepared by "dry method."

of Cs^+, which has a smaller valence and fewer bonding hand, compared to Sr^{2+} when Cs and Sr coexisted in zirconium phosphate, an immobilizer, during the simultaneous immobilization of Cs and Sr. Although the leaching amount of Cs increased more notably in the simultaneous immobilized samples than in the individual immobilized samples, the leaching amount of Cs and Sr are in the same digit. Thus, good Cs and Sr leaching resistance characteristics can be realized even in the simultaneous immobilized sample.

3.2 Cs + Sr immobilized sample prepared by "autoclave method"

Figure 4 illustrates the immobilized amount of Cs and Sr in the immobilized sample determined by X-ray fluorescence analysis. 0.5 mol of Cs and 0.25 mol of Sr added to 1 mol of $(H_3O)Zr_2(PO_4)_3$, thus up to 0.5 moles of Cs and 0.25 moles of Sr for 1 mole of $(H_3O)Zr_2(PO_4)_3$; immobilization of Cs and Sr was observed from 150 °C. The immobilized amount of Cs and Sr increased with an increase in the treated temperature; the immobilized amount of Cs and Sr was 0.3 and 0.2 mol, respectively, for 1 mol of $(H_3O)Zr_2(PO_4)_3$ at a treated temperature of 250 °C. Sr was immobilized more than Cs in the ratio of Cs or Sr immobilized to the maximum immobilized amount. Sr^{2+} (0.116 nm for 6-coordination) with a smaller ionic radius was easily immobilized in $(H_3O)Zr_2(PO_4)_3$ as compared to Cs^+ (0.170 nm for 6-coordination).[11] This tendency was also confirmed in the individual immobilization of Cs and Sr by the previously reported "autoclave method."[7)–9)]

Figure 5 demonstrates the XRD patterns of the Cs + Sr immobilized sample and $(H_3O)Zr_2(PO_4)_3$. The composition of the Cs + Sr immobilized sample was $(H_3O)_{1-x-2y}Cs_xSr_yZr(PO_4)_3$. Similar to that in section 3.1, all XRD peaks of the Cs + Sr immobilized sample were ascribed to the hexagonal crystal system with NASICON-type structure (space group: R3c). The relationship between the autoclave treatment temperature and the lattice constants of the Cs + Sr immobilized sample is illustrated in **Fig. 6**, along with the lattice constants of $(H_3O)Zr_2(PO_4)_3$ used as the immobilizer. Both *a*- and *c*-axes became smaller with the increasing treated temperature. This tendency was consistent with the lattice constant data of the ICDD card, wherein both the *a*- and *c*-axes of $SrZr_4(PO_4)_6$ ($a = 0.8693$ nm, $c = 2.3389$ nm, ICDD No. 34-1360) are smaller than those of $(H_3O)Zr_2(PO_4)_3$ ($a = 0.8760$ nm, $c = 2.3744$ nm, ICDD No. 38-67).[8)–10)] However, it does not match the ICDD card data wherein the *a*- and *c*-axes were smaller and larger, respectively, in $CsZr_2(PO_4)_3$ ($a = 0.8581$ nm, $c = 2.4965$ nm, ICDD No. 34-196) compared to that in $(H_3O)Zr_2(PO_4)_3$.[8)–10)] This is because Sr was more immobilized than Cs in the immobilization ratio in the Cs + Sr immobilized sample prepared by the "autoclave method." The lattice constant of the Cs + Sr immobilized sample thermal-treated at 250 °C with 0.3 and 0.2 mol of Cs and Sr, respectively, was almost similar to the lattice constant of the Cs + Sr immobilized sample with the Cs + Sr immobilization amount of 0.30 + 0.15 prepared by the "dry method" in section 3.1.

Figure 7 illustrates the relationship between the treated temperature and the leaching amounts of Cs and Sr in 1 mol·dm^{-3} of HCl solution at 160 °C for 24 h. The

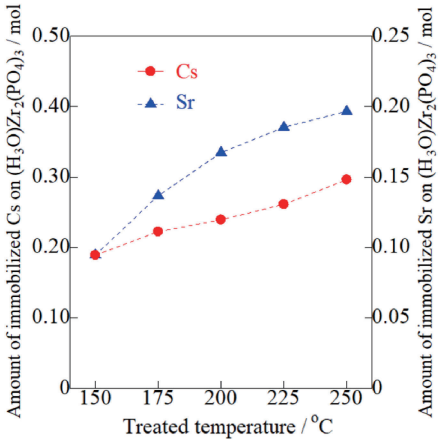


Fig. 4. Relationship between the treated temperature and the immobilized amount of Cs and Sr on $(H_3O)Zr_2(PO_4)_3$ after heating at 150–250 °C for 24 h in an autoclave.

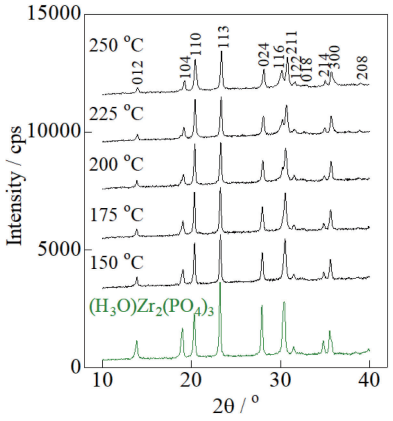


Fig. 5. X-ray diffraction patterns of $HZr_2(PO_4)_3$ and the Cs + Sr immobilized sample prepared by the "autoclave method" at various treated temperature. The number of each peak in the figure indicates the Miller index with reference to ICDD No. 34-1360 [$SrZr_4(PO_4)_6$].

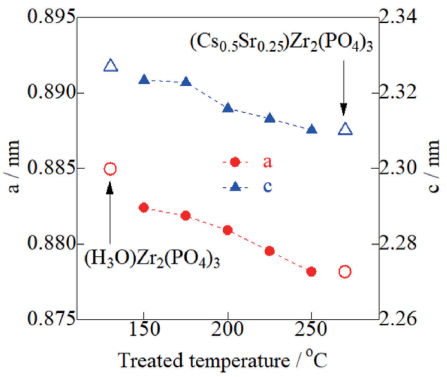


Fig. 6. Relationship between the lattice parameters and the treated temperature for (Cs + Sr) immobilized samples prepared by the "autoclave method."

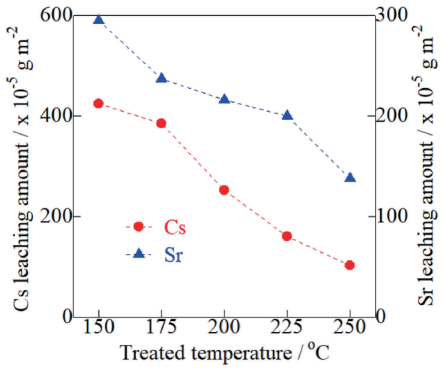


Fig. 7. Relationship between the treated temperature and the leaching amount of Cs and Sr in 1 mol·dm^{-3} of HCl after heating at 160 °C for 24 h per 1 m^2 of surface area of the (Cs + Sr) immobilized sample prepared by the "autoclave method."

immobilized sample of Cs and Sr thermal-treated at 250 °C exhibited the best leaching resistance. The leaching amounts of Cs and Sr decreased with the increasing treated temperature. However, the immobilized amount of Cs and Sr increased with the increasing treated temperature. The Cs + Sr immobilized at 250 °C immobilized 0.3 and 0.2 mol of Cs and Sr, respectively; the leaching amount of Cs and Sr were 1.0×10^{-3} g·m^{-2} (R_{Cs}: 5.3 wt %) and 1.4×10^{-3} g·m^{-2} (R_{Sr}: 16.9 wt %), respectively. The Cs and Sr immobilization stability was improved at higher treated temperatures. For the individually immobilized samples of Cs and Sr reported previously, the Cs immobilized sample treated at 250 °C had Cs immobilization and leaching amount of 0.37 mol and 1.2×10^{-3} g·m^{-2} (R_{Cs}: 5.6 wt %), respectively, while the Sr immobilized sample had Sr immobilization and leaching amount of 0.27 mol and 1.4×10^{-3} g·m^{-2} (R_{Sr}: 11.8 wt %), respectively.[9] Unlike the dry method, no significant difference in the leaching rate (R) was observed between the simultaneous and individual immobilized samples using the autoclave method. This may be ascribed to the tight and loose structure of the immobilized sample prepared by the dry and autoclave method, respectively. The cell volumes of the 0.2 + 0.1 and 0.3 + 0.15 Cs + Sr immobilized samples prepared by the dry method were 1.5277 and 1.5363 nm^3, respectively, whereas that prepared by the autoclave method at 250 °C were 1.5459 nm^3. Meanwhile, compared to the leaching amount of the Cs + Sr immobilized sample prepared by the "autoclave method" at 250 °C and that of the Cs + Sr immobilized sample with Cs + Sr immobilization amount of 0.3 + 0.15 prepared by the "dry method" (Cs: 2.9×10^{-4} g·m^{-2}, Sr: 3.9×10^{-4} g·m^{-2}), the leaching resistance of the sample prepared by the "dry method" was approximately five times better than that by the "autoclave method" for Cs and Sr. However, Cs and Sr immobilized by the "autoclave method" could be further heat-treated at 700 °C in the air to reduce the leaching amounts of Cs and Sr to 1/40 or less.[7]

4. Conclusion

The results of the simultaneous immobilization of Cs and Sr in $HZr_2(PO_4)_3$ and $(H_3O)Zr_2(PO_4)_3$ by the "dry method" and "autoclave method" demonstrated the following:

In the "dry method," the added Cs and Sr were almost completely immobilized in $HZr_2(PO_4)_3$. An excellent leaching resistance of Cs and Sr was exhibited in a 24 h leaching test in 1 mol·dm^{-3} of HCl solution at 160 °C when the amount of Cs + Sr immobilized was less than 0.3 + 0.15. In contrast, the immobilization of Cs and Sr was confirmed at 150 °C or higher in the "autoclave method," and the immobilized amount of Cs and Sr increased with the increasing treated temperature. The Cs + Sr immobilized sample at 250 °C exhibited the best leaching resistance, although the immobilized amount of Cs and Sr increased. The Cs and Sr leaching resistance of the immobilized sample prepared by the "dry method" was approximately five times better than that by the "autoclave method."

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