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Immobilization of Cs and Sr to $HZr_2(PO_4)_3$ using an autoclave

Chihiro Hashimoto *, Susumu Nakayama

Department of Applied Chemistry and Biotechnology, Niihama National College of Technology, 7-1 Yakumo-Cho, Niihama, Ehime 792-8580, Japan

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ABSTRACT

The proton-type crystalline zirconium phosphate, $HZr_2(PO_4)_3$, was prepared by a thermal decomposition of $NH_4Zr_2(PO_4)_3$ at about 450 °C, where $NH_4Zr_2(PO_4)_3$ was obtained in advance by a hydrothermal synthesis using a mixed solution of $ZrOCl_2$, H_3PO_4 and $H_2C_2O_4$. Cs or Sr ion was immobilized to $HZr_2(PO_4)_3$ by mixing $HZr_2(PO_4)_3$ with an aqueous solution of $CsNO_3$ or $Sr(NO_3)_2$ under the molar ratio $CsNO_3/HZr_2(PO_4)_3 = 1.0$ or $Sr(NO_3)_2/HZr_2(PO_4)_3 = 0.5$. The mixtures were treated thermally in an autoclave at different temperatures from 200 to 275 °C and Arrhenius equation was applied to the Cs and Sr immobilization process to $HZr_2(PO_4)_3$. The activation energy for the immobilization process of Cs or Sr was estimated as 179 kJ mol^{-1} and 186 kJ mol^{-1}, respectively.

1. Introduction

When spent nuclear fuels, produced as waste from nuclear power stations, are reprocessed, the high level radioactive wastes produced, contain fission products such as Cs, Sr as well as transuranic elements (such as Np, Pu and Am) with extremely long half-lives. Of particular concern, with regard to the potential for leaching during storage of these high level wastes, are the alkali metal Cs137 and the alkaline earth metal Sr90 which have a relatively long life of approximately 30 years. Immobilization methods employed for high level radioactive wastes should therefore produce compounds that are chemically and thermally stable, with respect to leachability of Cs137 and Sr90 [1,2].

Conventional methods of the immobilization of radioactive Cs and Sr are by forming a borosilicate glass or a ceramic such as supercalcine, SYNROC and titanium oxide $Ti(OH)_4$ [3–12]. A process based on borosilicate glass has been of practical use, but accompanied by drawbacks as follows. The borosilicate glass processing requires thermal treatment in excess of 1000 °C which causes partial volatilization of Cs, and the resultant gas could damage the processing equipment. In addition, heat caused by radioactive decay has a cumulative effect on the crystal structure, leading to changes in structure. This in turn leads to poor physical and chemical resistance (especially for salts, acids and alkalis) with resultant poor Cs and Sr leachability performance. Instead of this method, new techniques for the immobilization are expected to be examined.

One of the immobilization methods, using proton-type zirconium phosphate $HZr_2(PO_4)_3$ with the NASICON three dimensional structure (as shown in Fig. 1) is known to exhibit better immobilization efficiency than the borosilicate glass. $HZr_2(PO_4)_3$ readily exchanges its proton ion H_3O^+ for metal ion M^{n+} with relatively small radius such as Li^+ and Na^+ from aqueous mixtures. When $HZr_2(PO_4)_3$ is mixed with $M(NO_3)_n$ in a dry state and subsequently thermally treated at 700 °C, the obtained $HZr_2(PO_4)_3/M$ crystalline complex is stable, thermally and chemically resistant and exhibit excellent M^{n+} leaching resistance [13–15]. The immobilized amount of Cs or Sr is several times larger than that of the borosilicate glass, and the leachability performance of Cs or Sr is 100–1000 times better. However, the following problems for this method are pointed out; metal ions should form nitrate like $M(NO_3)_n$ and the nitrate should not be oxidized and decomposed prior to melting with heating. This immobilization method is a little complicated and troublesome. To resolve these problems, the following immobilization method has been explored by subjecting the mixture to high pressure steam at high temperature with an autoclave [16]. When $HZr_2(PO_4)_3$ was mixed with an aqueous solution of Cs^+ (e.g. $CsNO_3$, CsCl and Cs_2CO_3) and placed in an autoclave at 150–400 °C for 24 h, the immobilization of Cs^+ to $HZr_2(PO_4)_3$ was confirmed to be archived above 160 °C. In this study, the immobilization process of Cs and Sr to $HZr_2(PO_4)_3$ using an autoclave has been investigated at different temperatures from 200 to 275 °C and analyzed from the viewpoint of chemical kinetics based on the Arrhenius equation.

2. Experimental procedure

Reagent grades of zirconium oxychloride ($ZrOCl_2$), phosphoric acid (H_3PO_4) and oxalic acid ($H_2C_2O_4$) were dissolved in water and adjusted to pH 3 by aqueous ammonium. By a hydrothermal synthesis at 80 °C for 48 h, ammonium type zirconium phosphate ($NH_4Zr_2(PO_4)_3$) was prepared. This was then calcined at 450 °C to

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* Corresponding author. Tel.: +81 (0)897377782; fax: +81 (0)897377777.
E-mail address: hashimoto@chem.niihama-nct.ac.jp (C. Hashimoto).

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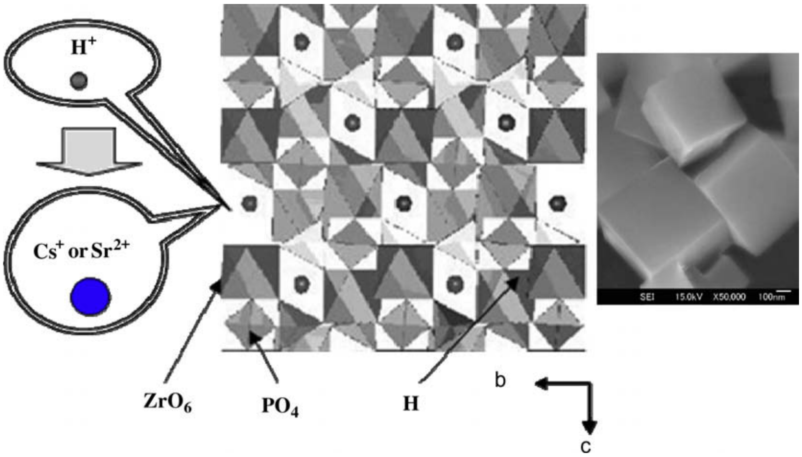

Fig. 1. Crystal structure proposed for $HZr_2(PO_4)_3$. The replacement of H^+ with Cs^{2+} or Sr^{2+} undergoes in the Cs or Sr immobilization process to $HZr_2(PO_4)_3$.

produce proton-type zirconium phosphate $HZr_2(PO_4)_3$. In this report, such $HZr_2(PO_4)_3$ was produced by Daiichi Kigenso Kagaku Kogyo Co. Ltd. (NZP-100).

Five grams of $HZr_2(PO_4)_3$ was mixed with the aqueous solution (20 cm^3) of $CsNO_3$ or $Sr(NO_3)_2$ with the molar ratio of Cs and Sr against $HZr_2(PO_4)_3$ as 1.0 and 0.5, respectively. The mixtures were thermally treated in an autoclave (TSC-006, Taiatsu Techno Co.) at 200–300 °C for 6–200 h to immobilize Cs or Sr to $HZr_2(PO_4)_3$. The immobilization process undergoes by replacing H^+ with Cs^+ or Sr^{2+} as shown in Fig. 1. The immobilized amount of Cs and Sr to $HZr_2(PO_4)_3$ was quantitatively analyzed by X-ray fluorescence spectroscopy (EDX-700, Shimazu). The crystalline structure for the Cs or Sr immobilized $HZr_2(PO_4)_3$ was measured by powder X-ray diffraction (MiniFlex, Rigaku) carried out with Cu Kα over the angles $2\theta = 10–70°$. The leachability performance of Cs^+ and Sr^+ from the immobilized products was studied as follows; the immobilized product ($HZr_2(PO_4)_3$/Cs or $HZr_2(PO_4)_3$/Sr complexes) of 2 g was mixed with 1 M HCl aqueous solution of 16 cm^3 was placed in the autoclave (TVS-N2, Taiatsu Techno Co.) at 160 °C for 24 h. After cooling to the room temperature, the mixture was filtrated and the amount of Cs^+ or Sr^+ leached from the immobilized material into the filtrate was measured by atomic absorption spectrophotometer (AA-6200, Shimazu).

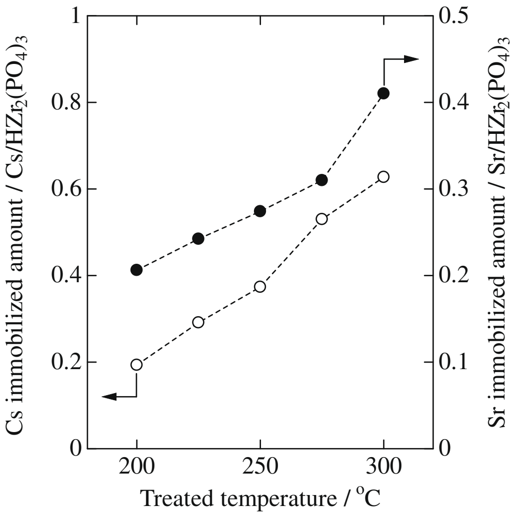

Fig. 2. Effect of treated temperature of the autoclave on the immobilized amount of Cs or Sr to $HZr_2(PO_4)_3$ measured by X-ray fluorescence spectroscopy.

3. Results and discussion

3.1. Immobilization of Cs and Sr to $HZr_2(PO_4)_3$

The mixture of $HZr_2(PO_4)_3$ and aqueous solution of $CsNO_3$ or $Sr(NO_3)_2$ was treated in the autoclave at different temperatures for 24 h. The immobilized amounts of Cs and Sr of the products were measured by X-ray fluorescence spectroscopy and plotted against the treated temperature as shown in Fig. 2. Both immobilized amounts of Cs and Sr increase with rising temperature from 200 to 300 °C. The molar ratio of Cs to $HZr_2(PO_4)_3$ is $Cs/HZr_2(PO_4)_3 = 0.63$ at 300 °C, while that of Sr is $Sr/HZr_2(PO_4)_3 = 0.41$. In comparison with the theoretically evaluated molar ratio of $Cs/HZr_2(PO_4)_3 = 1.0$ and $Sr/HZr_2(PO_4)_3 = 0.5$, Sr^{2+} is more immobilized to $HZr_2(PO_4)_3$ than Cs^+. The ion radii of Sr^{2+} and Cs^+ are 0.116 nm and 0.170 nm, respectively. It indicates that the metal ion with smaller ion radius could be more immobilized into $HZr_2(PO_4)_3$ [11].

3.2. Powder X-ray diffraction

Fig. 3 shows the X-ray diffraction patterns of the Cs^+ or Sr^{2+} immobilized $HZr_2(PO_4)_3$ treated thermally in an autoclave at 400 °C, together with $HZr_2(PO_4)_3$ and $(H_3O)Zr_2(PO_4)_3$. $(H_3O)Zr_2(PO_4)_3$ was obtained by treating $HZr_2(PO_4)_3$ in the autoclave

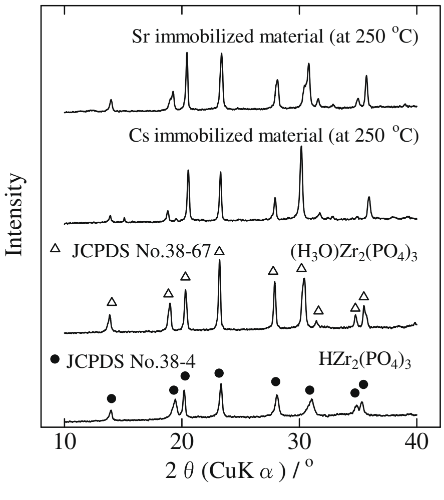

Fig. 3. X-ray diffraction patterns of the Cs or Sr immobilized material together with $HZr_2(PO_4)_3$ and $(H_3O)Zr_2(PO_4)_3$.

at 180 °C for 24 h. Since $HZr_2(PO_4)_3$ is readily converted to $(H_3O)Zr_2(PO_4)_3$ in pure water at room temperature for 3 days, $(H_3O)Zr_2(PO_4)_3$ is more adequate to be compared with the Cs or Sr immobilized material than $HZr_2(PO_4)_3$. As shown in Fig. 3, the X-ray diffraction patterns of the Cs or Sr immobilized material have only bands due to NASICON type structure of $(H_3O)Zr_2(PO_4)_3$, and any bands due to impurity such as $CsNO_3$ or $Sr(NO_3)_2$, Cs_3PO_4 or $Sr_3(PO_4)_2$, Cs_2O or SrO and Cs_2CO_3 or $SrCO_3$ are not seen. It indicates that a part of H_3O^+ is exchanged for Cs^+ or Sr^{2+} and the immobilized material such as $(Cs_x(H_3O)_{1-x})Zr_2(PO_4)_3$ or $(Sr_x(H_3O)_{1-2x})Zr_2(PO_4)_3$ are produced. The reason why the peak intensity of the Cs or Sr immobilized material and $(H_3O)Zr_2(PO_4)_3$ is larger than that of $HZr_2(PO_4)_3$ is considered to be due to that the crystallization proceeds by the thermal treatment in the autoclave.

Fig. 4 shows the effect of the treatment temperature on the lattice constants of the Cs or Sr immobilized material, referred to as *a* and *c*. In case of the Cs immobilized material, the lattice constant *a* decreases and *c* increases from the lattice constants of $(H_3O)Zr_2(PO_4)_3$ (*a*: 0.8760 nm, *c*: 2.3744 nm) [17] to that of $CsZr_2(PO_4)_3$ (*a*: 0.8581 nm, *c*: 2.4965 nm) [18] almost linearly with increasing the treatment temperature. It indicates that the immobilized amount of Cs increases with increasing treatment temperature, and this supports the result of X-ray fluorescence analysis in 3.1. On the other hand, for the Sr immobilized material, both lattice constants a and c decrease from the lattice constants of $(H_3O)Zr_2(PO_4)_3$ to that of $SrZr_4(PO_4)_6$ (*a*: 0.8693 nm, *c*: 2.3389 nm) [19] with increasing treatment temperature. The variation of *a* and *c* of the Sr immobilized material against treatment temperature is relatively smaller than that of the Cs immobilized one, and it will be due to a small difference between the lattice constants of $(H_3O)Zr_2(PO_4)_3$ and that of $SrZr_4(PO_4)_6$.

3.3. Cs and Sr leachability performance

Fig. 5 shows the leaching rate of Cs or Sr from its immobilized materials after 24 h by adding 1 M HCl at 160 °C, where the Cs or Sr immobilized materials are produced in an autoclave at different treatment temperatures from 200 to 300 °C. The leaching rates of Cs and Sr become lower in the treatment temperature range from 250 to 300 °C than that from 200 to 225 °C in spite of that the immobilized amount itself is larger at 250–300 °C than 200–225 °C as shown in Fig. 2. It indicates that the mixtures should be treated in the autoclave above 250 °C to immobilize and stabilize Cs or Sr. The fact that the immobilization and the stabilization of Cs and Sr is archived near 250 °C is convenient for the use of Teflon material with heat-resistance up to 250 °C.

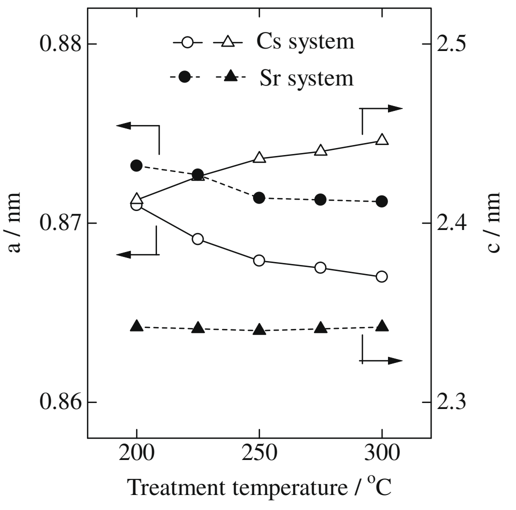

Fig. 4. Lattice constants *a* and *c* of the Cs or Sr immobilized material treated at 200–300 °C.

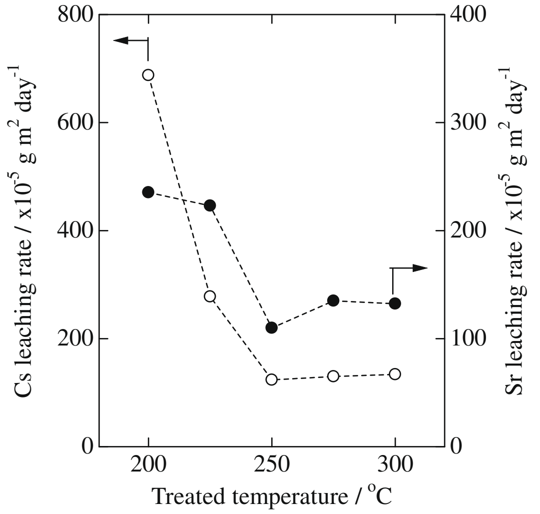

Fig. 5. Effect of treated temperature of the autoclave on the Cs or Sr leaching rate from its immobilized material.

3.4. Chemical kinetics for the Cs and Sr immobilization process

The amount of Cs and Sr immobilized to $HZr_2(PO_4)_3$ in the autoclave increases with time at 200–300 °C, then becomes almost constant after about 24 h. The chemical kinetics for the immobilization process of both Cs and Sr is discussed by the Arrhenius equation as follows. For the immobilization process as a reaction between $CsNO_3$ and $HZr_2(PO_4)_3$, such that:

$$CsNO_3 + HZr_2(PO_4)_3 \rightarrow CsZr_2(PO_4)_3 + HNO_3, \tag{1}$$

the rate of reaction is given by

$$-\frac{d[CsNO_3]}{dt} = k[CsNO_3][HZr_2(PO_4)_3], \tag{2}$$

where *k* is rate constant and *t* is time. Assuming that the concentration of $CsNO_3$ is always equal to that of $HZr_2(PO_4)_3$ like $[CsNO_3] = [HZr_2(PO_4)_3]$, Eq. (2) is replaced by

$$-\frac{d[CsNO_3]}{dt} = k[CsNO_3]^2 \tag{3}$$

and the solution is

$$[CsNO_3]^{-1} = kt + [CsNO_3]_0^{-1}, \tag{4}$$

where $[CsNO_3]_0$ is the concentration of $CsNO_3$ at $t = 0$. A plot of $[CsNO_3]^{-1}$ vs. *t* produces a straight line with slope *k* at different treatment temperature *T* as shown in Fig. 6. Based on the following Arrhenius equation, the activation energy E_a is determined by measuring the reaction rate *k* at different temperatures *T*, plotting the logarithm of *k* against $1/T$ on a graph as shown in Fig. 7, and determining the slope of the straight line that best fits the points.

$$\log k = -\frac{E_a}{2.303RT} + \log A \tag{5}$$

The evaluated activation energy E_a for the reaction of Cs (Eq. (1)) is 179 kJ mol^{-1}.

In a similar way, for the 2nd order reaction of $Sr(NO_3)_2$ and $HZr_2(PO_4)_3$ as

$$Sr(NO_3)_2 + 2HZr_2(PO_4)_3 \rightarrow SrZr_4(PO_4)_6 + 2HNO_3, \tag{6}$$

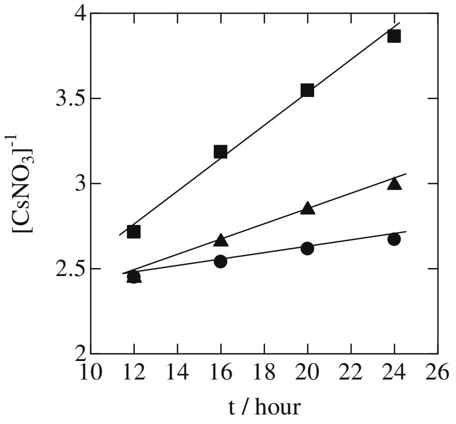

Fig. 6. Plot of $[CsNO)3]^{-1}$ against t in the Cs immobilization process at 225 °C(●), 250 °C(▲) and 275 °C(■), where $[CsNO_3]$ is the concentration of $CsNO_3$ and *t* is time.

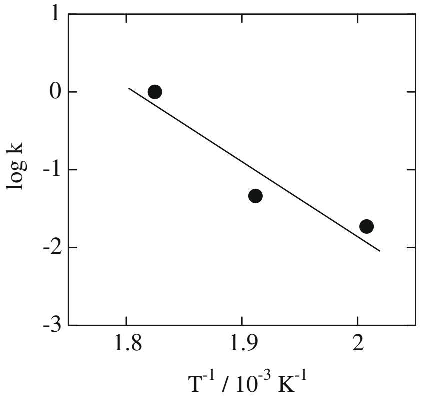

Fig. 7. Arrhenius plot for the Cs immobilization process to $HZr_2(PO_4)_3$. The logarithm of rate constant *k* is plotted against 1/*T*, where *T* is treatment temperature. The unit of *k* is $mol^{-1}\ dm^3\ h^{-1}$.

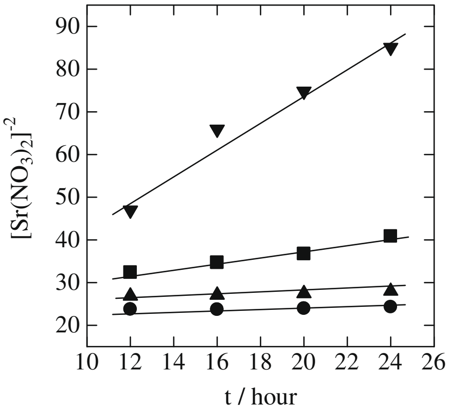

Fig. 8. Plot of $[Sr(NO_3)_2]^{-1}$ against time in the Cs immobilization process at 200 °C(●), 225 °C(▲), 250 °C(■) and 275 °C(▼), where $[Sr(NO_3)_2]$ is the concentration of $Sr(NO_3)_2$ and *t* is time.

the rate of reaction is given by

$$-\frac{d[Sr(NO_3)_2]}{dt} = k[Sr(NO_3)_2][HZr_2(PO_4)_3]^2 \tag{7}$$

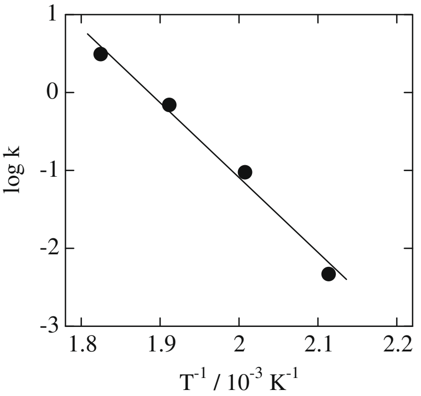

Fig. 9. Arrhenius plot for the Sr immobilization process to $HZr_2(PO_4)_3$. The logarithm of rate constant *k* is plotted against 1/*T*, where *T* is treatment temperature. The unit of *k* is $mol^{-1}\ dm^3\ h^{-1}$.

Assuming that the concentration of $Sr(NO_3)_2$ is always equal to half that of $HZr_2(PO_4)_3$ like $2[Sr(NO_3)_2] = [HZr_2(PO_4)_3]$, Eq. (7) is written as

$$-\frac{d[Sr(NO_3)_2]}{dt} = 4k[Sr(NO_3)_2]^3 \tag{8}$$

and the solution is

$$[Sr(NO_3)_2]^{-2} = 8kt + [Sr(NO_3)_2]_0^{-2} \tag{9}$$

where $[Sr(NO_3)_2]_0$ is the concentration of $Sr(NO_3)_2$ at $t = 0$. A plot of $[Sr(NO_3)_2]^{-2}$ vs. *t* produces a straight line with slope *k* at different treatment temperature *T* as shown in Fig. 8. By plotting the logarithm of *k* against 1/*T* on a graph as shown in Fig. 9 and determining the slope of the straight line of Eq. (9) that best fits the points, the activation energy E_a for the Sr reaction (Eq. (6)) is 186 kJ mol^{-1}. The activation energies for the Cs and Sr immobilization processes could be regarded as close to each other.

4. Conclusion

The immobilization process of Cs and Sr to $HZr_2(PO_4)_3$ using an autoclave has been investigated at different temperatures from 200 to 275 °C for 6–200 h. The immobilized amount of Cs and Sr increases with increasing temperature and time, and Sr is more readily immobilized than Cs. For the immobilization process of Cs to $HZr_2(PO_4)_3$, a reaction between $CsNO_3$ and $HZr_2(PO_4)_3$ as $CsNO_{3+}$ $HZr_2(PO_4)_3 \rightarrow CsZr_2(PO_4)_3 + HNO_3$ is applied to Arrhenius equation. From the temperature dependence of the rate constant, the activation energy of this reaction is evaluated as 179 kJ mol^{-1}. In a similar way, for the immobilization process of Sr to $HZr_2(PO_4)_3$, a reaction between $Sr(NO_3)_2$ and $HZr_2(PO_4)_3$ as $Sr(NO_3)_2 + 2HZr_2(PO_4)_3 \rightarrow SrZr_4(PO_4)_6 + 2HNO_3$, the evaluated activation energy is 181 kJ mol^{-1}. The activation energies for the Cs and Sr immobilization processes could be regarded as close to each other.

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