Journal of the European Ceramic Society 23 (2003) 1047–1052
www.elsevier.com/locate/jeurceramsoc

Immobilization of strontium by crystalline zirconium phosphate

Susumu Nakayama[a,*], Katsuhiko Itoh[b]

[a]*Department of Applied Chemistry and Biotechnology, Nihama National College of Technology, Niihama 792-8580, Japan*
[b]*Planning and Development Section, Daiichi Kigenso Kagaku Kogyo Co. Ltd., Osaka 541-0043, Japan*

Received 15 March 2002; received in revised form 22 June 2002; accepted 6 July 2002

Abstract

Mixtures of $HZr_2(PO_4)_3$ with varying amounts of $Sr(NO_3)_2$ were thermally treated at 600–1200 °C in order to investigate the immobilization of radioactive Sr. When the $Sr(NO_3)_2$ / $HZr_2(PO_4)_3 = 0.2$ mixture was thermally treated at 700 °C, the main product was postulated to be $SrZr_4(PO_4)_6$ from the XRD results. The $Sr(NO_3)_2/HZr_2(PO_4)_3 = 0.2$ immobilized product thermally treated at 700 °C containing the maximum amount of immobilized Sr (a 0.2 molar ratio of $Sr(NO_3)_2/HZr_2(PO_4)_3$ equates to approximately 4 wt.% of Sr) had minimal Sr leaching rates in several solvents at 160 °C in an autoclave. The leaching rate of Sr ion from that product was $<10^{-6}$, 1.3×10^{-4}, 1.4×10^{-4}, 1.1×10^{-3}, 2.0×10^{-3}, 8.8×10^{-3} and $<10^{-6}$ g m^{-2} day^{-1} in deionized water, sea water, 0.1 mol l^{-1}- HCl, 0.5 mol l^{-1}- HCl, 1 mol l^{-1}- HCl, 1.5 mol l^{-1}- HCl and 1 mol l^{-1}- NH_3 in an autoclave at 160 °C, respectively, indicating that $HZr_2(PO_4)_3$ reacts with $Sr(NO_3)_2$ to give a stable Sr-immobilized product.

Keywords: $HZr_2(PO_4)_3$; Mixing; Nuclear applications; Powders-solid state reaction; Sr-immobilisation

1. Introduction

The alkaline metal Cs 137 and the alkaline earth metal Sr 90, which have relatively long half lifes of approximately 30 years, are typical high level radioactive wastes generated from spent nuclear fuels in atomic power plants. The immobilization method of Cs and Sr should produce compounds that are chemically and thermally stable with respect to the leachability of Cs and Sr.[1,2] Conventional methods for the immobilization of radioactive Cs and Sr are accomplished by forming a borosilicate glass,[3–5] a phosphate glass[6,7] or a ceramic using a synroc,[8,9] a zeolite[10,11] and a phosphate.[12] The borosilicate glass process has a number of drawbacks, i. e., processing requires thermal treatment in excess of 1000 °C. This can cause partial volatilization of the Cs and the resultant gas could damage the processing equipment. Heat generated by the radioactive decay has a cumulative effect on the crystal structure, thus leading to changes in the structure. This in turn leads to poor chemical resistance with resultant poor Cs and Sr leachability performance. In addition to the ceramic immobilization method employing synroc, etc., that using zirconium phosphates with a three-dimensional structure [expressed by the chemical formula $CsZr_2(PO_4)_3$ and $SrZr_4(PO_4)_6$] has also been investigated by Ray et al.[13,14] The three-dimensional structure can be formed by two methods. One method involves the thermal treatment at 1000 °C of a gel formed from the aqueous solution of $CsNO_3$ or $Sr(NO_3)_2$, $ZrO(NO_3)_2$ and H_3PO_4. The second method involves ion exchange of Cs or Sr into γ-$Zr(HPO_4)_2{\cdot}2H_2O$ in aqueous solution followed by thermal treatment at 850–1000 °C. Although the Cs and Sr leaching resistance is significantly higher than in the borosilicate glass immobilization methods, the thermal treatment at 1000 °C causes impurity phases such as ZrP_2O_7 and $CsPO_3$ or $Sr(PO_3)_2$, resulting in poor Cs and Sr leaching resistance.[15–18] On the other hand, we recently investigated the immobilization of radioactive Cs using a crystalline proton-type zirconium phosphate, $HZr_2(PO_4)_3$, with a three-dimensional structure (as shown in Fig. 1).[19–22] (Ion exchange between H^+ and Cs^+ is effective in $\{CsNO_3/HZr_2(PO_4)_3\}$ mixture at 700 °C.) The $CsNO_3/HZr_2(PO_4)_3 = 0.36$ immobilized material, thermally treated at 700 °C, containing the

---

* Corresponding author. Fax: +81-897-37-7842.
E-mail addresses: nakayama@chem.niihama-nct.ac.jp (S. Nakayama), k_ito@dkkk.co.jp (K. Itoh).

0955-2219/03/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0955-2219(02)00237-6

maximum amount of immobilized Cs (a 0.36 molar ratio of Cs / $HZr_2(PO_4)_3$ equates to approximately 10 wt.% of Cs) had minimal Cs leaching rates (below the limits of detection by atomic adsorption photometry) in both deionized water and 0.1 mol l^{-1}-HCl at 100 °C in the open air.[19,22] Furthermore, the leaching rate of Cs ion from the $CsNO_3/HZr_2(PO_4)_3 = 0.4$ immobilized material, thermally treated at 700 °C, was $<10^{-6}$, 1.0×10^{-3}, $<10^{-6}$, $<10^{-6}$, 4.7×10^{-5}, 2.2×10^{-4} and 2.1×10^{-3} g m^{-2} day^{-1} in deionized water, sea water, 0.1 mol l^{-1}- HCl, 0.5 mol l^{-1}- HCl, 1 mol l^{-1}- HCl, 1.5 mol l^{-1}- HCl and 1 mol l^{-1}- NH_3 at 160 °C in an autoclave, respectively, indicating that $HZr_2(PO_4)_3$ reacts with $CsNO_3$ to give a stable Cs immobilized product.[21] On the other hand, we considered that the Cs leaching from the Cs immobilized material is not a dissolution reaction by the reaction with H_2O and is considered to be an ion substitution reaction of Cs ion and other ions.

In this study, the Sr immobilized materials were prepared by thermally treating mixtures of $HZr_2(PO_4)_3$ with varying amounts of $Sr(NO_3)_2$ at 600–1200 °C using the same technology as the Cs immobilizing method and the Sr leaching resistances in several solvents (deionized water, sea water, 0.1 mol l^{-1}- HCl, 0.5 mol l^{-1}- HCl, 1 mol l^{-1}- HCl, 1.5 mol l^{-1}- HCl and 1 mol l^{-1}- NH_3) have been examined in an autoclave at 160 °C.

2. Experimental procedure

Powders of NZP-100 grade, crystalline proton-type zirconium phosphate [$HZr_2(PO_4)_3$] prepared by the thermal decomposition of $NH_4Zr_2(PO_4)_3$ synthesized by a hydrothermal reaction from a solution containing $ZrOCl_2$, H_3PO_4 and $H_2C_2O_4$ at Daiichi Kigenso Kagaku Kogyo, Co., Ltd., were used as the Sr immobilizing agent.

The process of Sr immobilization has been performed as follows: Reagent grade strontium nitrate [$Sr(NO_3)_2$], believed to show the same behavior as radioactive Sr 90, was used. An aqueous solution of $Sr(NO_3)_2$ was added to 20 g of $HZr_2(PO_4)$ $_3$ powder in molar ratios of $Sr(NO_3)_2/HZr_2(PO_4)_3$ of between 0.1 and 0.5 and then completely mixed. This operation was performed twice. The mixture was dried and the immobilized $\{Sr(NO_3)_2/HZr_2(PO_4)_3\}$ material was prepared by thermal treatment in the temperature range of 750–1200 °C for 5 h. The obtained thermally treated powder was washed in 500 ml of deionized water for 1 h with stirring, filtered and dried at 120 °C. The Sr immobilized sample at a molar ratio of $Sr(NO_3)_2/HZr_2(PO_4)_3$ of 0.2 is labeled "Sr 0.2 immobilized material".

Powder X-ray diffraction (XRD) was performed using CuK_α radiation in the 2θ range of 10–70°. The crystal structure was observed using a scanning electron microscope (SEM). The surface area was determined by the BET method. Since no Sr leaching was observed (below the limits of detection by atomic adsorption photometry) from the Sr immobilized material in both deionized water and 0.1 mol l^{-1}- HCl at room temperature and 100 °C in open air, the test method for the leaching resistance of Sr was performed as follows. Five grams of the immobilized material was placed in 40 ml of each solvent, deionized water, sea water, 0.1–1.5 mol l^{-1}- HCl or 1.0 mol l^{-1}- NH_3 in an autoclave at 160 °C for 24 h. The concentrations of Sr in the filtrates after washing the thermally treated powders and those in the solvents after the leaching tests were checked using atomic absorption photometry. The thermal behaviors of the mixture of $Sr(NO_3)_2/HZr_2(PO_4)_3$ were examined by thermogravimetric analysis (TG) and differential thermal analysis (DTA) under a static atmosphere of air at a heating rate of 10 °C min^{-1} from room temperature to 1000 °C.

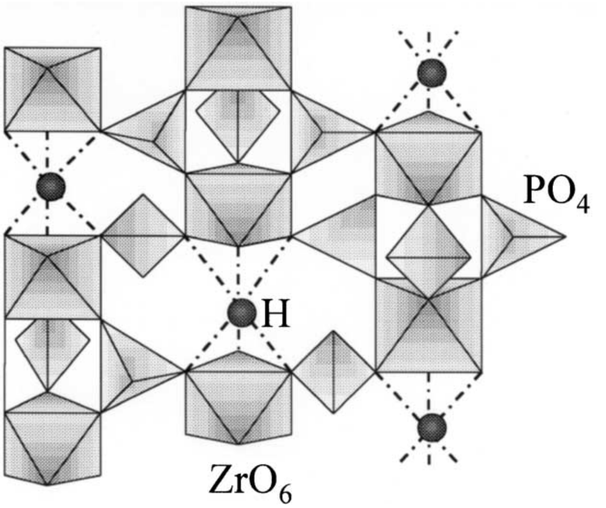

Fig. 1. Crystal structure proposed for $HZr_2(PO_4)_3$.

3. Results and discussion

3.1. Powder X-ray diffraction

Fig. 2 shows the XRD results for the Sr 0.2 immobilized material thermally treated at temperatures between 600 and 1200 °C. Although the diffraction peaks at 600, 650 or 700 °C are attributed to $SrZr_4(PO_4)_6$, some diffraction peaks of zirconium pyrophosphate (ZrP_2O_7) are observed at 800 °C. [It is mostly in agreement with the XRD pattern of $SrZr_4(PO_4)_6$.] At the thermal treatment temperature of 1200 °C, the diffraction peaks are chiefly those of Zr pyrophosphate. In all the Sr immobilized materials thermally treated at 700 °C for the $Sr(NO_3)_2/HZr_2(PO_4)_3$ mixtures in molar ratios between 0.1 and 0.5, the diffraction peaks observed are mainly of $SrZr_4(PO_4)_6$.

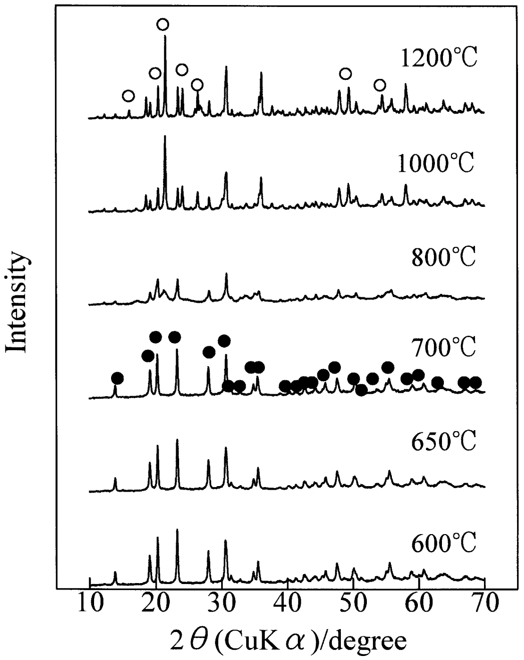

Fig. 2. X-ray diffraction patterns of the $Sr(NO_3)_2/HZr_2(PO_4)_3 = 0.2$ immobilized materials thermally treated from 600 to 1200 °C; ● $SrZr_4(PO_4)_6$ and ○ ZrP_2O_7.

3.2. Scanning electron microscopy

The SEM photographs of the synthesized $HZr_2(PO_4)_3$ and 0.2 immobilized material, thermally treated at 1200 °C are shown in Fig. 3. The crystal form of $HZr_2(PO_4)_3$ is cubic with a side length of approximately 1 μm. The specific surface area was measured at approximately 4 m^2 g^{-1}. Although the 0.2 immobilized materials thermally treated below 800 °C had the same crystal state as $HZr_2(PO_4)_3$, the sintering of particles occurred at 1000 and 1200 °C. On the other hand, no difference in the crystal state was observed for the 0.1–0.5 immobilized materials thermally treated at 700 °C.

3.3. Fluorescence X-rays analysis

Table 1 summarizes the amount of Sr and Zr in the Sr immobilized materials after the thermal treatment at 700 °C. The measured amounts of Sr and Zr were near the calculation amounts. On the other hand, the amount of Sr elution in the washing water per 1 g Sr in the immobilized materials were below 4 mg g^{-1}.

3.4. Leaching resistance in various solvents

The results of various leaching tests are shown in Figs. 4–6. Fig. 4 shows the relationship between the Sr leaching rate in 0.1 mol l^{-1}- HCl and the thermal treatment temperature for the Sr 0.2 immobilized material. In the thermal treatment temperature region of 800 °C or more, the Sr leaching rate is higher than 10^{-3} g m^{-2} day^{-1}. This is probably due to the formation of ZrP_2O_7 observed in Fig. 2. The result for the Cs 0.4 immobilized material [$CsNO_3/HZr_2(PO_4)_3 = 0.4$] previously reported is also shown by the dashed line. The Sr 0.2 immobilized material showed the best leaching resistance of Sr in the thermal treatment temperature range of 600–700 °C, while that for the Cs 0.4 immobilized material was above 700 °C. Since Cs and Sr are targets of the immobilized elements for $HZr_2(PO_4)_3$ in the future, it is suitable that the thermal treatment temperature is 700 °C.

As seen in Fig. 5, the Sr leaching rates in deionized water for the Sr 0.1, 0.2 and 0.3 immobilized materials are 10^{-3} g m^{-2} day^{-1} or less and those for the Sr 0.4 and 0.5 immobilized materials are 10^{-4} g m^{-2} day^{-1}. This result is excellent compared with the following reports. Beradzikowski et al.[1] reported a borosilicate glass in which the Sr leaching rate in deionized water at 90 °C was 1×10^{-3} g m^{-2} day^{-1} in the 28-day leaching test. Audero et al.[4] reported an aluminoborosilicate glass with a leaching rate at 70 °C of 1.8×10^{-1} g m^{-2} day^{-1} for 7 days. Sales and Boatner[6] reported a borosilicate glass and a phosphate glass that at 90 °C had

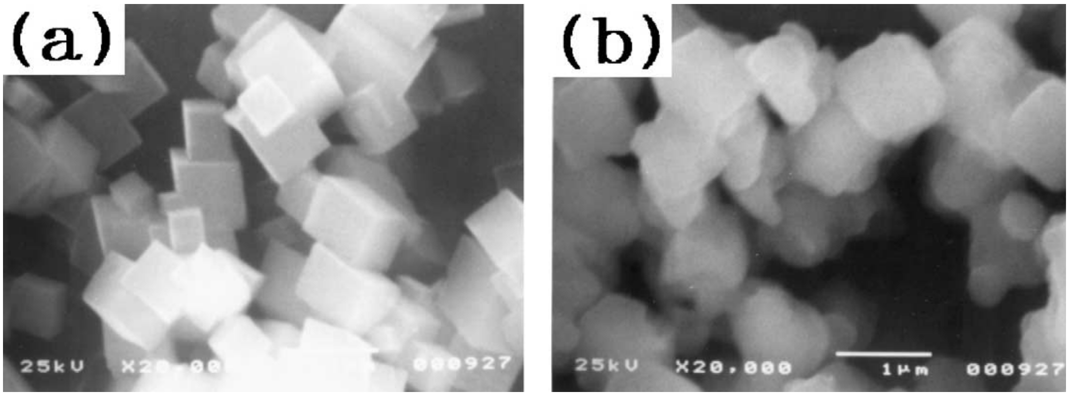

Fig. 3. SEM photographs of (a) crystalline proton-type zirconium phosphate [$HZr_2(PO_4)_3$] and (b) the $Sr(NO_3)_2/HZr_2(PO_4)_3 = 0.2$ immobilized materials thermally treated at 1200 °C.

Table 1
X-ray fluorescence results of the Sr immobilized materials thermally treated at 700 °C

$Sr(NO_3)_2/HZr_2(PO_4)_3$ molar ratio	Atomic ratio Sr/Zr
0.1	0.048 (0.050)
0.2	0.101 (0.100)
0.3	0.154 (0.150)
0.4	0.193 (0.200)
0.5	0.251 (0.250)

( ) : Theoretical values.

leaching rates of 3×10^{-2} and 2×10^{-2} g m^{-2} day^{-1} for 30 days, respectively. Roy et al.[14,16,17] and Ishida et al.[18] reported a zirconium phosphate ceramic that at 70 and 90 °C had leaching rates of 10^{-2} and 2×10^{-2} g m^{-2} day^{-1}, respectively. On the other hand, the Sr leaching rates in sea water of the Sr 0.1 and 0.2 immobilized materials and the Sr 0.3, 0.4 and 0.5 immobilized materials were 10^{-4} and 10^{-3} g m^{-2} day^{-1}, respectively, and was the highest leaching rate observed when compared with deionized water. However, the leaching resistance of Sr 0.1 and 0.2 immobilized materials was excellent compared with that of a borosilicate glass. It has been reported by Beradzikowski et al.[1] that the Sr leaching rates in sea water at 90 and 150 °C are 1.3×10^{0} g m^{-2} day^{-1} for the 28-day leaching test, respectively.

The test results of the Sr leaching resistance by acid (HCl) or alkali (NH_3) are shown in Fig. 6. The Sr leaching rates in 0.1 mol l^{-1}- HCl and, 0.5, 1 and 1.5 mol l^{-1}- HCl of the Sr 0.1 0.2 and 0.3 immobilized materials are 10^{-4} and 10^{-5} g m^{-2} day^{-1}, respectively and that increased with the increasing molar ratio of $Sr(NO_3)_2/HZr_2(PO_4)_3$ and the HCl concentration. On the other hand, no leaching was observed in 1 mol l^{-1}-NH_3 for the Sr 0.2 immobilized material. (the detection limit of the atomic absorption photometry is 10^{-7} g m^{-2} day^{-1}.)

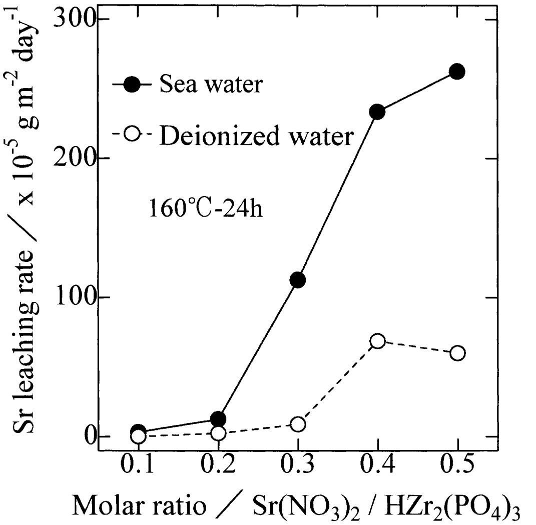

Fig. 5. Effect of molar ratio ($Sr(NO_3)_2/HZr_2(PO_4)_3$) on Sr leaching rate for the Sr immobilized materials thermally treated at 700 °C.

For the Sr 0.2 immobilized material thermally treated at 700 °C, the relationship between the Sr leaching amount in deionized water and time (6–169 h) in an autoclave at 160 °C is shown in Fig. 7. The Sr leaching amount became constant in 6 h and no additional Sr leaching was detected after 6 h.

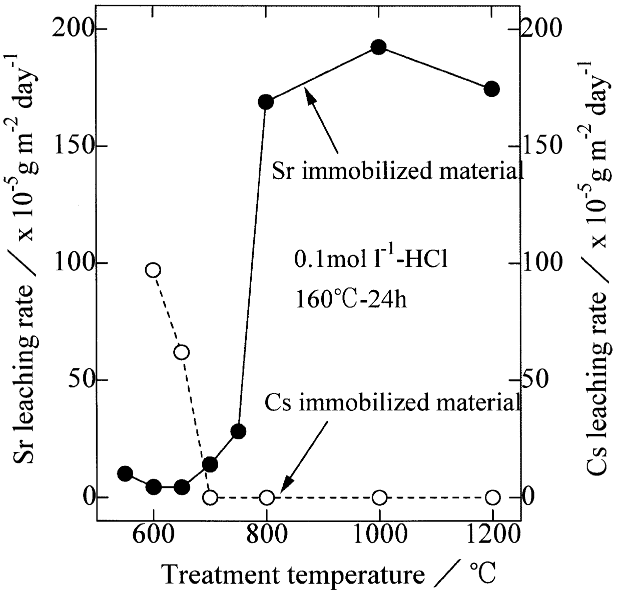

Fig. 4. Effect of treatment temperature on Sr or Cs leaching rate for the $Sr(NO_3)_2/HZr_2(PO_4)_3 = 0.2$ and $CsNO_3/HZr_2(PO_4)_3 = 0.4$ immobilized materials thermally treated at 700 °C.

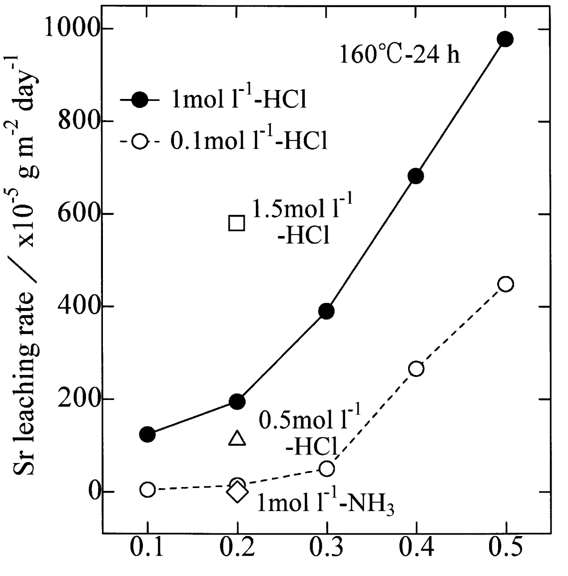

Fig. 6. Effect of molar ratio ($Sr(NO_3)_2/HZr_2(PO_4)_3$) on Sr leaching rate for the Sr immobilized materials thermally treated at 700 °C.

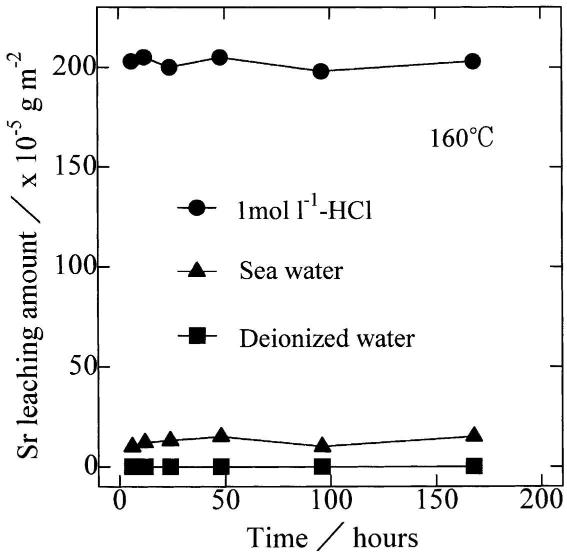

Fig. 7. Relationship between Sr leaching amount and time for the $Sr(NO_3)_2/HZr_2(PO_4)_3 = 0.2$ immobilized material thermally treated at 700 °C.

3.5. Thermal decomposition behavior

Fig. 8 shows the TG-DTA result for the mixture of $Sr(NO_3)_2/HZr_2(PO_4)_3 = 0.2$. Two endothermic peaks around 80 and 210 °C and the broad endothermic peak around 400–900 °C with a weight loss were observed. The endothermic peaks at 80 and 210 °C are due to the release of adsorbed water and the change of $(H_3O)Zr_2(PO_4)_3$ to $HZr_2(PO_4)_3$ produced when mixed with an aqueous solution of $Sr(NO_3)_2$, respectively. In the broad endothermic peak temperature range of 400–900 °C, it is considered that the following ion substitution reaction of H^+ in $HZr_2(PO_4)_3$ and Sr^{2+} in $Sr(NO_3)_2$ in the following equation is occurred by the melting of $Sr(NO_3)_2$ and the pyrolysis of a nitric acid group.

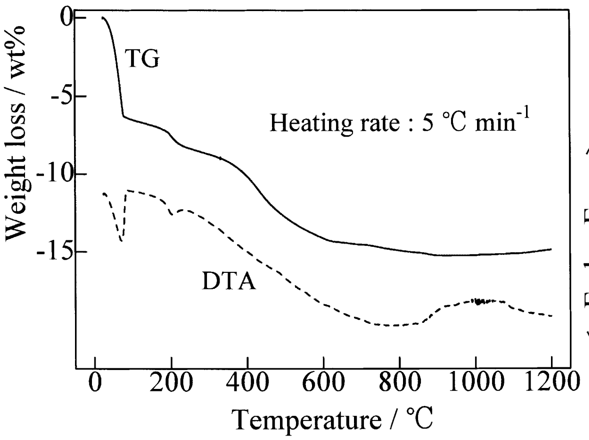

Fig. 8. TG and DTA curves for the mixture of $Sr(NO_3)_2/HZr_2(PO_4)_3 = 0.2$ under a static atmosphere of air.

$$2HZr_2(PO_4)_3+Sr(NO_3)_2 \rightarrow SrZr_4(PO_4)_6+2HNO_3$$

Therefore, the Sr immobilized material may not be completely formed under 400 °C.

3.6. Powder X-ray diffraction before and after leaching test

As seen in Fig. 9, only a slight change was seen in the observed XRD results of the 0.2 immobilized material before and after the leaching test in deionized water, sea water, 1 mol l^{-1}- HCl and 1 mol l^{-1}- NH_3, except for the peak intensity becoming stronger after the leaching test, and the observed main diffraction peaks belonged to those of $SrZr_4(PO_4)_3$. The change in peak intensity is probably attributable to the progress of crystallization during the leaching test at 160 °C for 24 h.

4. Conclusions

The investigation of the treatment conditions for the immobilization of Sr and the Sr leaching resistance in the Sr immobilized material was performed for the purpose of immobilizing radioactive Sr using the crystalline proton type zirconium phosphate ($HZr_2(PO_4)_3$). The following findings show that the Sr immobilized material is thermally and chemically resistant, and the excellent Sr leaching resistance is attained and the quantity

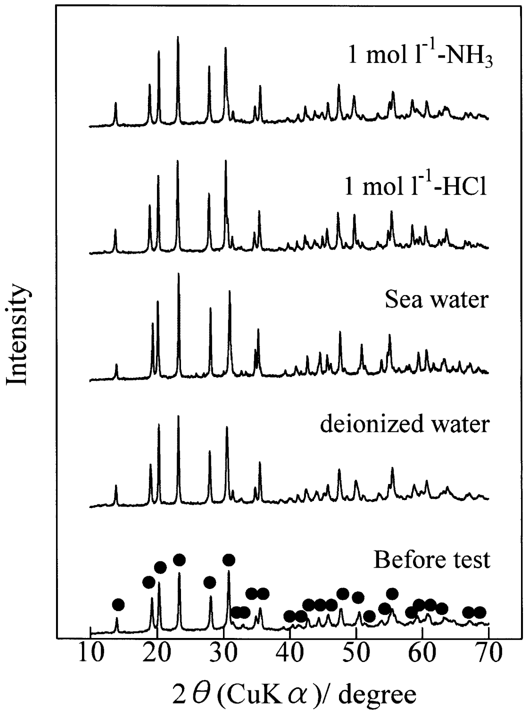

Fig. 9. X-ray diffraction patterns before and after the leaching tests in various solutions for the $Sr(NO_3)_2/HZr_2(PO_4)_3 = 0.2$ immobilized material thermally treated at 700 °C; ● $SrZr_4(PO_4)_6$.

of Sr maximized in the Sr 0.2 immobilized material thermally treated at 700 °C. A 0.2 molar ratio of $Sr(NO_3)_2/HZr_2(PO_4)_2$ equates to approximately 4 wt.% of Sr.

Acknowledgements

This work was supported by The Mazda Foundation's Research Grant and a Grant-in-Aid (12558057, 14380281) from the Ministry of Education, Science and Culture.

References

1. Bernazikowski, T. A., Allender, J. S., Stone, J. A., Gordon, D. E., Gould, T. H. Jr. and Westberry, C. F. III, High-level nuclear waste form performance evaluation. *Am. Ceram. Soc. Bull.*, 1983, **62**, 1364–1390.
2. Donald, I. W., Metcalfe, B. L. and Taylor, R. N. J., Review—The immobilization of high level radioactive wastes using ceramics and glasses. *J. Mater. Sci.*, 1997, **32**, 5851–5887.
3. Kahl, L., The hydrolytic durability of two high-level waste oxide borosilicate glasses (GP 98/12 and GP 98/26). *Nucl. Chem. Waste Management*, 1981, **2**, 143–146.
4. Audero, M. A., Bevilacqua, A. M., de Bernasconi, N. B. M., Russo, D. O. and Sterba, M. E., Immobilization of simulated high-level waste in sintered glasses. *J. Nucl. Mater.*, 1995, **233**, 151–156.
5. Plodinec, M. J., Borosilicate glases for nuclear waste imobilisation. *Glass Tech.*, 2000, **41**, 186–192.
6. Sales, B. C. and Boatner, L. A., Lead phosphate glass as a stable medium for immobilization and disposal of high-level nuclear waste. *Mater. Lett.*, 1984, **2**, 301–304.
7. Reis, S. T. and Martinelli, J. R., Cs immobilization by sintered lead iron phosphate glasses. *J. Non-cryst. Solids*, 1999, **247**, 1224–1247.
8. Mitamura, H., Matsumoto, S., Miyazaki, T., White, T. J., Nukaga, K., Togashi, Y., Sagawa, T., Tashiro, S., Levins, D. M. and Kikuchi, A., Self-irradiation damage of a curium-doped titanate ceramic containing sodium-rich high-level nuclear waste. *J. Am. Ceram. Soc.*, 1990, **73**, 2433–3441.
9. Bhattacharyya, D. K. and Dutta, N. C., A study of the immobilization of strontium over crystalline titania. *J. Mater. Sci.*, 1995, **30**, 2248–2250.
10. Komarneni, S. and Roy, R., Zeolites for fixation of cesium and strontium from radwastes by thermal and hydrthermal treatments. *Nucl. Chem. Waste Management*, 1981, **2**, 259–264.
11. Mimura, H. and Kanno, T., Distribution and fixation of cesium and strontium in zeolite A and chabaite. *J. Nucl. Sci. Tech.*, 1985, **22**, 284–291.
12. Hayashi, H., Ebina, T., Onodera, Y. and Iwasaki, T., Strontium immobilization by fibrous cerium(IV) bis(monohyrogenphosphate) under hydrothermal conditions. *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1701–1708.
13. Roy, R., Vance, E. R. and Alamo, J., [NZP], a new radiophase for ceramic nuclear waste forms. *Mat. Res. Bull.*, 1982, **17**, 585–589.
14. Scheetz, B. E., Agrawal, D. K., Breval, E. and Roy, R., Sodium zirconium phosphate (NZP) as a host structure for nuclear waste immobilizaition : a review. *Waste Management*, 1994, **14**, 489–505.
15. Vance, E. R. and Ahmad, F. L., Dissolution and reaction studies of $CsZr_2(PO_4)_3$ and Zr phosphate in aqueous media. *Mater. Res. Soc. Symp. Proc.*, 1983, **15**, 105–112.
16. Komarneni, S. and Roy, R., γ-zirconium phosphate as Cs-waste form for partitioned wastes. *Mater. Res. Soc. Symp. Proc.*, 1983, **26**, 77–82.
17. Yang, L. J., Komarneni, S. and Roy, R., Gel adsorption processing for waste solodification in 'NZP' ceramics. *Mater. Res. Soc. Symp. Proc.*, 1984, **26**, 567–574.
18. Ishida, M., Kikuchi, K., Yanagi, T. and Terai, R., Leaching behavior of crystalline phosphate waste forms. *Nucl. Chem. Waste Management*, 1986, **6**, 127–131.
19. Nakayama, S., Takahashi, N. and Itoh, K., Leaching property of cesium immobilized by zirconium phosphate under high temperature. *J. Mater. Sci. Lett.*, 2001, **20**, 513–515.
20. Ioth, K. and Nakayama, S., Perparation of various NASICON-type crystalline zirconium phosphates. *J. Ceram. Soc. Jpn.*, 2001, **109**, 355–358.
21. Nakayama, S., Sasaki, K. and Itoh, K., Immobilization technique of cesium by crystalline zirconium phosphate. *J. Atomic Energy Soc. Jpn.*, 2001, **43**, 718–723.
22. Itoh, K. and Nakayama, S., Immobilization of cesium by crystalline zirconium phosphate. *J. Mater. Sci.*, 2002, **37**, 1701–1704.