Immobilization of Strontium by Cerium Hydrogen Phosphate

Hiromichi Hayashi, Takeo Ebina, and Kazuo Torii
Tohoku National Industrial Research Institute, Nigatake 4-2-1, Miyagino-ku, Sendai 983

(Received June 28, 1995)

The effect of heat-treatment temperature on the immobilization of strontium by cerium hydrogen phosphate was studied. Effective immobilization was achieved when calcined at the temperature from 300 to 500 °C, whereas strontium leached out accompanying with the formation of $CePO_4$ above 600 °C

Caesium and strontium with a long half-life close to 30 years are the main troublesome fission products in radioactive wastes from nuclear power plants. Among the various processes proposed for the disposal of the high-level radioactive wastes,[1-10] one of the promising methods is to convert the radioactive wastes into a vitrified solid mass which is then embedded deep in a stable stratum of ground so as to be isolated from the biosphere. However, a problem in this method is that some of the radioactive nuclides such as Cs, Sr, and the like having high solubility in water are always under a risk of leaching out from the vitrified solid mass when intrusion of the underground water takes place into the stratum. In view of this situation, tetravalent metal phosphates are anticipated to be an immobilizer for Sr^{2+} ions owing to a strong affinity for alkaline earth metal ions compared with silicate or titanate ion-exchangers. Especially, cerium(IV) hydrogen phosphate is a fibrous ion-exchanger, which can be employed to prepare ion-exchange filters without binder, suitable for column operation. In this letter, the effect of heat-treatment on the immobilization of Sr^{2+} by cerium hydrogen phosphate has been examined and discussed in terms of the crystalline structure of the products.

Cerium hydrogen phosphate, $Ce(HPO_4)_2 \cdot 3H_2O$ (abbreviated as CeP) was prepared according to the literature.[11] The adsorption and leaching tests of Sr^{2+} ions were carried out by batchwise operation; A 4 g portion of CeP was immersed in 200 cm^3 of 0.01 mol dm^{-3} aqueous Sr^{2+} solution at 25 °C for 7 days. The Sr^{2+}-bearing CeP was separated by filtration and dried at 50 °C for 24 h. The amount of the Sr^{2+} ions taken up was 0.82 mmol g^{-1} as determined by analyzing the filtrate for the residual Sr^{2+} ions. Each 0.5 g portion of thus prepared Sr^{2+}-bearing CeP was taken in a porcelain crucible and heated for 2 h at a constant temperature ranging from 100 °C to 1000 °C. A 0.1 g portion of the heated Sr^{2+}-bearing CeP was treated with 10 cm^3 of 1 mol dm^{-3} HCl solution at 25 °C for 24 h. After filtration of the solid, the filtrate was analyzed for the content of Sr^{2+} ions leaching out from the solid.

The effect of heat-treatment temperature on the leaching of Sr^{2+} ions is shown in Figure 1. The amount of Sr^{2+} ions leached from the sample heated at 50 °C was equivalent to the amount of Sr^{2+} ions taken up, indicating that Sr^{2+} ions are thoroughly extracted with the HCl solution. The amount of the leaching decreased with an increase in the heat-treatment temperature and reached a minimum value of 0.014 mmol g^{-1} at 400 °C, suggesting that the immobilization of Sr is substantially effective in the temperature range from 300 °C to 500 °C. However, there was an increase of the amount in the temperature range above 600 °C. X-ray diffraction patterns of the Sr^{2+}-bearing CeP after heating at 50, 200, 400, 600 and 800 °C are shown in Figure 2. XRD pattern at 50 °C exhibits a strongest peak at a basal spacing of 11.2 Å with some other weak peaks. Basal spacing of the sample heated at 200 °C was shifted to 9.6 Å and simultaneously the leaching amount of Sr^{2+} remarkably decreased to less than 10 % of the adsorbed amount (Fig.1). The XRD pattern at 400 °C reveals that the layered structure was converted into an amorphous phase. Therefore, Sr^{2+} ions seem to be exchanged with the hydrogen ions of the interlayer phosphate groups and subsequently to be immobilized by being confined in the interlayer space which is closed by heat-treatment.

Crystalline phases CeP_2O_7 and $CePO_4$ are clearly evident by XRD for the sample heated at 600 °C and $CePO_4$ is confirmed to be dominant phase accompanied by the formation of $Sr(PO_3)_2$ at 800 °C. Thus, valency of cerium appears to change from tetravalent to trivalent as the temperature increased. This is supported by the result of the X-ray photoelectron spectroscopy (XPS). The XPS spectra of Ce 3d for the samples heated at 50, 400, and 800 °C are shown in Figure 3. The spectrum of the sample heated at 50 °C shows a complex feature which is peculiar to the compounds containing cerium in tetravalent state. Namely, each spin-orbit component showed a splitting due to the following different final states; $4f^0$, $4f^1$.[12] The peaks attributing to $4f^1$ component of the spectrum at 400 °C were somewhat bigger than those at 50 °C, indicating that a part of tetravalent cerium converted to the trivalent state. Owing to the presence of Ce in framework of the exchanger, redox reactions may accompany the degradation of the layer structure and an amorphous product is obtained. In the spectrum at 800 °C, the peaks attributing to $4f^0$ component disappeared which is typical for trivalent cerium, suggesting that most of the cerium was reduced to trivalent state. Reduction of cerium from tetravalent to

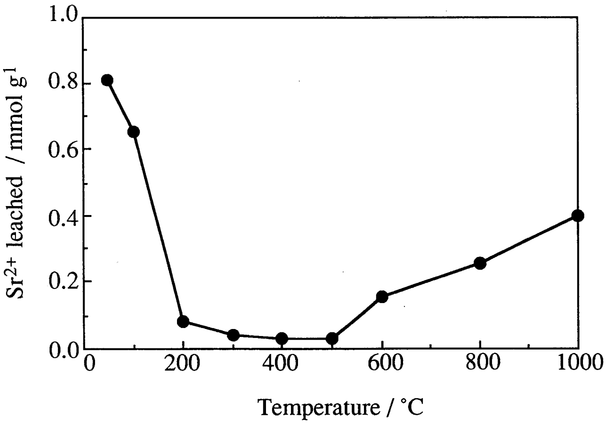

Figure 1. Plots of Sr^{2+} leached vs. heat-treatment temperature. Leaching test was carried out with 1 mol dm^{-3} HCl solution at 25 °C for 24 h.

trivalent leads to conversion of the amorphous phase into a crystalline $CePO_4$ phase. Accordingly, Sr^{2+} ions should be disclosed as $Sr(PO_3)_2$. Therefore, the increase of leaching amount above 600 °C as shown in Fig. 1 may arise from the dissolution of $Sr(PO_3)_2$. In conclusion, a heat-treatment temperature between 300 and 500 °C is recommended for the immobilization of Sr^{2+} ion by the cerium hydrogen phosphate.

It is important to evaluate the hydrothermal stability of the immobilizer. We are now investigating that strontium sorption behavior by cerium hydrogen phosphate under hydrothermal conditions. The results will be published elsewhere in the near furture.

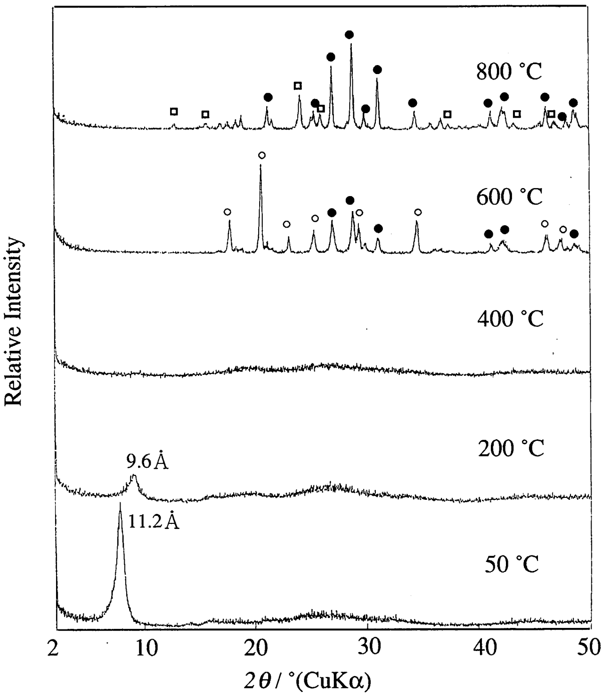

Figure 2. X-Ray diffraction patterns of Sr-bearing cerium hydrogen phosphate after heating at various temperatures in air for 2h. Diffraction peaks corresponding to CeP_2O_7, $CePO_4$ and $Sr(PO_3)_2$ are labeled ○, ● and □, respectively.

References and Notes

1 T. B. Bernadzikowski, J. S. Allender, J. A. Stone, D. E. Gordon, T. H. Gould Jr. and C. F. West III, *Am. Ceram. Soc. Bull.*, **62**, 1364(1983).

2 T. Kanno, H. Mimura, and T. Kitamurara, *Nihon Genshi -ryoku Gakkai Shi*, **18**, 518(1976).

3 H. Mimura and T. Kanno, *Nihon Genshi-ryoku Gakkai Shi*, **19**, 170(1977).

4 D. M. Stachan and W.W. Schulz, *Ceram. Bull.*, **58**, 865 (1979).

5 Y. Fujiki, Y. Komatsu, and N. Ohta, *Chem. Lett.*, **1980**, 1023.

6 Y. Komatsu and Y. Fujiki, *Chem. Lett.*, **1980**, 1525.

7 T. Sasaki, Y. Komatsu, and Y. Fujiki, *Chem. Lett.*, 1981, 957.

8 N. Yamasaki, K. Yanagisawa, S. Kanahara, M. Nishioka, K. Matsuoka, and J. Yamazaki, *J. Nucl. Sci. Technol.*, **21(1)**, 71(1984).

9 D. K. Bhattachayya and N. C. Dutta, *J. Nucl. Sci. Technol.*, **28**, 1041(1991).

10 D. K. Bhattachayya and N. C. Dutta, *J. Mater. Sci.*, **30**, 2248(1995).

11 G. Alberti, M. A. Massucci and E. Torracca, *J. Inorg. Nucl. Chem.*, **30**, 579(1967).

12 A. Fujimori, *Phys. Rev. B*, **28**, 4489(1983).

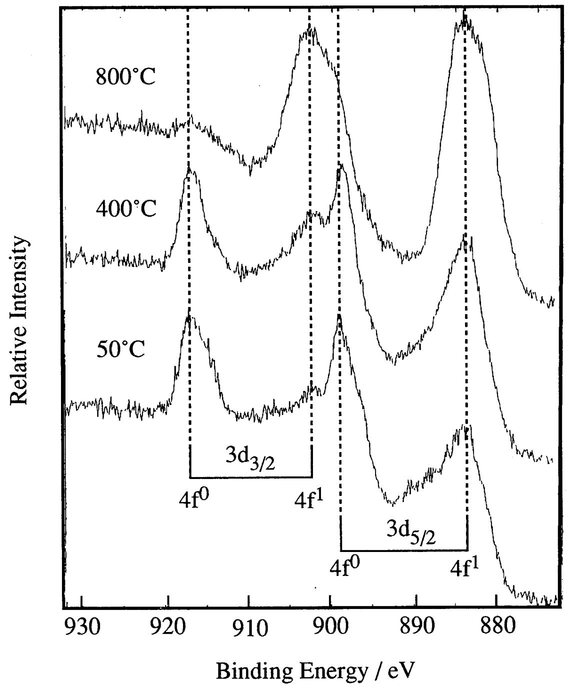

Figure 3. XPS spectra of Ce 3d for Sr-bearing cerium hydrogen phosphate after heating in air for 2h at 50, 400 and 800 °C.