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Immobilization of cesium by crystalline zirconium phosphate

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$HZr_2(PO_4)_3$ was prepared by the thermal decomposition of $NH_4Zr_2(PO_4)_3$ which was synthesized in advance by a hydrothermal reaction from a mixed solution of $ZrOCl_2$, H_3PO_4 and $H_2C_2O_4$. Mixtures of $HZr_2(PO_4)_3$ with various amounts of $CsNO_3$ were treated at 700–1200°C, in order to investigate the immobilization of Cs ion. When a mixture of $CsNO_3/HZr_2(PO_4)_3$ in a molar ratio of 0.36 was treated at 700°C, the main product was suggested to be $CsZr_2(PO_4)_3$ from XRD measurements. The leaching rate of Cs ion from this product was less than 10^{-11}g · cm^{-2} · day^{-1} in 0.1 mol · 1^{-1} HCl solution at 100°C, indicating that $HZr_2(PO_4)_3$ reacts with $CsNO_3$ to give a stable Cs-immobilized product.

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, is the alkaline metal, Cs 137, which has a relatively long half life of approximately 27 years. Immobilization methods employed for high level radioactive wastes should therefore produce compounds that are chemically and thermally stable, with respect to leachability of Cs 137 [1].

Conventional methods of immobilization of radioactive Cs are by forming a borosilicate glass [2–4], a phosphate glass [5] or a ceramic using a zeolite [6]. A process based on borosilicate glass is expected to be chosen as the first commercial process [7]. The borosilicate glass process has a number of drawbacks; 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 caused by radioactive decay has a cumulative effect on the crystal structure, leading to changes in structure. This in turn leads to poor chemical resistance with resultant poor Cs leachability performance. In addition to the ceramic immobilization method employing zeolite, a number of methods using zirconium phosphates have also been investigated.

One of these methods, using amorphous $Zr(HPO_4)_2 \cdot nH_2O$ with a two dimensional layer structure is already known to exhibit the property of ready selective adsorption of alkaline metal ions in aqueous solutions, consequently giving high recovery rates of alkaline metal ions from aqueous mixtures [8]. On the negative side, the finished characteristics of amorphous Zr phosphate can vary greatly, based on minor changes in processing conditions, and is also readily hydrolysable [9]. Adsorbed ions such as Cs can be dissolved in acid solution. Zr phosphate, with two dimensional structure, is therefore not applicable for semi-permanent immobilization of Cs.

Ray *et al.* have reported that Cs can be immobilized by making a crystalline Zr phosphate with a three dimensional structure (expressed by the chemical formula $CsZr_2(PO_4)_3$ [10, 11]. 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 $CsNO_3$, $ZrO(NO_3)_2$ and H_3PO_4. The second method involves ion exchange of Cs into γ-$Zr(HPO_4)_2 \cdot 2H_2O$ in aqueous solution followed by thermal treatment at 850–1000°C. Although the Cs leaching resistance is significantly higher than in borosilicate glass immobilization methods, the thermal treatment at 1000°C causes impurity phases such as ZrP_2O_7 and $CsPO_3$ to be formed, resulting in poor Cs leaching resistance [12, 13].

In this study, a method by which Cs is readily immobilized has been found whereby crystalline proton type zirconium phosphate $HZr_2(PO_4)_3$ with three dimensional structure (as shown in Fig. 1) is mixed with $CsNO_3$ in a dry state and subsequently thermally treated at 700°C. The following findings show that the obtained

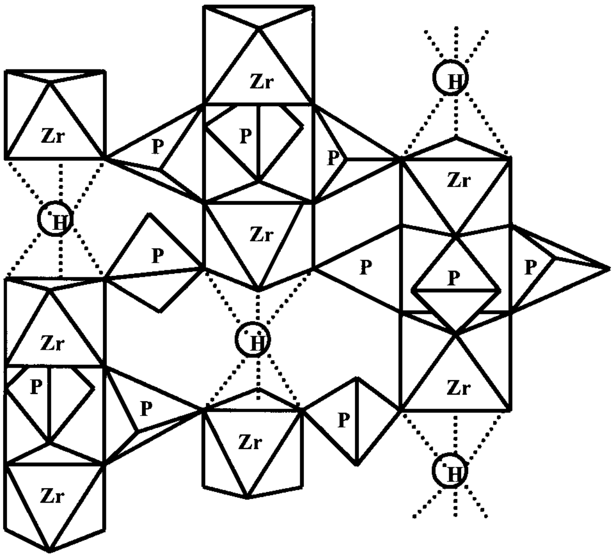

Figure 1 Crystal structure proposed for $HZr_2(PO_4)_3$.

zirconium phosphate/Cs crystalline complex is stable, thermally and chemically resistant and exhibit excellent Cs leaching resistance.

2. Experimental procedure

Reagent grades of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$), oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) and phosphoric acid (H_3PO_4) are dissolved in water and adjusted to pH 3 by aqueous ammonia. By a hydrothermal synthesis at 80°C for 48 hours, ammonium type zirconium phosphate $\{NH_4Zr_2(PO_4)_3\}$ is prepared. This is then calcined at 680°C to produce $HZr_2(PO_4)_3$.

Although ion exchange between H^+ and Cs^+ is good in $Zr(HPO_4)_2$ with two dimensional structure in aqueous solution, it is limited in $HZr_2(PO_4)_3$. Due to this fact, the process of immobilization of Cs is performed as follows: Reagent grade cesium nitrate ($CsNO_3$), believed to show the same behavior as radioactive Cs 137, is used. The prepared $HZr_2(PO_4)_3$ is put into deionized water at room temperature for 72 hours and specified quantities of $CsNO_3$ aqueous solution are added then agitated, in molar ratios of $CsNO_3/HZr_2(PO_4)_3$ of between 0.2 to 1.2. The mixture is dried and the immobilized $\{CsNO_3/HZr_2(PO_4)_3\}$ material is prepared by thermal treatment at a range of tempeatures between 600°C and 1200°C for five hours. The Cs immobilized sample at a molar ratio of $CsNO_3/HZr_2(PO_4)_3$ of 0.36 is named the "0.36 immobilized material".

The crystal structure of $HZr_2(PO_4)_3$ is observed using a scanning electron microscope (SEM). The surface area is determined by BET method. Quantitative analysis of Cs and Zr in the immobilized material is by x-ray fluorescence (XRF). Powder X-ray diffraction (XRD) is performed with CuK alpha-rays in the range 2 theta = 10 to 70°. Test method for leaching resistance of Cs is performed as follows: 5 g of the immobilized material is placed in 100 ml deionised water or 0.1 $mol \cdot l^{-1}$ HCl at room temperature and also at 100°C, agitated for 7 hours by using a magnetic stirrer and left to stand for a further 17 hours. The stirring/standing process is repeated a further six times to give a total leaching time of seven days. The concentration of Cs in the solvent is checked using atomic absorption photometry.

TABLE I X-ray fluorescence results

$CsNO_3/HZr_2(PO_4)_3$ molar ratio	Atomic ratio Cs/Zr
0.36	0.19(0.180)
0.6	0.31(0.300)

※ Treatment temperature: 700°C.
( ):theoretical values.

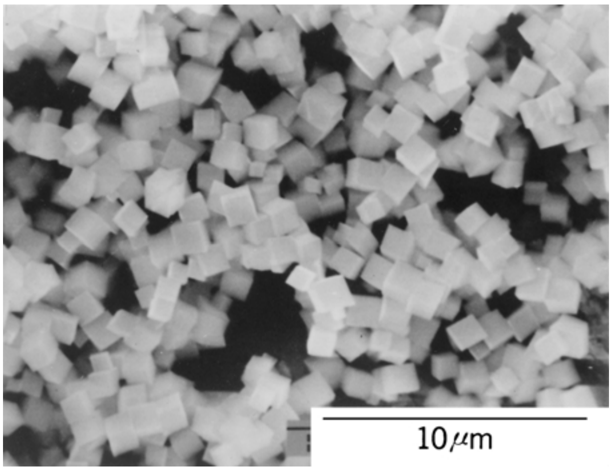

Figure 2 SEM photograph of $HZr_2(PO_4)_3$.

3. Results and discussion

The SEM photograph of synthesized $HZr_2(PO_4)_3$ is shown in Fig. 2. The crystal form is cubic of side length of approximately 1 micron. Specific surface area was measured at approximately 4 $m^2 \cdot g^{-1}$. Table I shows the XRF results for Cs and Zr contents in the 0.36 and 0.6 immobilized material treated at 700°C. Both results show near theoretical values and therefore it can be assumed that the Cs is immobilized in the two samples.

Fig. 3 shows XRD measurement results of immobilized materials, thermally treated at 700°C for $CsNO_3/HZr_2(PO_4)_3$ mixtures in molar ratios between 0.2 and 1.2. In the 0.2 immobilized material, the diffraction peaks observed are mainly of $HZr_2(PO_4)_3$. In the 0.36 immobilized material, diffraction peaks of $CsZr_2(PO_4)_3$ are observed. As the $CsNO_3/HZr_2(PO_4)_3$ molar ratio increases, the diffraction peaks are primarily of $CsZr_2(PO_4)_3$. In the 1.0 and 1.2 immobilized material, diffraction peaks of soluble cesium compounds (Cs_3PO_4, Cs_2O, Cs_2CO_3 etc) are also observed. Fig. 4 shows the XRD results for 0.36 immobilized material, thermally treated at temperatures between 600°C and 1200°C. At 600°C the diffraction peaks are mainly of $HZr_2(PO_4)_3$, with some $CsZr_2(PO_4)_3$ observed. At 800°C diffraction peaks are primarily $HZr_2(PO_4)_3$, while some zirconium pyrophosphate (ZrP_2O_7) is observed. At the thermal treatment temperature of 1200°C, the diffraction peaks are chiefly of the Zr pyrophosphate.

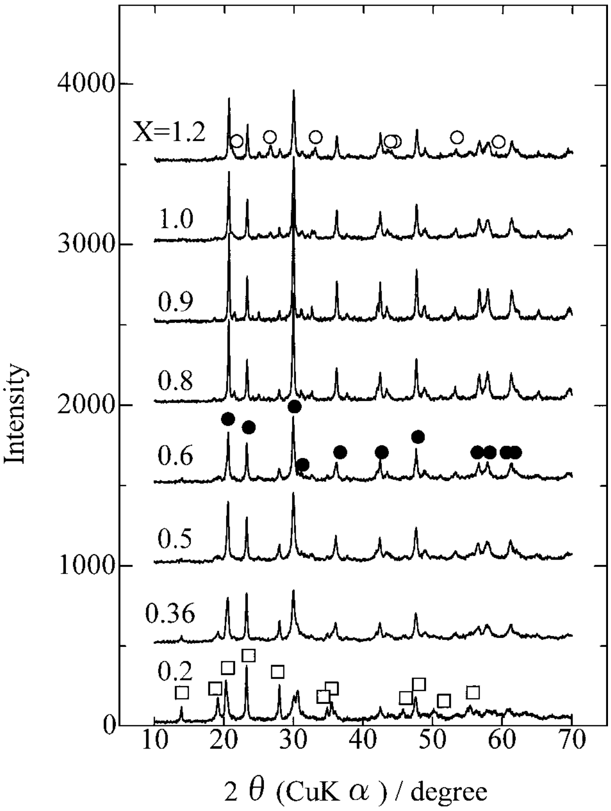

Figure 3 X-ray diffraction patterns of products of $CsNO_3$ and $HZr_2(PO_4)_3$ treated at 700°C ($X = CsNO_3/HZr_2(PO_4)_3$); ○ soluble Cs compounds, ● $CsZr_2(PO_4)_3$ and □ $HZr_2(PO_4)_3$.

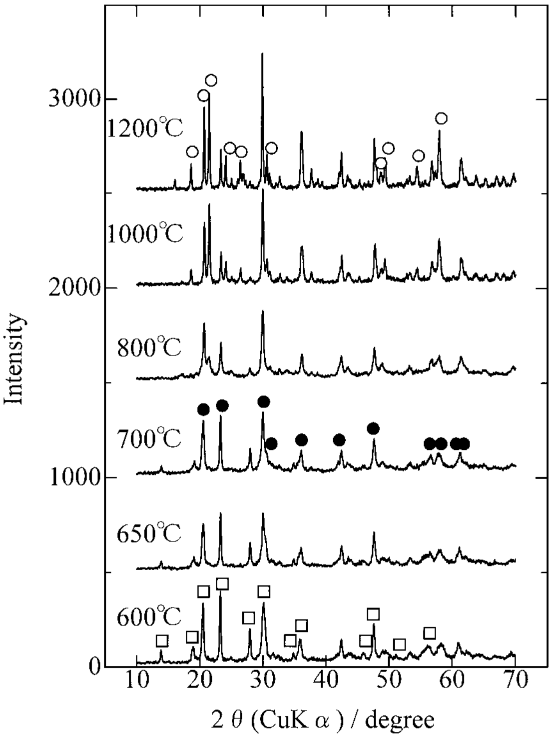

Figure 4 X-ray diffraction patterns of products of $CsNO_3$ and $HZr_2(PO_4)_3$ treated at 600°C to 1200°C ($CsNO_3/HZr_2(PO_4)_3 = 0.36$); ○ ZrP_2O_7, ● $CsZr_2(PO_4)_3$ and □ $HZr_2(PO_4)_3$.

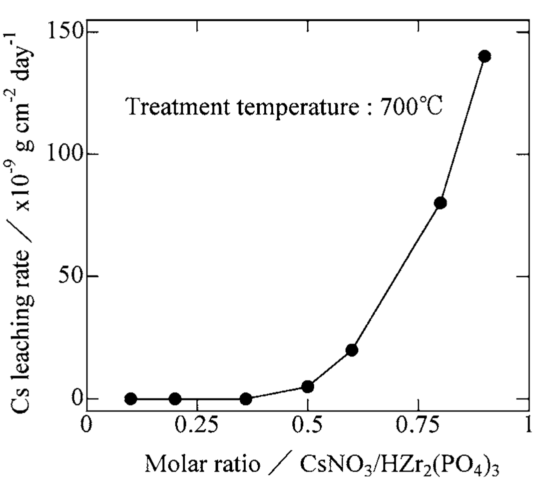

Figure 5 Effect of molar ratio ($CsNO_3/HZr_2(PO_4)_3$) on Cs leaching rate.

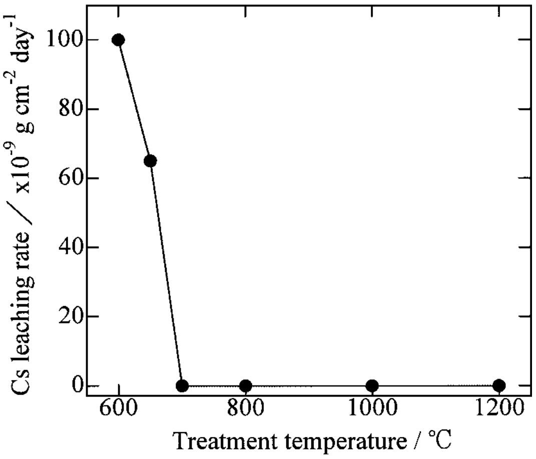

Figure 6 Effect of treatment temperature on Cs leaching rate for mixtures of $CsNO_3$ and $HZr_2(PO_4)_3$ ($CsNO_3/HZr_2(PO_4)_3 = 0.36$).

Test results of leaching resistance of Cs are noted as follows (the detection limit of the atomic absorption photometry is $10^{-11} g \cdot cm^{-2} \cdot day^{-1}$). In deionized water at room temperature and at 100°C and in 0.1 $mol \cdot l^{-1}$ HCl at room temperature, in both the 0.36 and 0.6 immobilized material, thermally treated at 700°C, no leaching was observed. Fig. 5 shows the Cs leaching rate in 0.2 to 1.0 immobilized material, thermally treated at 700°C in 0.1 $mol \cdot l^{-1}$ HCl at 100°C. No leaching was observed in immobilized material at or below a molar ratio of 0.36 but is observed in the 0.5 immobilized material and above. The leaching rate of Cs in the 1.0 immobilized material was measured at $1.3 \times 10^{-7} g \cdot cm^{-2} \cdot day^{-1}$. It is believed that this is caused by the presence of the soluble Cs compounds (Cs_3PO_4, Cs_2O and Cs_2CO_3 as observed by XRD) in the 1.0 and 1.2 immobilized material. Fig. 6 shows the Cs leaching resistance of the 0.36 immobilized material in 0.1 $mol \cdot l^{-1}$ HCl at 100°C and in the range of thermal treatment temperatures of 600°C and 1200°C. A Cs leaching rate of the order of $10^{-6} g \cdot cm^{-2} \cdot day^{-1}$ was observed in the thermally treated materials at 600°C and 650°C, but at thermal treatment temperatures of 700°C and greater, no leaching was observed.

From the results noted above, it has been determined that excellent Cs leaching resistance is attained, and quantity of Cs maximized, in the 0.36 immobilized material, thermally treated at 700°C. This material exhibits superb Cs leaching resistance in comparison to both borosilicate glass immobilized material (with a leaching rate of approximately 10^{-4}g · cm^{-2} · day^{-1} in deionized water at 100°C [4]) and to the zirconium phosphate method as used by Ray *et al.* [10–12] (where a Cs leaching rate of some 10^{-6}g · cm^{-2} · day^{-1} in deionized water was reported). In an acid solution of pH 1, Vance and Ahmad reported results showing Cs leaching rates were increased by a factor of 10 in the immobilized zirconium phosphate material produced by the Ray *et al.* method. A 0.36 molar ratio of $CsNO_3/HZr_2(PO_4)_2$ equates to approximately 10 wt% of Cs.

4. Conclusions

The object of this study was to investigate the permanent immobilization of radioactive Cs by use of crystalline proton type zirconium phosphate $\{HZr_2(PO_4)_3\}$. The method of manufacture of this immobilizing agent has been described together with the treatment conditions for immobilization of Cs, and testing of the leaching resistance of Cs in the immobilized material.

1. Cs can be readily immobilized by heating a powder mix of the immobilizing agent $\{HZr_2(PO_4)_3\}$ and $CsNO_3$.
2. In the immobilized material, treated at 700°C, it has been shown by XRD that $CsZr_2(PO_4)_3$ is predominant up to 0.9 immobilized material and that soluble Cs compounds appear in the 1.0 immobilized material.
3. In the 0.36 immobilized material it has been shown by XRD that when the thermal treatment temperature of 800°C is achieved, ZrP_2O_7 is observed and at higher temperatures is the primary structural phase.
4. The 0.36 immobilized material, thermally treated at 700°C contains the maximum amount of immobilized Cs at minimal Cs leaching rates (below the limits of detection by atomic adsorption photometry) in both deionized water and 0.1 mol · 1^{-1}HCl at 100°C.

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