# Strontium Immobilization by Fibrous Cerium(IV) Bis(monohydrogenphosphate) under Hydrothermal Conditions

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The uptake of strontium ions from an aqueous solution by fibrous cerium(IV) bis(monohydrogenphosphate) has been studied from the viewpoints of the immobilization of strontium in radioactive waste by a batchwise operation in the temperature range from 25 to 250  $^{\circ}$ C. Strontium ions can be exchanged below 100  $^{\circ}$ C following an ion-exchange reaction between hydrogen ions of the phosphate groups. In contrast, strontium ions can be effectively immobilized under hydrothermal conditions accompanied by a structural change of the exchanger, where divalent strontium ions are incorporated into the monazite-like compound to compensate tetravalent cerium ions in trivalent cerium orthophosphate system. This phenomenon is peculiar to alkaline earth metal ions, since the monazite-like compounds were obtained in the presence of  $Ca^{2+}$  and  $Ba^{2+}$ , while this phenomenon was absent in the presence of  $Cu^{2+}$  or  $Ni^{2+}$ .

One of very serious issues in the atomic industry is the disposal of high-level radioactive waste coming from spent nuclear fuels in atomic power plants. One of the promising methods among the various methods for the disposal of the radioactive waste so far proposed is to convert it into a vitrified solid mass embedded deep in a stable stratum of ground so as to be isolated from the biosphere. Since some radioactive nuclides, such as caesium, strontium, and the like have high solubility in water, one problem in this method is that these nuclides are always under a risk of leaching out from a vitrified solid mass when an intrusion of underground water takes place into the stratum. It thus seems interesting to separate these nuclides from primary waste in a way that is suitable for further storage under safe conditions. The immobilization of strontium ions by inorganic exchangers from a waste solution is a promising separation method, since such products are generally radiation resistant and stable enough for long-term storage. 1—6) These materials, however, usually require a heat treatment at a high temperature of 1000 °C, or even higher, for the immobilization of strontium ions.

Cerium(IV) bis(monohydrogenphosphate), Ce(HPO<sub>4</sub>)<sub>2</sub>·nH<sub>2</sub>O, is a fibrous ion-exchanger having an affinity for strontium ions. We have found that stountium ions can be immobilized by fibrous cerium(IV) bis(monohydrogenphosphate) when a Sr<sup>2+</sup>-bearing exchanger is subjected to a dry heat treatment in the temperature range from 300 to 500 °C. This is accompanied by a structural change of the exchanger. To Compared with a solid-state reaction, a hydrothermal reaction is expected to be a useful technique for the immobilization of strontium ions, because the hydrothermal products generally possess high resistance to severe hydrothermal conditions; also, in-situ immobilization from the waste solution can be achieved.  $^{8)}$ 

The present study aims to demonstrate the effectiveness and mechanism of strontium immobilization by fi-

brous cerium(IV) bis(monohydrogenphosphate) under hydrothermal conditions. The effect of the reaction temperature on the strontium uptake by the fibrous cerium(IV) bis(monohydrogenphosphate) was examined by batchwise experiments, and the immobilization mechanism is discussed from the point of view of the crystalline structure of the products.

### **Experimental**

**Materials.** Fibrous cerium(IV) bis(monohydrogenphosphate), (abbreviated as f-CeP) was prepared according to the literature. A fibrous product having a 10—40 nm width was confirmed to be cerium(IV) bis(monohydrophosphate) trihydrate by chemical and thermal analyses (Found: Ce, 35.2; P, 15.8%; Ig loss, 18.6%. Calcd for Ce(HPO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O: Ce, 36.3; P, 16.1%; Ig loss, 18.7%).

**Distribution Coefficient.** The distribution coefficients for metal ions  $(K_d)$  were measured at various pHs adjusted with a 0.1 mol dm<sup>-3</sup> HCl solution. The equilibration of f-CeP with metal ions was carried out by a batchwise operation; 0.05 g of f-CeP was immersed in a sealable teflon tube with 10 cm<sup>3</sup> of a  $10^{-4}$  mol dm<sup>-3</sup> metal solution at a constant temperature ranging from 25 to 200 °C for 168 h. After cooling to room temperature, the solid was filtered off, and the filtrate was analyzed concerning the metal-ion concentration and pH. The distribution coefficient for the metal ions was calculated using

$$K_{\rm d} \, ({\rm cm}^3 \, {\rm g}^{-1}) = (C_0 - C)V/WC,$$

where  $C_0$  and C represent the initial and final concentration of metal ion and V and W are volume (10 cm<sup>3</sup>) and weight of f-CeP.

**Uptake and Leaching Test.** A 0.1 g portion of f-CeP was taken into a sealable teflon tube or a glass ample together with 10 cm<sup>3</sup> of an aqueous  $Sr(NO_3)_2$  solution (0.01—0.5 mol dm<sup>-3</sup>), and kept for 168 h at a constant temperature of 25, 100, 150, 200, and 250 °C. After cooling to room temperature the solid was recovered by filtration and dried at 60 °C. After the solid was digested with concd hydrochloric acid, the diluted solution was analyzed in order to determine the amount of  $Sr^{2+}$  ions taken by f-CeP to-

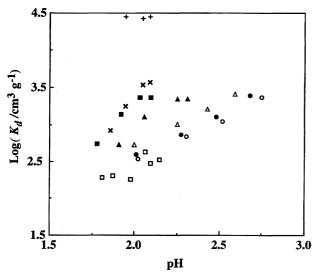


Fig. 1. Distribution coefficients of strontium ion as a function of pH at various temperatures. The exchanger is 0.05 g of f-CeP. The aqueous strontium ion solution is  $10 \text{ cm}^3$  with the initial concentration of  $1 \times 10^{-4} \text{ mol dm}^{-3}$ . Temperature:  $\bigcirc$ , 25;  $\bullet$ , 50;  $\triangle$ , 75;  $\blacktriangle$ , 100;  $\square$ , 125;  $\blacksquare$ , 150;  $\times$ , 175; +, 200 °C.

gether with the concentration of cerium and phosphorus. The solid residues were retained for X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron micrography (SEM) analyses. A 0.05 g portion of the thus-obtained Sr-bearing f-CeP was taken into a glass bottle with  $10~\rm cm^3$  of a 0.1 mol dm $^{-3}$  HCl solution as an eluent. The bottle was shaken at 25 °C for 24 h. After equilibration the solid was allowed to settle, and the supernatant was taken and analyzed concerning the concentration of  $\rm Sr^{2+}$  ions leached out from the solid.

**Method of Analysis.** The concentration of metal ion in an aqueous solution was determined using a Seiko Densi ICP emission spectrometer (model SPS 1500R). XRD powder patterns of the samples were recorded using a Rigaku RAD-C diffractometer with Ni-filtered Cu  $K\alpha$  radiation. A measurement of XPS was carried out using an ULVAC-Phi ESCA 5600Ci spectrometer on which the powdred sample was fixed on a piece of adhesive tape. SEM was performed with a Hitachi S-800 electron microscope, operating at 15 kV

### **Results and Discussion**

Temperature Dependence of Distribution Coefficients for Metal Ions. The temperature dependence of the distribution coefficient ( $K_d$ ) for the  $Sr^{2+}$  ion as a function of the

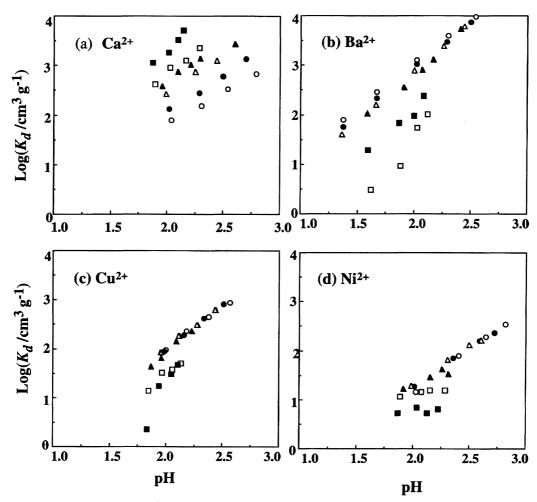


Fig. 2. Distribution coefficients of (a)  $Ca^{2+}$ , (b)  $Ba^{2+}$ , (c)  $Cu^{2+}$ , and (d)  $Ni^{2+}$  ions as a function of pH at various temeratures. The exchanger is 0.05 g of f-CeP. The aqueous metal ion solution is 10 cm<sup>3</sup> with the initial concentration of  $1\times10^{-4}$  mol dm<sup>-3</sup>. Temperature:  $\bigcirc$ , 25;  $\bigcirc$ , 50;  $\triangle$ , 75;  $\triangle$ , 100;  $\square$ , 125;  $\bigcirc$ , 150 °C.

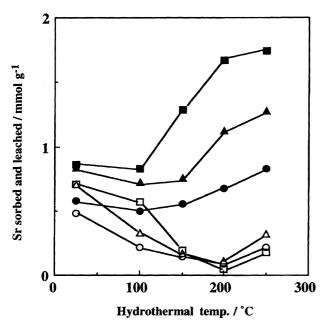


Fig. 3. Hydrothermal temperature dependence of strontium uptake on the f-CeP and strontium leached from the strontium-bearing solid. Uptake; strontium ion concn; ●, 0.01; ▲ 0.05; ■ 0.5 mol dm<sup>-3</sup>. f-CeP: 0.1 g, solution: 10 cm<sup>3</sup>, reaction time: 72 h. Leaching; strontium-bearing solid: 0.05 g, leachant: 0.1 mol dm<sup>-3</sup> HCl solution, solution: 10 cm<sup>3</sup>, tempeature: 25 °C, reaction time: 24 h, strontium ion concn. at the uptake: ○, 0.01; △, 0.05; □, 0.5 mol dm<sup>-3</sup>.

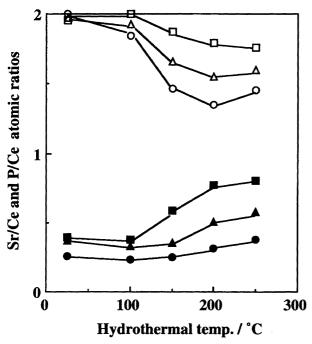


Fig. 4. Hydrothermal temperature dependence of Sr/Ce and P/Ce atomic ratios of the products. f-CeP: 0.1 g, solution: 10 cm<sup>3</sup>, reaction time: 72 h. Sr/Ce atomic ratio; strontium ion concn: ●, 0.01; ▲, 0.05; ■, 0.5 mol dm<sup>-3</sup>. P/Ce atomic ratio: ○, 0.01; △, 0.05; □, 0.5 mol dm<sup>-3</sup>.

pH is shown in Fig. 1. Plots of  $\log K_d$  vs. pH shifted towards a lower pH as the temperature increased up to 100 °C. This indicates that an ion-exchange between Sr2+ and H+ is an endothermic reaction. 11) Above 100 °C, the K<sub>d</sub> value dropped at 125 °C, and recovered again at 150 °C, suggesting that there was an inflection point in the  $K_d$  value at 125 °C. The temperature dependence of the  $K_d$  values for some other divalent metal ions was examined in order to confirm that the abovementioned phenomenon was specific to the Sr<sup>2+</sup> ion. The results for Ca<sup>2+</sup>, Ba<sup>2+</sup>, Cu<sup>2+</sup>, and Ni<sup>2+</sup> ions are shown in Fig. 2. In the case of the  $Ca^{2+}$  ion, although the  $K_d$  value increased with the temperature, the rate of increment varied with the temperature range. Below 100 °C, the K<sub>d</sub> value increased constantly due to an endothermic reaction, 11) then slightly increased between 75 and 125 °C, and increased at 150 °C with a larger rate than that at 125 °C. In the case of the Ba<sup>2+</sup> ion, the plot of  $\log K_d$  vs. pH slightly shifted downward below 100 °C due to the fact that the Ba<sup>2+</sup> and H<sup>+</sup> exchange is an exothermic reaction. 11) Above 100 °C, the plot decreased at 125 °C, then increased at 150 °C. In contrast, the  $K_d$  values for the Cu2+ and Ni2+ ions scarcely depended on the temperature below 100 °C; there was no enhancement of  $K_d$  above 100 °C. Accordingly, anomalous phenomena, such as the increases in the  $K_d$  value under hydrothermal conditions, are expected to be peculiar to alkaline earth metal ions. The evidence has been demonstrated by the XRD results afterwards. The distribution coefficients of f-CeP for metal ions at 150  $^{\circ}$ C increases in the order Ni<sup>2+</sup> <Cu<sup>2+</sup> <Ba<sup>2+</sup> <Ca<sup>2+</sup> <Sr<sup>2+</sup>. Thus, Sr<sup>2+</sup> ions are anticipated to be preferentially taken under hydrothermal conditions, even in the presence of other divalent metal ions.

# Strontium Uptake under Hydrothermal Conditions. To elucidate the mechanism of the $Sr^{2+}$ uptake under hydrothermal conditions, a sorption experiment was carried out using $Sr^{2+}$ solutions at a concentration range of between 0.01 and 0.5 mol dm<sup>-3</sup>. The temperature dependence of the $Sr^{2+}$ uptake by f-CeP is shown in Fig. 3. The $Sr^{2+}$ uptake increases with along an increase in the hydrothermal temperature and the $Sr^{2+}$ concentration of the solution. The highest $Sr^{2+}$ uptake obtained by a hydrothermal reaction with 0.5 mol dm<sup>-3</sup> at 250 °C amounts to 1.74 mmol $g^{-1}$ .

Leaching experiments were conducted in order to examine the reversibility of the Sr<sup>2+</sup> sorption using a 0.1 mol dm<sup>-3</sup> HCl solution as a leachant. The leached amounts of Sr<sup>2+</sup> from the Sr<sup>2+</sup>-bearing solids reacted at various temperatures are shown in Fig. 3. More than 80% of Sr<sup>2+</sup> taken by the f-CeP could be leached out from the Sr<sup>2+</sup>-bearing solid reacted at 25 °C. This indicates that Sr<sup>2+</sup> ions taken by the f-CeP at lower temperature are reversibly exchanged with hydrogen ions. The leached amount of the Sr<sup>2+</sup> ions decreased along with an increase in the hydrothermal temperature, and reached a minimum value at 200 °C. The minimum value corresponded to less than 5% of the amount of Sr<sup>2+</sup> uptake. Most of the Sr<sup>2+</sup> taken by the f-CeP could no longer be leached out substantially, even when the Sr<sup>2+</sup>-bearing solid was contacted with a diluted acidic medium. Thus, the Sr<sup>2+</sup> uptake under hydrothermal conditions is not a simple ion-

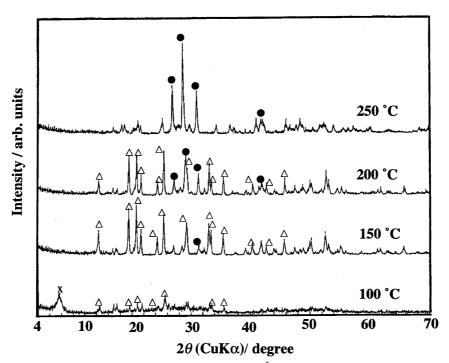


Fig. 5. X-Ray diffraction patterns of the products reacted in  $0.5 \text{ mol dm}^{-3}$  strontium ion solution at various hydrothermal temperatures. Diffraction peaks corresponding to Cerium(IV) bis(monohydrogenphosphate), Ce(OH)(PO<sub>4</sub>), and monazite-like phase are labeled  $\times$ ,  $\triangle$ , and  $\blacksquare$ , respectively.

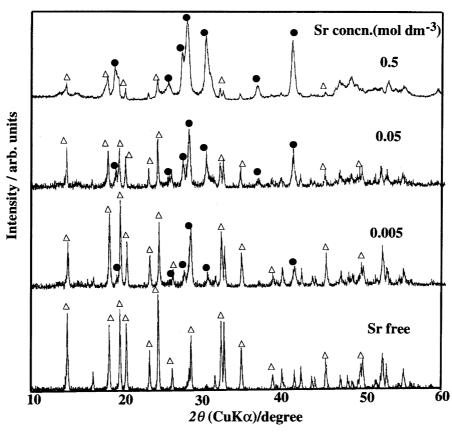


Fig. 6. X-Ray diffraction patterns of the products reacted at 200 °C in various strontium ion solution with the concentration ranging from 0.01 to 0.5 mol dm<sup>-3</sup>. Diffractin peaks corresponding to Ce(OH)(PO<sub>4</sub>) and monazite-like phase are labeled  $\triangle$  and  $\blacksquare$ , respectively.

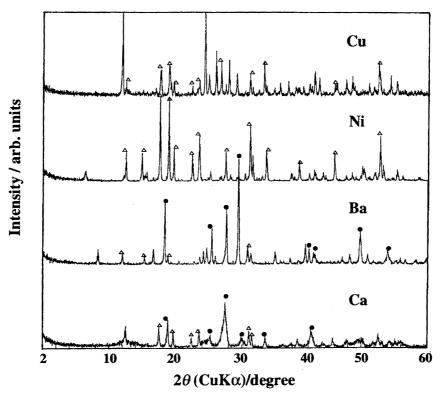


Fig. 7. X-Ray diffraction patterns of the products reacted at 200  $^{\circ}$ C in some divalent metal ions solutions (0.5 mol dm<sup>-3</sup>). Diffraction peaks corresponding to Ce(OH)(PO<sub>4</sub>) and monazite-like phase are labeled  $\triangle$  and  $\blacksquare$ , respectively.

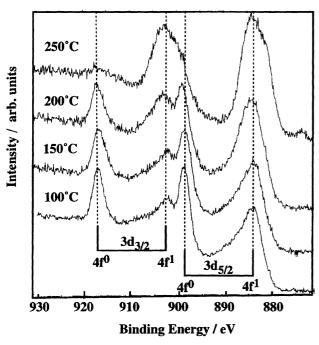


Fig. 8. X-Ray photoelectron spectra of Ce 3d for the products reacted in 0.5 mol dm<sup>-3</sup> strontium ion solution at various hydrothermal temperatures.

exchange reaction, but a type of chemisorption. The leached amounts from solids reacted at 250 °C are somewhat larger than those from solids reacted at 200 °C. In this case, the leaching of cerium and phosphorus from the solids reacted at 250 °C was evident, indicating that the solid might have

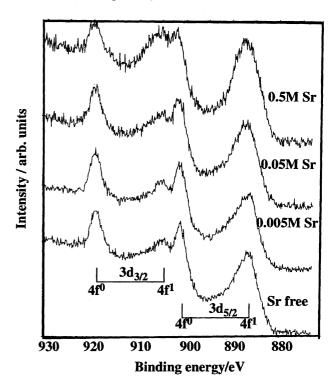


Fig. 9. X-Ray photoelectron spectra of Ce 3d for the products reacted at 200 °C in various strontium ion solution with the concentration ranging from 0.01 to 0.5 mol dm<sup>-3</sup>.

been partly dissolved in the acid solution. The reason for the dissolution of the solid is discussed later. Consequently, in order to immobilize Sr<sup>2+</sup> ions by f-CeP, the suitable hydro-

thermal temperature should be around 200 °C.

During the Sr<sup>2+</sup> uptake process under hydrothermal conditions, phosphate release from the solid was evident, whereas in the case of cerium it did not occur. The P/Ce atomic ratios of the products reacted at various temperatures, and the Sr<sup>2+</sup> concentrations are shown in Fig. 4 together with the Sr/Ce atomic ratio of the products. The P/Ce atomic ratio decreased along with an increase in the hydrothermal temperature, and reached a minimum at 200 °C. However, the P/Ce atomic ratio increased along with an increase in the Sr<sup>2+</sup> concentration of the solution, suggesting that the Sr<sup>2+</sup> uptake suppressed the release of phosphate from the solid. Accordingly, f-CeP might be converted to a compound with a different P/Ce atomic ratio, corresponding to the Sr/Ce atomic ratio. This is discussed later from the standpoint of the mechanism of the strontium immobilization.

X-Ray Powder Diffractmetry. XRD patterns of the products reacted with a 0.01 mol dm <sup>-3</sup> Sr(NO<sub>3</sub>)<sub>2</sub> solution at various hydrothermal temperatures are shown in Fig. 5. The XRD pattern of the product reacted at 100 °C exhibited a mixture of a crystalline phase and the original f-CeP with the strongest peak at 1.12 nm. In the pattern of the product reacted at 150 °C, the peak at 1.12 nm disappeared and the crystalline phase predominated. The peaks of the crystalline phase matched with the data of the cerium(IV) hydroxide orthophosphate reported by Herman et al. 12,13) This compound was prepared under the conditions of a lower phosphate concentration at the refluxing temperature. Peaks attributed to the monazite-like phase were observed in the pattern of the product reacted at 200 °C. The XRD pattern of the product reacted at 250 °C revealed that the cerium-(IV) hydroxide orthophosphate phase almost disappeared, and that the monazite-like phase predominated. Accordingly, the formation of the monazite-like phase seems to be related to the immobilization of Sr<sup>2+</sup> ions.

The XRD patterns of the products reacted in  $Sr^{2+}$  solutions with different concentrations at 200 °C are shown in Fig. 6. In the absence of  $Sr^{2+}$  ions, only cerium(IV) hydroxide orthophosphate was constructed. As the  $Sr^{2+}$  concentration increased, the cerium(IV) hydroxide orthophosphate phase was reduced and the monazite-like phase predominated. No peak which could be attributed to any kind of strontium compound was observed in the XRD pattern of the product, even at a relatively high content of  $Sr^{2+}$  ions. It has therefore been found that the immobilization of  $Sr^{2+}$  ions by f-CeP under hydrothermal conditions is an incorporation of  $Sr^{2+}$  ions into the monazite-like compound.

Monoclinic cerium(III) orthophosphate is a synthetic analogue of naturally occurring mineral monazite, which contains large amounts of tetravalent metal ions, such as thorium and uranium. These substitutions are accompanied by a charge balancing substitution of divalent metal ions, such as calcium and lead. <sup>14)</sup> In this regard, Sr<sup>2+</sup> ions can be incorporated into the monazite-like compound in order to compensate for the tetravalent cerium due to a similar ionic radius of the lead ion. The irregular coordination around the cerium ions may enable divalent metal ions to be accommodated into

the monazite-type structure without any severe constraints. This feature is favorable for the use of materials as hosts for nuclear waste. The diffraction peaks of the pattern of the product which reacted with a 0.5 mol dm<sup>-3</sup> Sr<sup>2+</sup> solution at 200 °C could be indexed on the basis of the primitive monoclinic cell of cerium(III) orthophosphate. The lattice parameters (a=6.83, b=6.97, and c=6.38 Å,  $\beta$ =105.1°) are comparable with those of anhydrated cerium(III) orthophosphate (a=6.8004, b=7.0231, and c=6.4717 Å,  $\beta$ =103.46°. Irrespective of the solid solution, strontium ions could be accommodated into the monazite-like compound without any remarkable lattice change of the cerium(III) orthophosphate due to a distorted arrangement of the monazite structure.

The XRD patterns of the products which reacted with some other divalent metal ions are shown in Fig. 7. The patterns of the products that reacted in the presence of Ca<sup>2+</sup> and Ba<sup>2+</sup> ions were similar to the monazite-like pattern as well as in the presence of Sr<sup>2+</sup> ions. In contrast, cerium(IV) hydroxide orthophospahte predominated in the presence of Cu<sup>2+</sup> and Ni<sup>2+</sup> ions as well as in the absence of Sr<sup>2+</sup> ions, whereas unidentified strong peaks were observed in the case of Cu<sup>2+</sup> ions. Therefore, monazite-like compounds seem to form in the presence of alkaline earth metal ions

X-Ray Photoelectron Spectorscopy. As is shown in Figs. 5 and 6, the monazite-like crystalline phase is clearly evident by XRD for products reacted under hydrothermal conditions. Therefore, the valency of cerium is anticipated to change from tetravalent to trivalent as the formation of the monazite-like phase proceeds. XPS is a powerful technique for studying a mixed-valence system; especially, trivalent and tetravalent cerium are distinguishable from the shape of the spectra. The XPS of Ce 3d for products reacted in a 0.5 mol dm<sup>-3</sup> Sr(NO<sub>3</sub>)<sub>2</sub> solution at various hydrothermal temperatures are shown in Fig. 8. The spectrum of the product reacted at 100 °C shows a feature which is peculiar to compounds containing cerium in the tetravalent state. Namely, each spin-orbit component shows a splitting due to different final states: 4f<sup>0</sup> and 4f<sup>1</sup>. 16,17) As the hydrothermal temperature increases, peaks corresponding to 4f1 are gradually intensified, and, conversely, those of 4f<sup>0</sup> are weakened, indicating that a part of tetravalent cerium is converted to the trivalent state. In the spectrum of the product at 250 °C, the peaks attributed to the 4f<sup>0</sup> component disappeared, which is typical for trivalent cerium, suggesting that most of the cerium was reduced to the trivalent state. The product which reacted at 250 °C seems to have contained much trivalent cerium, which is more easily dissolved in acid solution than that of a tetravalent cerium compound. Therefore, Sr<sup>2+</sup> ions should be leached out from the product reacted at 250 °C, as is shown in Fig. 3, due to the degradation of the product by the acid solution.

The XPS of Ce 3d for the products reacted with different  $Sr(NO_3)_2$  concentration at 200 °C are shown in Fig. 9. Concerning the XRD results in Fig. 6, where the CePO<sub>4</sub> phase predominated in the products as the  $Sr^{2+}$  concentration increased, XPS revealed that the Ce 3d spectra changed with the  $Sr^{2+}$  concentration. It is noteworthy that peaks corresponding

to  $4f^1$  increased along with an increase in the  $Sr^{2+}$  concentration, indicating that the  $Sr^{2+}$  ion affected the reduction of cerium. However, tetravalent cerium predominates, even in the case that only the monazite-like compound was recognized in the XRD spectra. This implys that the monazite-like compound consisted of a mixed valence state of cerium accompanied by the divalent—tetravalent charge balancing substitution,  $(Sr_yCe(IV)_yCe(III)_{2-2y})(PO_4)_2$ . Since the redox potential of  $Ce^{3+}/Ce^{4+}$  is higher than that for the reaction of water oxidation  $(2H_2O\longrightarrow 4e^-+4H^++O_2)$ , oxygen evolution presumably takes place under hydrothermal conditions in the presence of strontium ions accompanied by the reduction of cerium.

Scanning Electron Microscopy. SEM photographs of the products which reacted with a 0.5 mol dm<sup>-3</sup> Sr<sup>2+</sup> solution at various temperatures are shown in Fig. 10. The product reacted at 25 °C shows that a fibrous structure remained, as expected from the XRD pattern, whereas fibers having a width of 10—30 nm condensed to form wide strips, as compared with that of the original f-CeP. It can be seen that there was a remarkable change in the morphology of the products reacted under hydrothermal conditions, where small crystallites exhibited a platelet morphology, suggesting that the fibrous structure was converted into a plate texture, which is typical for the monazite-like compound.<sup>18)</sup> It is apparent that the reaction is not a topotactic exchange reaction, but,

rather, a chemisorption reaction. The SEM analysis shows that the crystalline size of particles enlarged with the hydrothermal temperature. It can thus be concluded that the secondary reason for Sr<sup>2+</sup> immobilization was a process of crystal growth of the monazite-like compound.

**Strontium Immobilization Mechanism.** Table 1 summarizes the chemical composition of the products which reacted at 200 °C in a solution with different Sr<sup>2+</sup> ions concentrations. In the absence of Sr<sup>2+</sup> ions, the atomic ratio of P/Ce is close to unity. From the XRD result in Fig. 6, the formation of cerium(IV) hydroxide orthophosphate was evident. It was thus considered that a hydrothermal treatment causes f-CeP to convert into cerium(IV) hydroxide orthophosphate. During this process, half of hydrogenphosphate groups was released from the solid.

$$Ce(HPO_4)_2 \cdot nH_2O \longrightarrow Ce(OH)(PO_4) \cdot mH_2O + H_3PO_4$$
 (1)

In the presence of Sr<sup>2+</sup> ions, the released amount of phosphate groups decreased along with an increase in the Sr<sup>2+</sup> uptake. As is shown in Fig. 6, the XRD patterns of the products reacted with Sr<sup>2+</sup> solutions revealed mixtures of the patterns of the cerium(IV) hydroxide orthophosphate and that of monazite-like phase. Also, as the Sr concentration of the solution increased, the monazite-like phase predominated. The atomic ratio of P/Ce is roughly proportional to the ratio of Sr/Ce. In the case that the Sr/Ce ratio is close to unity, the

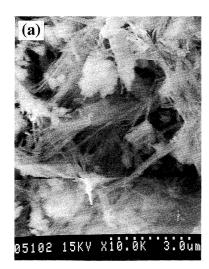






Fig. 10. Scanning electron microghaphs of the products reacted in 0.5 mol dm<sup>-3</sup> strontium ion solution at (a): 25 °C, (b): 100 °C, and (c): 250 °C.

Table 1. Composition of the Products Reacted at 200 °C with Strontium Ion Solutions

Sample	Found (%)			Cald (%)			Atomic ratio	
	Sr	P	Ce	Sr	P	Ce	Sr/Ce	P/Ce
No addition		11.3	50.5					1.01
Sr concn								
0.05	14.0	11.8	31.5				0.71	1.70
0.1	15.5	11.6	29.5				0.84	1.78
0.5	16.7	11.6	27.2				0.98	1.93
$Ce(OH)(PO_4) \cdot 0.5H_2O$					11.5	51.9		1.00
$SrCe(PO_4)_2 \cdot H_2O$				20.1	14.2	32.2	1.00	2.00

product appears to be the composition of  $SrCe(PO_4)_2$ . From the above results,  $Sr^{2+}$  ions seem to be primarily exchanged with the hydrogen ions of the interlayer phosphate groups, and, subsequently, to be immobilized by being incorporated into the monazite-type structure.

$$Ce(HPO_4)_2 + Sr^{2+} \longrightarrow Ce(Sr_{0.5}PO_4)_2 + 2H^+ \tag{2} \label{eq:2}$$

$$Ce(Sr_{0.5}PO_4)_2 \longrightarrow (Ce, Sr)(PO_4)_2$$
 (3)

Since a part of tetravalent cerium was reduced to trivalent accurately, Eq. 3 can be represented by a solid solution,  $(Ce_{2-2y}^{3+}Ce_y^{4+}Sr_y^{2+})(PO_4)_2$ , where the  $Sr^{2+}$  ions are incorporated into the monazite-like compound to compensate for the tetravalent cerium.

The Sr<sup>2+</sup> ion uptake on synthetic cerium(III) orthophosphate was examined using the same procedure as that for the f-CeP at 150 °C. The Sr<sup>2+</sup> uptake was 0.03 mmol g<sup>-1</sup>, a smaller amount than that of f-CeP. The XRD pattern of the product was unchanged after the hydrothermal reaction at 150 °C. Accordingly, synthetic monazite-type cerium(III) orthophosphate does not possess an immobilization property for strontium ions. Consequently, f-CeP was proven to be suitable as a host for the immobilizer of Sr<sup>2+</sup> ions.

Strontium immobilization can be achieved by a hydrothermal reaction with fibrous cerium(IV) bis(monohydrogen-phosphate) as the host material. A possible immobilization method based on the new mechanism can be proposed. The proposed method is used for the immobilization of strontium ions from an aqueous solution with the efficiency at a relatively low temperature under hydrothermal conditions. It should thus be a possible way for the in situ immobilization of strontium ions from radioactive waste.

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