

Reactive Sintering of the Thorium Phosphate-Diphosphate. Study of Physical, Thermal, and Thermomechanical Properties and Chemical Durability during Leaching Tests

N. Dacheux,^{*,†} B. Chassagneux,[†] V. Brandel,[†] P. Le Coustumer,[‡] M. Genet,[†] and G. Cizeron[§]

Groupe de Radiochimie, Institut de Physique Nucléaire, Université de Paris-Sud, Bât 100, 91406 Orsay, France, CDGA, Université de Bordeaux I, BP 19, Avenue des facultés, 33405 Talence, France, and Laboratoire de Structure des Matériaux Métalliques, Université de Paris-Sud, 91405 Orsay, France

Received November 13, 2001. Revised Manuscript Received March 20, 2002

Taking into account some attractive properties of the thorium phosphate–diphosphate ($\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$), called TPD, we focused our research on its potential use as a ceramic for the long term storage of some radionuclides including trivalent and tetravalent actinides. In this objective, we already investigated with success several ways of preparation of the pure TPD and solid solutions with tetravalent actinides either by wet or dry chemical methods. In the field of nuclear applications and considering handling operations on the radioactive materials, the preparation of this compound in the ceramic form was developed. Therefore, a precursor of TPD was especially synthesized in order to get sintered samples after performing an uniaxial pressing at room temperature followed by a heat treatment at high temperature. The synthesis, the characterization, and the sintering procedure of the precursor are described in this paper. The influence of the heating temperature on the specific area of the powder is examined and then correlated with the granulometry and the densification of the solid. For all of the samples, the apparent and effective relative densities obtained are in the range of 87–99% of the value calculated from XRD data. Moreover, some physical properties such as thermal diffusivity, thermal conductivity, and specific heat were measured from room temperature up to 1000 °C. The main results are given in this paper. Finally, the durability of the sintered TPD samples during leaching tests was studied. The apparent dissolution rates remain low even in very corrosive media ($1.25(2) \times 10^{-3} \text{ g d}^{-1}$ in 5 M HNO_3 at 25 °C) which shows that the TPD can be considered as a promising candidate for the immobilization of actinides and some fission products for a long-term storage.

Introduction

The disposal of nuclear waste for an underground repository is currently considered as a likely option for the immobilization of long-lived radionuclides. From a waste management point of view, it is necessary to stabilize these radionuclides in solids (e.g., ceramics) of low solubility in order to delay their release in water and finally their migration to the biosphere.

In this context, considering the very interesting properties reported for several phosphate-based matrixes,^{1–20} the synthesis and the characterization of thorium and

uranium phosphate compounds were studied several years ago.^{21–26} These prospective studies revealed the

* To whom correspondence should be addressed. Phone: + 33 1 69 15 73 46. Fax: + 33 1 69 15 71 50. E-mail: dacheux@ipno.in2p3.fr.

† Institut de Physique Nucléaire, Université de Paris-Sud.

‡ Université de Bordeaux.

§ Laboratoire de Structure des Matériaux Métalliques, Université de Paris-Sud.

(1) Carpene, J.; Audubert, F.; Bernache, D.; Boyer, L.; Donazzon, B.; Lacout, J. L.; Senamaud, N. *Mater. Res. Soc. Proc.* **1998**, *506*, 543.

(2) Bros, R.; Carpene, J.; Sere, V.; Beltritti, A. *Radiochim. Acta* **1996**, *74*, 277.

(3) Soulet, S.; Carpene, J.; Chaumont, J.; Krupa, J. C.; Ruault, M. O. *J. Nucl. Mater.* **2001**, *289*, 194.

(4) Poitrasson, F.; Oelkers, E.; Schott, J.; Montel, J. M. *Geochim. Cosmochim. Acta* Submitted for publication.

(5) Valsami-Jones, Ragnarsdottir, K. V.; Putnis, A.; Bosbach, D.; Kemp, A. J.; Cressey, G. *Chem. Geol.* **V** **1998**, *151*, 215.

(6) Ryerson, F. J. *J. Am. Ceram. Soc.* **1984**, *67*, 75.

(7) Ringwood, A. E.; Kesson, S. E. *Nature* **1979**, *278*, 219.

(8) Boatner, L. A.; Sales, B. C. In *Radioactive Waste Forms for the Future*; Lutze, W., Ewing, R. C., Eds.; North-Holland Physics: Amsterdam, 1988; p 495.

(9) Audubert, F.; Carpene, J.; Lacout, J. L.; Tetard, F. *Solid State Ion* **1997**, *95*, 113.

(10) McCarthy, White, W. B.; Pfoertsch. *Mater. Res. Bull.* **1978**, *13*, 1239.

(11) Ewing, R. C. *Am. Mineral.* **1975**, *60*, 728.

(12) Hawkins, H. T.; Scheetz, B. E.; Guthrie, G. D., Jr. *Mater. Res. Soc. Symp. Proc.* **1996**, *465*, 387.

(13) Hawkins, H. T.; Spearing, D. R.; Guthrie, G. D., Jr. *Chem. Mater.* **1999**, *11*, 2851.

(14) Orlova, A. I.; Zyryanov, V. N.; Kotel'nikov, A. R. *Radiochem.* **1993**, *35*, 717.

(15) Roy, R.; Vance, E. R.; Alamo, J. *J. Mater. Res. Bull.* **1982**, *17*, 585.

(16) Bois, L.; Guittet, M. J.; Carrot, F.; Trocellier, P.; Gautier-Soyer, M. *J. Nucl. Mater.* **2001**, *297*, 129.

(17) Podor, R.; Cuney, M. *Am. Miner.* **1997**, *82*, 765.

(18) Podor, R.; Cuney, M.; Trung, C. N. *Am. Miner.* **1995**, *80*, 1261.

(19) Poitrasson, F.; Cheney, S.; Sheperdt, J. *Geochim. Cosmochim. Acta* **2000**, *64*, 3283.

(20) Meldrum, A.; Boatner, L. A.; Weber, W. J.; Ewing, R. C. *Geochim. Cosmochim. Acta* **1998**, *62*, 2509.

existence of a material of very low solubility: the thorium phosphate-diphosphate (TPD) for which a general formula can be written as $\text{Th}_4\text{P}_6\text{O}_{23}$, as yet mentioned before.²⁶ We evidenced that the TPD is especially appropriated for the retention of small amounts of trivalent actinides and large quantities of tetravalent actinides because it allows the formation of solid solutions with uranium (IV), neptunium (IV), and plutonium (IV) by replacement of thorium in the structure of TPD as already reported.^{27–31} Moreover, the high durability of the powder during leaching tests led to low normalized dissolution rates even in acid solutions.^{32–35}

The main objective of using this material deals with the immobilization of some long-lived actinides such as ^{239}Pu ($T_{1/2} = 2.5 \times 10^4$ yr) and ^{237}Np ($T_{1/2} = 2.1 \times 10^6$ yr) for a long-term storage. These radionuclides could be incorporated in situ during the synthesis of TPD (in large amount) or can be adsorbed on a precursor: the thorium phosphate hydrogenphosphate (TPHP), $\text{Th}_2(\text{PO}_4)_2(\text{HPO}_4) \cdot 3-7\text{H}_2\text{O}$, (small amounts of radionuclides in contaminated liquid waste). Both ways led to the formation of the loaded TPD after heating at 1150–1250 °C.^{27,36,37}

For safety considerations, the immobilization of radionuclides must be performed in sintered samples. For this reason, the preparation of pellets of TPD involving two successive steps is described in this paper. It consists of the synthesis of a precursor of the TPD prepared in the powdered form at room temperature. This solid leads to the final ceramic required by heating at 1150–1250 °C for 10 h. During the sintering procedure, several parameters such as the grain size distribution, the specific area, the crystallization state, and the apparent and effective relative densities were studied.

We benefited from getting the TPD in the sintered form to determine some thermal and physical proper-

- (21) Bénard, P.; Louër, D.; Dacheux, N.; Brandel, V.; Genet, M. *Chem. Mater.* **1994**, *6*, 1049.
- (22) Brandel, V.; Dacheux, N.; Genet, M. *J. Solid State Chem.* **1996**, *121*, 467.
- (23) Bénard, P.; Louër, D.; Dacheux, N.; Brandel, V.; Genet, M. *Anal. Chim. *1996**, *92*, 79.
- (24) Dacheux, N.; Brandel, V.; Genet, M.; Bak, K.; Berthier, C. *New J. Chem.* **1996**, *20*, 301.
- (25) Brandel, V.; Dacheux, N.; Genet, M.; Podor, R. *J. Solid State Chem.* **2001**, *159*, 139.
- (26) Bénard, P.; Brandel, V.; Dacheux, N.; Jaulmes, S.; Launay, S.; Lindecker, C.; Genet, M.; Louër, D.; Quarton, M. *Chem. Mater.* **1996**, *8*, 181.
- (27) Dacheux, N.; Podor, R.; Chassaigneux, B.; Brandel, V.; Genet, M. *J. Alloys Compd.* **1998**, *271*, 236.
- (28) Dacheux, N.; Podor, R.; Brandel, V.; Genet, M. *J. Nucl. Mater.* **1998**, *252*, 179.
- (29) Dacheux, N.; Thomas, A. C.; Chassaigneux, B.; Pichot, E.; Brandel, V.; Genet, M. *Mater. Res. Soc. Symp. Proc.* **1999**, *556*, 85.
- (30) Dacheux, N.; Thomas, A. C.; Chassaigneux, B.; Brandel, V.; Genet, M. In *Environmental and Waste Management technologies in the Ceramic and Nuclear Industries*; Chandler, G. T., Feng, X., Eds.; **2000**, *107*, 333.
- (31) Dacheux, N.; Thomas, A. C.; Brandel, V.; Genet, M. *J. Nucl. Mater.* **1998**, *257*, 108.
- (32) Thomas, A. C.; Dacheux, N.; Le Coustumer, P.; Brandel, V.; Genet, M. *J. Nucl. Mater.* **2000**, *281*, 105.
- (33) Fourest, B.; Lagarde, G.; Perrone, J.; Brandel, V.; Dacheux, N.; Genet, M. *New J. Chem.* **1999**, *23*, 645.
- (34) Thomas, A. C.; Dacheux, N.; Aupiais, J.; Brandel, V.; Genet, M. *J. Nucl. Mater.* To be published.
- (35) Thomas, A. C.; Dacheux, N.; Le Coustumer, P.; Brandel, V.; Genet, M. *J. Nucl. Mater.* **2001**, *295*, 249.
- (36) Brandel, V.; Dacheux, N.; Pichot, E.; Genet, M.; Emery, J.; Buzaré, J. Y.; Podor, R. *Chem. Mater.* **1998**, *10*, 345.
- (37) Pichot, E.; Dacheux, N.; Brandel, V.; Genet, M. *New J. Chem.* **2000**, *24*, 1017.

ties. These intrinsic parameters such as thermal diffusivity and conductivity need to be considered first, to estimate the dispersion of the heat produced from the high radioactivity level in the repository and second, to get a better knowledge of the mechanical behavior of ceramics in highly radioactive storage conditions. By this way, the specific heat of the TPD was also obtained and can be compared to that calculated using the molecular dynamics approach.

Experimental Section

Thorium chloride solution was from Rhône-Poulenc (France). Other chemical reagents were supplied by Merck and Aldrich-Fluka. High-temperature treatments of the samples were performed up to 1300 °C in alumina boats in air in a Pyrox MDB15 furnace or under inert atmosphere (argon) in a Pyrox HM40 or in an Adamel FR 20 furnace.

The electron probe microanalyses (EPMA) were carried out using a Cameca SX 50 apparatus with an acceleration voltage of 15 kV and a current of 10 nA using the following calibration standards: ThO_2 (M_α ray of thorium) and $\text{KTi}_2(\text{PO}_4)_3$ (K_α ray of phosphorus). The grain size distribution of the powdered samples was determined with a Coulter LS 230 laser particle size apparatus. The specific area was measured using the BET method (nitrogen adsorption at 77 K) with a Coulter SA 3100 apparatus.³⁸ TG and DT analyses were done with a Metszsch STA 409 apparatus equipped with a platinum furnace.

The TPD sintered samples were obtained using an uniaxial pressing at room temperature followed by a heat treatment at 1250 °C. The initial pressing was performed between 100 and 800 MPa with a Graseby/Specac press supplied by Eurolab and using tungsten carbide dies purchased by Siametir in order to get rectangular ($5 \times 5 \times 20$ mm) or cylindrical ($\varnothing = 5-13$ mm) pellets. The dilatometer was a DI 24 apparatus supplied by MTS Instruments working in air atmosphere from room temperature to 1100 °C. The density of the sintered samples was measured at room temperature using xylene ($\rho = 0.868 \text{ g cm}^{-3}$ at 25 °C), water ($\rho = 0.997 \text{ g cm}^{-3}$ at 25 °C), and/or helium pycnometry. For measurements with helium, two kinds of apparatus were used: Multi pycnometer and Ultra pycnometer from Quantachrome. SEM micrographs were carried out with a Philips XL30 scanning electron microscope (SEM).

The hardness of the TPD was measured using a Leco M400 Micro computerized Hardness meter. The thermal diffusivity measurements were realized in argon atmosphere on cylindrical pellets of TPD ($\varnothing = 8$ mm and 1–2 mm thick). The samples were heated on the largest possible surface by flash technique with a CO_2 pulse laser ($\lambda = 10.5 \mu\text{m}$; pulse duration, 0.02 s; energy pulse, $\approx 5 \text{ J}$). The temperature was measured with an optical pyrometer (HgCdTe). The sample heating was performed with a furnace built on a carbon graphite resistor device.³⁹ The thermal diffusivity values were determined with an accuracy of $\pm 4\%$ for each temperature considered.

Specific heat measurements were achieved in argon atmosphere on powdered TPD in an alumina sample holder using a Setaram DSC-111 apparatus. The monitoring was done with sapphire provided by NBS as a reference material. The specific heat was determined from 20 to 800 °C with a step of 20 °C and an acquisition time of 600 s (the heating rate between two steps was equal to 5 °C min⁻¹).

During the leaching tests, the thorium concentrations were determined in the leachate at regular intervals. Because the durability of TPD is very high, the thorium ions release is slow. Consequently, its concentration in the leachate remains low (10^{-5} – 10^{-9} M). It was thus necessary to choose an analytical technique of high sensitivity. We opted for an α -liquid scintil-

(38) Brunauer, S.; Emmet, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.

(39) Demange, D. *Métallurgie-CIT/ Sciences et génie des matériaux*, **1999**.

Table 1. Variation of the Average Grain Size of Powdered TPD versus the Heating Temperature

heating temp, °C	average grain size, μm^a	average grain size, μm^b
900	5 \pm 1	6 \pm 1
950	9 \pm 1	9 \pm 1
1000	10 \pm 1	11 \pm 1
1050	12 \pm 1	11 \pm 1
1100	18 \pm 1	14 \pm 1
1150	15 \pm 1	15 \pm 1
1200	14 \pm 1	14 \pm 1
1250	16 \pm 1	15 \pm 1

^a TPD prepared by evaporation of solutions in acidic medium.
^b TPD prepared by precipitation of TPHP in neutral medium.

lation technique with rejection of β/γ emitters using the PERALS (photon electron rejecting alpha liquid scintillation) system supplied by Ordela (Oak Ridge, TN). The operating conditions have been already described in previously published works.^{40–42}

Results and Discussion

Preparation and Characterization of the Powdered TPD. The synthesis of the precursor of TPD was prepared via a wet chemistry method starting from a mixture of concentrated solutions of thorium nitrate (1–1.5 M) and phosphoric acid (5 M) in the mole ratio $\text{Th}/\text{PO}_4 = 2/3$. After the complete evaporation of the mixture at 120–150 °C in a sand bath to eliminate the major part of volatile products, the residue was manually ground, heated at 400–500 °C for 2 h, and then finally heated at 1250 °C for 10 h. From electron probe microanalysis (EPMA), the samples appeared homogeneous and single phase. The elementary weight % and mole ratios Th/P were in good agreement with that expected, considering the general formula $\text{Th}_4\text{P}_6\text{O}_{23}$. Thorium–uranium (IV) phosphate–diphosphate (TUPD) solid solutions of formula $\text{Th}_3\text{UP}_6\text{O}_{23}$ were prepared using the same procedure. However, in this case, the solids were synthesized using hydrochloric acid medium instead of nitric acid in order to prevent the oxidation of uranium (IV) into uranyl ion.

The grain size distribution of the powdered TPD was determined as a function of several parameters such as the heating temperature and the holding time. The average grain sizes determined after heating the initial solid for 10 h at several temperatures are gathered in Table 1. The particle size distribution of TPD obtained at 1250 °C (Figure 1) reveals a nonuniform distribution between 1 and 40 μm , with an average grain size equal to 10–20 μm . This distribution slightly depends on the chemical way of synthesis considered for getting the final TPD.

The specific area of the powder was also determined for several initial conditions after heating the solid between 900 and 1300 °C for 10 h (Table 2). The specific area of the powder obtained from the direct evaporation of the solution at 150 °C is equal to about 3 $\text{m}^2 \text{g}^{-1}$. It first increases up to about 4–5 $\text{m}^2 \text{g}^{-1}$ for temperatures between 400 and 700 °C when the solid is amorphous and then slightly decreases for higher temperatures due

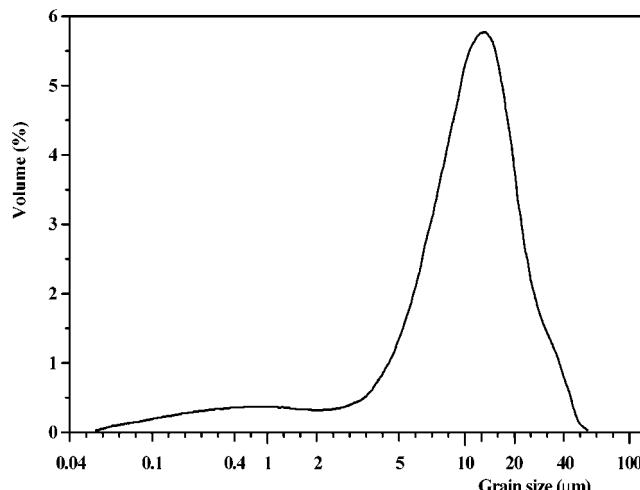


Figure 1. Grain size distribution of powdered TPD ($\theta = 1250$ °C, 10 h).

Table 2. Variation of the Specific Area of Powdered TPD as a Function of the Heating temperature

heating temp, °C	specific area, $\text{m}^2 \cdot \text{g}^{-1}$ ^a	specific area, $\text{m}^2 \cdot \text{g}^{-1}$ ^b
100–150 °C	3.0 \pm 0.3	150 \pm 5
400	4.9 \pm 0.5	N.D. ^c
600	4.6 \pm 0.5	N.D. ^c
700	3.9 \pm 0.4	N.D. ^c
800	3.8 \pm 0.4	N.D. ^c
900	3.5 \pm 0.3	10.4 \pm 0.3
1000	2.8 \pm 0.2	3.2 \pm 0.2
1050	2.1 \pm 0.2	2.2 \pm 0.1
1100	1.2 \pm 0.2	1.2 \pm 0.1
1150	0.9 \pm 0.1	0.9 \pm 0.1
1200	0.5 \pm 0.1	0.7 \pm 0.1
1250	0.4 \pm 0.1	0.5 \pm 0.1
1300	0.2 \pm 0.1	N.D. ^d

^a TPD prepared by evaporation of solutions in acidic medium.

^b TPD prepared by precipitation of TPHP in neutral medium.

^c N.D.: not determined. ^d N.D.: not determined due to the beginning of the TPD decomposition at this temperature.

to the TPD crystallization (associated to the primary natural sintering of TPD). This behavior was also observed for $\text{Th}_{4-x}\text{U}_x\text{P}_6\text{O}_{23}$ with low x values ($x \leq 1.2$). After heating at 1250 °C, the solid synthesized shows a very low specific area (0.2 – $0.5 \text{ m}^2 \text{ g}^{-1}$) which does not decrease significantly when increasing the holding time up to 60 h. The variation of the specific area as a function of the heating temperature is similar when the TPD is synthesized using a second way of preparation involving the precipitation of the thorium phosphate–hydrogenphosphate (TPHP) in neutral medium (Table 2). Nevertheless, the specific area is higher at 900 °C because of the higher value measured for the initial solid ($150 \text{ m}^2 \text{ g}^{-1}$). Moreover, the specific area decreases more strongly for lower heating temperatures when using the precipitation procedure. This phenomenon was attributed to the crystallization of TPD and to the beginning of the natural sintering step which starts at lower temperatures (800–850 °C) than using the first way of preparation (900–1000 °C).

To establish some correlation with the TPD behavior during the calcination, we investigated the system through TG and DT analyses. We especially tried to point out the chemical transformation associated to the heating process in terms of weight loss linked to exo-

(40) Dacheux, N.; Aupiais, J. *Anal. Chem.* **1997**, 69, 2275.

(41) Aupiais, J.; Dacheux, N. *Radiochim. Acta* **2000**, 88, 391.

(42) Dacheux, N.; Aupiais, J.; Courson, O.; Aubert, C. *Anal. Chem.* **2000**, 72, 3150.

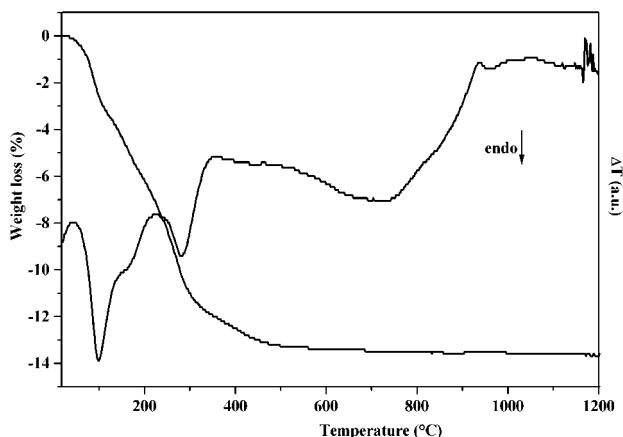
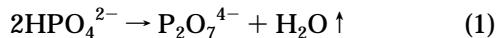


Figure 2. DT and TG analysis of powdered TPD.

or endothermic reactions. TGA and DTA curves obtained, from room temperature to 1200 °C, on powdered TPD samples prepared by direct evaporation of aqueous solutions in acidic medium are reported in Figure 2. Three main endothermic peaks at 100, 160, and 280 °C are clearly observed in the low-temperature range. They were assigned to the dehydration process and to the elimination of remaining acid and water from the residue obtained. This step goes on up to 360 °C where a maximum weight loss is obtained. Between 360 and about 750 °C, the weight loss is less significant, but simultaneously, an endothermic reaction takes place. It could correspond to the slow transformation of hydrogenphosphate ions into diphosphate groups according to the reaction:



It is hard to say if the water molecule departure is recorded on the TGA curve because the amplitude of the weight loss decreases slowly in this temperature range and the associated relative mass loss should be small. In these conditions, we explained that the expected effect on the mass variation must be very weak. As a general remark drawn from several TGA and DTA experiments, we concluded that the intensity of the various peaks observed can vary with the dryness conditions applied to the initial sample used.

The reaction corresponding to the condensation of hydrogenphosphate ions into diphosphate was already observed in several analogous compounds in which the transformation occurs between 400 and 800 °C. According to the literature, the greater the oxidation state of the cation is, higher the temperature of the dehydration-condensation process.⁴³ Beyond 850 °C, an exothermic process assigned to the crystallization of TPD begins with a maximum value at 938 °C. This temperature depends on the way of synthesis. Indeed, from the studies performed on TPHP, we know that the TPD crystallization is obtained at about 860 °C.^{25,36}

Preparation of the Sintered TPD. To avoid any hot pressing which could be difficult to apply in the nuclear industry, the sintering procedure was based on two successive steps. The solid was initially heated with a rate of 2–5 °C min⁻¹ up to 400 °C and held for 2–4 h

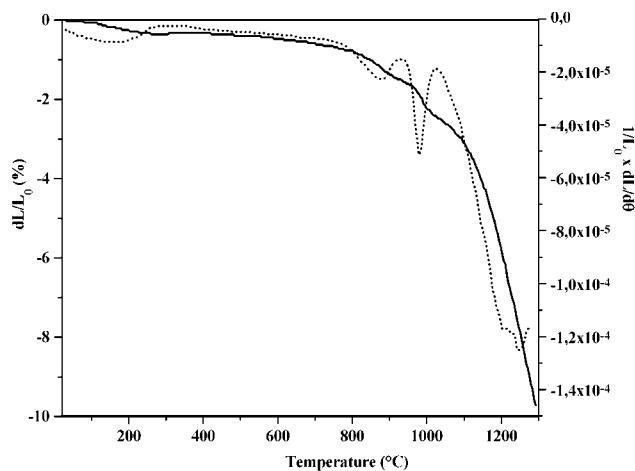


Figure 3. Dilatometric curve of TPD ($P = 500$ MPa): relative shrinkage (solid line) and derivative dL/L_0 (dot line).

in order to eliminate the major part of volatile products which could alter the properties of the sintered samples (at this temperature, the specific area of the solid is maximum: $4\text{--}5\text{ m}^2\text{ g}^{-1}$). It was then pressed at room temperature between 100 and 800 MPa in a tungsten carbide die and then finally heated at 1250 °C for 10–30 h (this temperature corresponds to the lower specific area value for the solid synthesized without any chemical decomposition of TPD). However, several experiments were also achieved for longer heating times. This quite simple procedure was applied with success to pure TPD, TPD doped with small amounts of cations simulating fission products (6.5–7.0 total weight % of 23 different cations), and TUPD solid solutions.^{44,45} We checked that in these operating conditions all of the apparent and effective relative densities reached 87–99% of the value calculated from the XRD data as shown in the next sections.

Shrinkage Variation during the Sintering. The dimensional changes of a parallelepiped pellet pressed at 500 MPa then heated at 5 °C min⁻¹ were studied by dilatometry. The powder was previously made by evaporation in acidic medium and dried at 400 °C for 5 h. The variation of the length (L) of the pellet (expressed in dL/L_0), versus temperature consists of three parts (Figure 3). The first contraction (100–300 °C) corresponds to the initial elimination of volatile products in agreement with the weight loss and the DTA results. The second part is connected to a second contraction (800–900 °C) which corresponds to the transformation of ions into groups with the elimination of one molecule of water as mentioned previously. The third contraction (900–1000 °C) was assigned to the exothermic peak of crystallization on the DTA curve. The substantially greater shrinkage observed between 1000 and 1250 °C corresponds to the sintering process (densification and improvement of the cohesion between the grains) and can be correlated to the decrease of the specific area.

(44) Brandel, V.; Dacheux, N.; Genet, M.; Pichot, E.; Thomas, A. C. In *Proceedings of the International Conference on Future Nuclear Systems*, Global 1999; American Ceramic Society: Westerville, OH, 1999; CD-ROM.

(45) Brandel, V.; Dacheux, N.; Genet, M.; Pichot, E.; Thomas, A. C. In *The Environmental Challenges of Nuclear Disarmament*; Bacac, T. E., Florkowski, T., Eds.; Kluwer Academic Press Publishers: Amsterdam, The Netherlands, 2000; p 85.

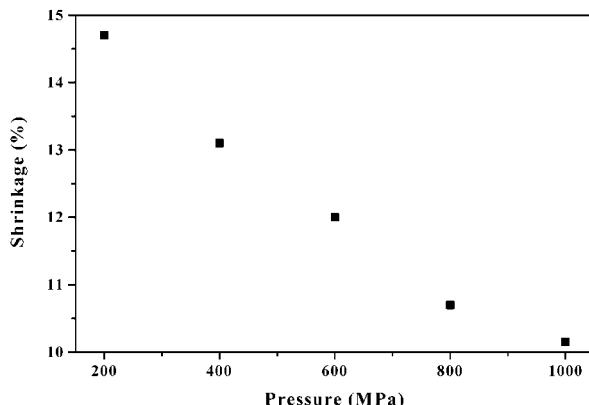


Figure 4. Variation of the pellet length (linear shrinkage) versus the initial forming pressure ($\theta = 1250$ °C, 10 h).

By comparison between TGA, DTA, and dilatometry results, the agreement in terms of temperature range in which the three main processes occur (primary dehydration, hydrogenphosphate transformation and final TPD crystallization) is rather good. The small differences observed are mainly due to the various experimental conditions: TGA and DTA were performed on powder dried with a heating rate of 20 °C min⁻¹, whereas the dilatometry was achieved on a pellet with a heating rate of 5 °C min⁻¹. These differences have no significant effect on the quality of the final ceramic produced. Simultaneously, the variation of the pellet dimensions after heating at high temperature was studied as a function of the initial forming pressure. The linear shrinkage of the material was roughly observed on the rectangular shaped pellet by measurement of the sample length before ($L = 20$ mm) and after heat treatment. The variation of the total shrinkage has been also studied versus the uniaxial pressure (Figure 4). As it was expected, for the same heating conditions, the shrinkage variation is lower when the initial pressure is more important.

Determination of the Density of the Sintered Material. To show the influence of the initial pressure on the TPD densification, we studied the variation of the relative apparent and effective densities of the samples in terms of the uniaxial pressure. The first one was determined after immersion of the sample in a given fluid (water or xylene), whereas the second was measured after outgassing the sample in the fluid. These experimental densities were compared to the value calculated from crystallographic data ($d_{\text{calc}} = 5.19$ for $V = 949$ Å³, $Z = 2$, and $M = 1482$ g mol⁻¹).^{26,46} For all sintered samples, we checked that the values obtained for the effective relative densities using water, xylene, or helium pycnometry were consistent. The values determined after pressing at 500 MPa then heating at 1250 or 1150 °C versus holding times are reported in Figure 5. The variation of the apparent relative density with the heating time and the compaction pressure is reported in Table 3. Those of the apparent and effective relative densities versus the initial pressure are reported in Table 4. For all operating conditions considered, the sintering appeared good as it was also reported for lanthanide orthophosphates.⁴⁷⁻⁴⁹

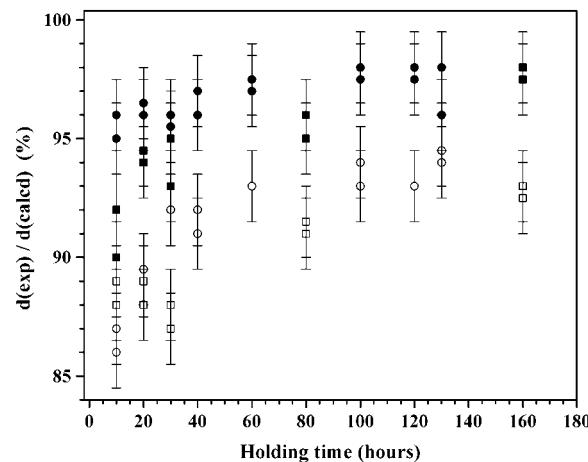


Figure 5. Variation of the apparent (open symbols) and effective (solid symbols) relative densities of sintered TPD obtained after heating at 1250 (○) or 1150 °C (□) as a function of holding time (initial pressing at 500 MPa).

Table 3. Variation of the Relative Apparent Densities (Compared to Calculated Density in %) of the TPD Pellets versus the Heating Time for $\theta = 1250$ °C

initial pressure, MPa	holding time, hours		
	10	20	80
100	87.0 ± 1.5	91.0 ± 1.5	N.D. ^a
200	90.0 ± 1.5	93.0 ± 1.5	N.D. ^a
300	92.0 ± 1.5	92.0 ± 1.5	92.0 ± 1.5
400	91.5 ± 1.5	91.5 ± 1.5	N.D. ^a
500	88.0 ± 1.5	90.0 ± 1.5	94.0 ± 1.5
600	92.0 ± 1.5	93.0 ± 1.5	N.D. ^a
700	92.0 ± 1.5	93.0 ± 1.5	94.0 ± 1.5
800	92.0 ± 1.5	93.0 ± 1.5	94.5 ± 1.5

^a N.D.: not determined.

Table 4. Variation of the Relative Apparent and Effective Densities (Compared to Calculated Density in %) of the TPD Pellets versus the Initial Pressure ($\theta = 1250$ °C, $t = 30$ Hours)

initial pressure, MPa	$d_{\text{app}}/d_{\text{calc}}$, %	$d_{\text{eff}}/d_{\text{calc}}$, %	open porosity, vol %	closed porosity, vol %
100	90.0 ± 1.5	96.0 ± 1.5	6	4
200	91.0 ± 1.5	97.0 ± 1.5	6	3
300	92.0 ± 1.5	95.0 ± 1.5	3	5
400	91.5 ± 1.5	95.5 ± 1.5	4	4.5
500	92.0 ± 1.5	96.0 ± 1.5	4	4
600	91.5 ± 1.5	95.0 ± 1.5	3.5	5
700	92.0 ± 1.5	94.0 ± 1.5	4	6
800	93.0 ± 1.5	97.0 ± 1.5	4	3

On the basis of the results obtained, the open and close porosities were evaluated to 3–6 vol % each, which seems to be enough to ensure significantly the decrease of the apparent leaching rate during the leaching tests (due to the low specific area of the sample) as well as the elimination of helium produced in situ by the disintegration of α emitter radionuclides, mainly actinide isotopes in the case of the actinide immobilization.

(47) Petek, M.; Abraham, M. M.; Boatner, L. A. In *The Scientific Basis for Nuclear Waste Management*; Topp, S. V., Eds.; Elsevier Science Publishing: Amsterdam, The Netherlands, 1982; p 181.

(48) Abraham, M. M.; Boatner, L. A.; Quinby, T. C.; Thomas, D. K.; Rappaz, M. *Radioact. Waste Manage.* **1980**, 1, 181.

(49) Floran, R. J.; Abraham, M. M.; Boatner, L. A.; Rappaz, M. In *Scientific Basis for Nuclear Waste Management*; Moore, J. G., Ed.; **1980**, 3, 507.

Table 5. Results of EPMA for Sintered TPD

operating conditions	calcd	expt					
holding temperature, °C	1150	1150	1250	1250	1250	1250	1250
heating time, hours	30	80	10	20	40	120	30
initial pressure, MPa	500	500	500	500	500	500	700
Th, wt %	62.6	63.0 ± 0.5	62.6 ± 0.8	63.1 ± 0.7	62.3 ± 0.7	62.8 ± 0.8	61.9 ± 0.5
P, wt %	12.6	12.3 ± 0.5	12.5 ± 0.3	12.3 ± 0.2	12.4 ± 0.2	12.2 ± 0.2	12.6 ± 0.2
O, wt %	24.8	24.7 ± 0.3	24.8 ± 0.3	24.6 ± 0.3	24.7 ± 0.3	24.4 ± 0.2	24.9 ± 0.3
mole ratio Th/P	0.67	0.68 ± 0.02	0.67 ± 0.02	0.68 ± 0.01	0.67 ± 0.01	0.69 ± 0.02	0.66 ± 0.01
							0.68 ± 0.02

The same study was applied with success on $\text{Th}_3\text{UP}_6\text{O}_{23}$. The preliminary results obtained for several sintered samples heated for 30 h at 1250 °C showed that the relative densities are almost the same than for TPD. The apparent and effective relative densities reach 93 and 97%, respectively, irrespective of the initial pressure considered. For both kinds of solids, the good properties of sintering observed eliminate the need for any sintering aid or organic binder in the compaction process as already observed for lanthanide orthophosphates (monazite structure).^{8,48,49}

Characterization of the Sintered TPD Samples. All of the sintered samples were extensively characterized by EPMA. The results obtained for various conditions concerning the pressure, the heating temperature, or the holding time are gathered in Table 5. From this table, it appears that for all of the initial conditions the elementary wt % and the corresponding mole ratios are consistent with that calculated considering the chemical formula of the TPD. Moreover, no secondary phase was detected in the samples. The orthorhombic structure of TPD was already determined by X-ray and neutron powder diffraction²⁶ and recently refined considering ³¹P NMR results.⁴⁶ The XRD performed on sintered samples confirmed that the system was always single phase.

SEM Observations. Either powdered or sintered TPD samples and fractured surface were observed using scanning electron microscopy (Figure 6). These observations of broken ceramic material provided information on the porosity and the size of residual pores in the TPD. In Figure 6a, a homogeneous material in its bulk exhibits small grains (average diameter of about 1 μm) which form compact clusters of 10 μm . The surface of the material appears homogeneous too (Figure 6b), and it is possible to observe some boundary grains where smallest crystals (less than 1 μm) subsist. This is due to the sintering which induces a crystal growth. No porosity can be detected. The fractured surface (Figure 6 parts d and f) demonstrates that the material is not ductile (mirrors of fracture typical of brittle material). The inner part of the sample (Figure 6 parts c and e) gives information about the size and the shape of the pores. Open pores are large (several μm) but rare, whereas closed ones, more numerous, are smaller (less than 1 μm). They are formed during the sintering (grain growth) for the larger ones. On the contrary, the smaller ones are generated by crystal defects or by elimination of volatile products. Thus, the first increase of the density is mainly due to the minimization of the size and the number of open pores. We checked by TEM observations that the solid was perfectly crystallized. However, a thin amorphous layer around the crystal (2 nm), probably caused by the process of the sample preparation, was observed.

Properties of the Sintered TPD. *Determination of the Vickers Hardness.* The Vickers hardness of the sintered samples was found between 350 and 500 HV for all of the samples studied. The average value reaches 450 HV when pressing at 500 MPa. This value is of the same order of magnitude than that reported for monazite (560 HV for LaPO_4)⁵² can be compared to those obtained for several metals (200 and 400 HV for molybdenum and tungsten, respectively) or alloys or oxides (1400 and 2000 HV for Si_3N_4 and Al_2O_3 , respectively). This mechanical property favors handling of the TPD containing radioactive materials during the disposal operations.

Thermal Expansion. Launay et al.⁵⁰ recently reported an unusual property of TPD already observed for zirconium oxide monophosphate: $\text{Zr}_2\text{O}(\text{PO}_4)_2$.⁵¹ Indeed, these authors measured the cell parameter variations on sintered TPD, between 20 and 800 °C, by dilatometry and high-temperature X-ray diffraction. They found an ultralow thermal expansion coefficient value: about $1.9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ in the temperature range studied. From this analysis, the behavior of TPD is specific and cannot be compared to the known families of other compounds. They assigned the observed thermal shrinkage as a "somewhat complex structural mechanism generated by the thorium–thorium Coulombic repulsions".⁵⁰ The same interpretation has been suggested for $\text{Zr}_2\text{O}(\text{PO}_4)_2$. As a comparison, the values reported for monazites (LaPO_4 , CePO_4 , NdPO_4 , and SmPO_4) are between 9.7 and $10 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$.⁵²

Thermal Diffusivity. The thermal diffusivity values are reported in Figure 7. We know from the densification study of the TPD (Tables 3 and 4) that the average apparent density of these samples is equal to about 4.8 which corresponds to 92% of the calculated value, with the porosity being composed of about 4% of open and 4% of closed porosity. Thermal diffusivity value α stands from $5.2 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ at 29 °C to $3.32 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ at 1000 °C. The fit of the variation of the diffusivity versus the absolute temperature led to the following equation:

$$\alpha = 5.26 \times 10^{-7} - 3.28 \times 10^{-10} T + 1.35 \times 10^{-13} T^2 \quad (2)$$

The observed smooth decrease with temperature as well as the order of magnitude of the diffusivity values are in good agreement with that expected for an insulator like TPD.

(50) Launay, S.; Wallez, G.; Quarton, M. *Chem. Mater.* **2001**, *13*, 2833.

(51) Wallez, G.; Launay, S.; Quarton, M. *Chem. Mater.* Submitted.

(52) Montel, J. M. Technical Report *Faisabilité Scientifique des matrices nouvelles de conditionnement des radionucléides à vie longue*; DEN/DDIN/DPRGD/2001/03, 2001.

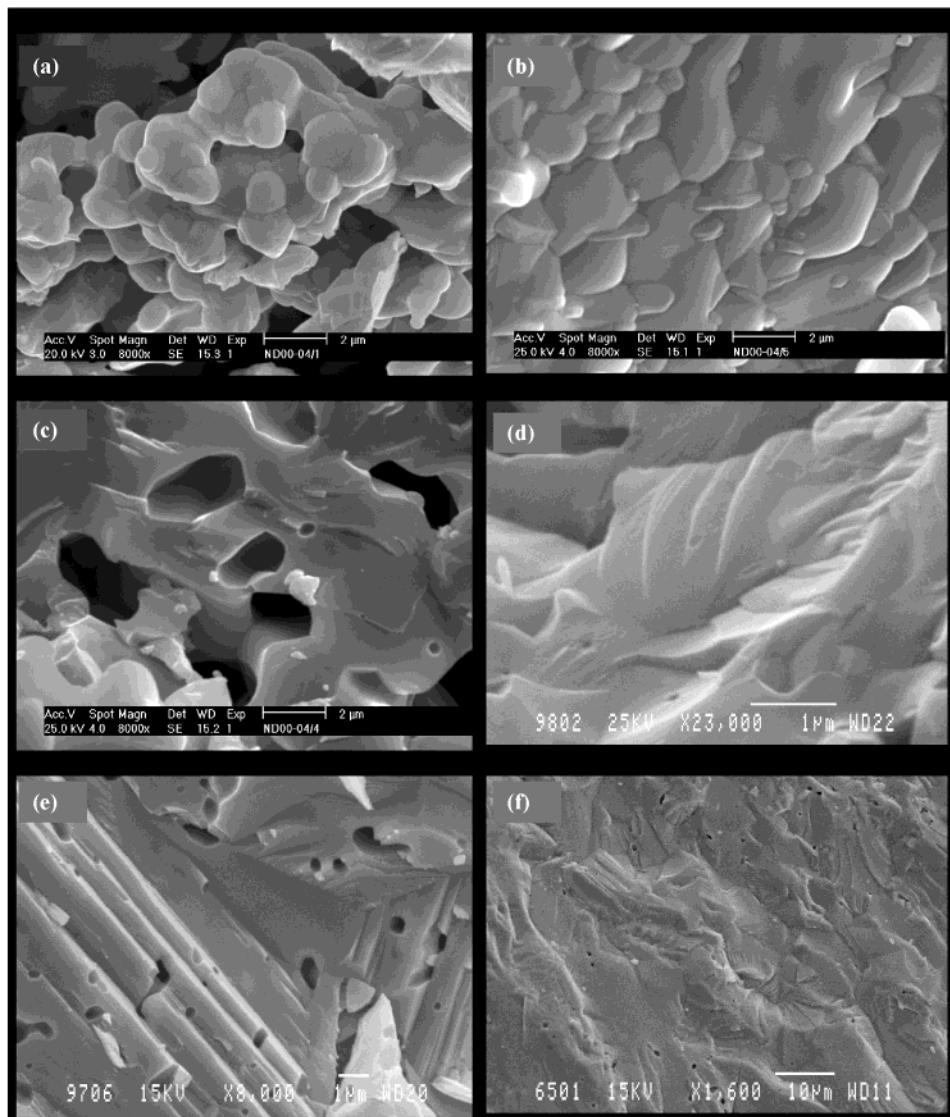


Figure 6. Scanning electron micrographs of powdered (a) and sintered TPD (b–f).

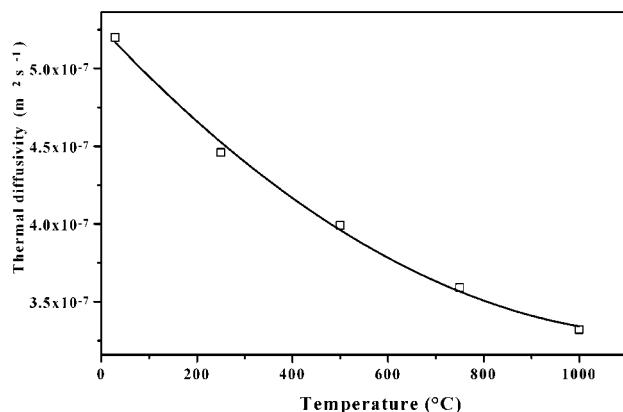


Figure 7. Variation of the thermal diffusivity of sintered TPD versus temperature.

Specific Heat and Thermal Conductivity. The thermal conductivity λ was determined considering the following equation:

$$\lambda = \alpha C_p \rho \quad (3)$$

where α is the thermal diffusivity, C_p is the specific heat,

and ρ is "the volumic mass" of the sample (considered as constant whatever the temperature). For the specific heat determination, about 200 mg of sintered TPD (500 MPa, 10 h at 1250 °C) broken in small pieces was used. The experimental values (Figure 8) ranged from 0.380 J g⁻¹ K⁻¹ at 28 °C to 0.528 J g⁻¹ K⁻¹ at 789 °C. The fit of the variation of C_p versus the absolute temperature led to the following relationship:

$$C_p = 0.58 - 6.10 \times 10^{-2} T^{-1} + 1.83 \times 10^{-4} T^{-2} \quad (4)$$

From molecular dynamics approach, the value of C_p was estimated to be 0.397 J g⁻¹ K⁻¹ at room temperature.⁵³ The Debye approximation is in rather good accordance with the experimental results up to 500 °C. Beyond this temperature, the calculated values are too small to be significant in terms of the model used which is based on a perfect harmonic oscillator for a monoatomic solid, whereas TPD is polyatomic, and the anharmonicity could play an important role. The Debye temperature was found to be about 770 K.

In these conditions, the thermal conductivity values were calculated for several temperatures (Figure 9). They range from 0.98 to 0.85 W m⁻¹ K⁻¹ respectively

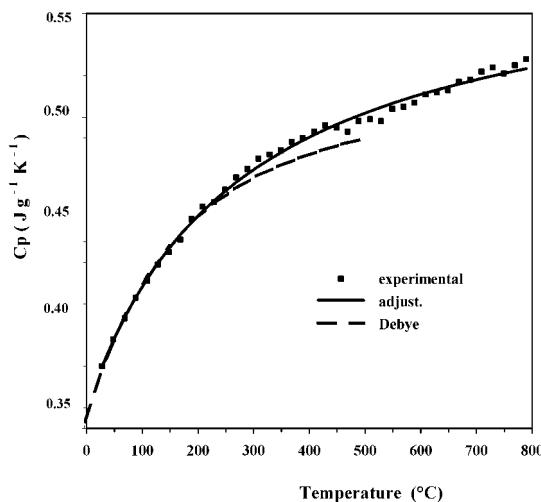


Figure 8. Variation of the specific heat (C_p) of TPD versus temperature: experimental results (■), fit (solid line), Debye approximation (dash line)

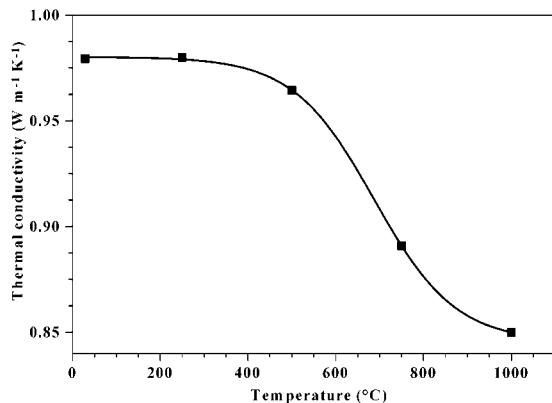


Figure 9. Variation of the thermal conductivity of sintered TPD versus temperature.

Table 6. Thermal Conductivity of Several Compounds at 500 °C

compound	thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$
UO_2	7
U_3O_8	3.5
CePO_4	1.8
ZrO_2	1.8–2.5
apatite	2.0–2.2
TPD	0.9

for 29 and 1000 °C (with an accuracy of about $\pm 15\%$). Furthermore, the thermal expansion coefficients do not take into account any corrections of the density variation. Moreover, their influence should be small because the cell volume of TPD is almost constant between room temperature and 800 °C.⁵⁰

Besides oxides, the thermal conductivity is known only for few compounds (Table 6). In addition, the presence of irradiation defects or loading of the material by other elements than the constitutive ones, as it is planned for TPD loading by radioactive wastes, should lead to a decrease of the λ parameter value as it was already shown.⁵⁴

Durability of Sintered TPD during Leaching Tests. One of the main properties of interest for using TPD as a host material for the radioactive waste storage con-

cerns its high durability when the solid is in contact with an aqueous solution (water or acid media).^{32,34,35} This high durability is correlated to very low normalized dissolution rates even in very acidic media as already reported in our previously published works.^{32,35} However, the apparent dissolution rate r (expressed in g d^{-1}) depends on the surface of the solid in contact with the solution.⁵⁵ For this reason, we compared the r values obtained for powdered and for sintered TPD in very corrosive medium (5 M HNO_3) for two temperatures (25 and 90 °C) (Table 7). As it was expected, the apparent leaching rate is lower for sintered TPD because of the decrease of the surface of solid in contact with the solution. In these conditions, it was possible to evaluate the specific area of the sintered pellets leached. The results led to $700\text{--}800 \text{ cm}^2 \text{ g}^{-1}$ which is coherent with the values determined by the BET method ($800\text{--}950 \text{ cm}^2 \text{ g}^{-1}$) after heating the pellet for 30 h at 1250 °C and with that calculated from the determination of the open porosity and the morphology of the pores ($\approx 450 \text{ cm}^2 \text{ g}^{-1}$). It corresponds to an effective surface in contact with the solution during leaching tests about two to three hundred times greater than the geometrical specific area ($\approx 2.5 \text{ cm}^2 \text{ g}^{-1}$). On this basis, for a given temperature (e.g., 1250 °C), the sintered TPD should delay the release of the radionuclides in the biosphere. This good behavior was recently confirmed by the leaching results of sintered samples of TUPD solid solutions in acidic media.^{34,35,56–58}

With respect to the apparent leaching rate reported in Table 7, it was possible to determine the activation energy of the dissolution process, E_A , according to a simple Arrhenius law. For sintered and powdered TPD, it was found to be equal to 41.5 kJ mol^{-1} and 41.6 kJ mol^{-1} , respectively, which is in good agreement with that obtained for powdered TPD ($E_A = 42 \pm 2 \text{ kJ mol}^{-1}$) leached in 5 M HNO_3 between 4 and 120 °C, for TUPD solid solutions leached in 10^{-1} M HNO_3 ($E_A = 40 \text{ kJ mol}^{-1}$), and for thorium–plutonium (IV) phosphate–diphosphate solid solutions leached in deionized water ($E_A = 41 \text{ kJ mol}^{-1}$) under dynamic conditions.^{32,34,35} Thus, we can conclude that the kinetics of the dissolution of TPD is controlled by the chemical nature of the TPD and its morphology. It appears to be dependent only on the surface in contact with the liquid phase. The durability is not degraded by the elaboration of TPD pellets which is required for proposing TPD as a potential ceramic for the immobilization of radioactive waste. In this field, we developed a systematic study of the kinetics of dissolution of TPD in acidic, on one hand, and in basic media, on the other hand.³⁴ The extrapolation of the results obtained to neutral solutions led to a

(53) Chartier, A.; Meis, C.; Dacheux, N.; Genet, M. In *Plutonium Future—The Science*; Pillay, K. K. S., Kim, K. C., Eds.; Santa Fe, AIP Conference proceedings; AIP: Melville, NY, 2000; Vol. 532, p 360.

(54) Minato, K.; Shiratori, T.; Serizawa, H.; Hayashi, K.; Une, K.; Nogita, K.; Hirai, M.; Amaya, M. *J. Nucl. Mater.* **2001**, 288, 57.

(55) Lasaga, A. C. *J. Geophys. Res.* **1984**, 89, 4009.

(56) Thomas, A. C. Ph.D. Thesis, University of Paris-XI, France, IPNO-T-00.09, **2000**.

(57) Dacheux, N.; Clavier, N.; Terra, O.; Le Coustumer, P.; Thomas, A. C.; Brandel, V.; Genet, M.; Podor, R. In *Proceeding of the International Conference on Future Nuclear Systems, Global 2001*; American Nuclear Society Inc.: La Grange Park, IL, 2001; CD-ROM.

(58) Dacheux, N.; Thomas, A. C.; Brandel, V.; Genet, M.; Le Coustumer, P.; Podor, R. In *Proceeding of the 8th International Conference on Radioactive Waste Management and Environmental Remediation*, (CD-ROM), 2001.

Table 7. Apparent Dissolution Rate, r (expressed in g day^{-1}) Measured for Powdered and Sintered TPD in 5M HNO_3 at 25 °C and 90 °C

TPD sample	time to saturation	r (25 °C), g day^{-1}	r (90 °C), g day^{-1}	E_A , kJ mol^{-1}
sintered TPD	17 days	$(1.25 \pm 0.02) \times 10^{-3}$	$(2.51 \pm 0.03) \times 10^{-2}$	(41.5 ± 0.5)
powdered TPD	4 days	$(6.9 \pm 0.3) \times 10^{-3}$	$(1.4 \pm 0.1) \times 10^{-1}$	(41.6 ± 1.6)
$S(\text{powdered TPD})/S(\text{sintered TPD})$		5.5 ± 0.3	5.6 ± 0.5	

normalized dissolution rate equal to $5-7.5 \times 10^{-6} \text{ g m}^{-2} \text{ d}^{-1}$ which is lower than that reported for the other ceramics studied in the same field such as apatites, zirconolites, synrock, or zircons and of the same order of magnitude than for monazites.^{4,5,10,47,59-61}

Conclusion

Out of the regular study of physical and chemical parameters, some thermal and thermomechanical properties are necessary to qualify the TPD as a potential candidate for the long-term storage of radioactive waste. Thus, the preparation and the characterization of powdered TPD were undertaken to get a better understanding of its behavior during the sintering process. In this objective, DT and TG analyses were performed on TPD. Endothermic dehydration is observed from room temperature up to 360 °C, and then hydrogen-phosphate ions are transformed into diphosphate groups between 400 and about 750 °C. Finally, an exothermic peak at 938 °C was assigned to the crystallization of TPD.

The sintering was studied in terms of the uniaxial pressure used at room temperature and of the temperature of the heating treatment. The macroscopic shrinkage associated with the natural sintering of TPD was followed by dilatometry. The different steps of dL/L_0 were correlated to DTA and TGA results. With the optimum conditions of sintering being determined (500 MPa, 1250 °C), the variation of the density of the

sintered TPD was studied for various heating times (10–180 h).

The average hardness value of the pellets was found to be equal to 450 HV and leads to a convenient mechanical handling of this compound.

The thermal properties of TPD were determined in order to estimate how the heat can be transmitted through the solid in a highly radioactive material. The diffusivity was measured from room temperature to 1000 °C. The knowledge of the specific heat in the same range of temperature allowed us to determine the thermal conductivity. The values obtained ($\approx 0.98 \text{ W m}^{-1} \text{ K}^{-1}$) show that the thermal conductivity of the TPD is not very sensitive to the temperature up to 500 °C. It decreases to $0.85 \text{ W m}^{-1} \text{ K}^{-1}$ for 1000 °C. The density of the sample studied was equal to 92%, but it could be decreased to improve the conductivity of the heat. Nevertheless, we cannot expect to increase the value of the thermal conductivity in a large extent.

The determination of the best sintering conditions of TPD and its thermal conductivity values need to be taken into account among various decisive criteria to select a matrix for the immobilization of radioactive waste. Some of them, like the chemical durability, have been already determined. All of the leaching tests performed have confirmed the good resistance of powdered TPD to aqueous corrosion. The same experiments achieved on sintered samples of TPD confirmed that these good properties are not degraded by the sintering process. The study of some other properties, like resistance to radiation damages, are now in progress.

(59) Ringwood, A. E.; Oversby, V. M.; Kesson, S. E.; Sinclair, W.; Ware, N. G.; Hibberson, W. D.; Major, A. *Nucl. Chem. Waste Mana.* **1981**, 2, 287.

(60) Ringwood, A. E.; Kesson, S. E.; Reeve, K. D.; Levins, D. M.; Ramm, E. J. In *Radioactive Waste Forms for the Future*; Lutze, W., Ewing, R. C., Eds.; North-Holland Physics: Amsterdam, The Netherlands, 1988; p 233.

(61) Helean, K. B.; Lutze, W.; Ewing, R. C. *Environ. Issues Waste Manage. Technol. Ceramics Nuclear Ind. IV* **1999**, 93, 297.

Acknowledgment. The authors would like to thank Dr. Renaud PODOR from Laboratoire de Chimie du Solide Minéral, Nancy, France for making the EPMA and SEM experiments on sintered pellets.

CM011277G