

THORIUM PHOSPHATE-DIPHOSPHATE AS A CERAMIC FOR THE IMMOBILIZATION OF TETRAVALENT URANIUM, NEPTUNIUM AND PLUTONIUM

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ABSTRACT

In the framework of radwaste storage, the thorium phosphate-diphosphate $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ (TPD) has been synthesized in the $\text{ThO}_2 - \text{P}_2\text{O}_5$ system. This material is very resistant to aqueous corrosion. In this paper we report the conditions of synthesis of TPD doped with small amounts of trivalent actinides and of solid solutions with uranium (IV), neptunium (IV) and plutonium (IV).

Sintered samples of TPD and $\text{Th}_{4-x}\text{U}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$ (TUPD) have been prepared after pressing at 100-800 MPa at room temperature then heating at 1250°C for 10 hours. The corresponding density varies from 87 to 93% of the calculated value from crystal data.

Leaching tests of $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ doped with Am^{3+} or Cm^{3+} and solid solutions $\text{Th}_{4-x}\text{U}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$ (TUPD) or $\text{Th}_{4-x}\text{Pu}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$ (TPPD) have been performed in water and in several acidic media at room temperature and at 90°C. The dependence of the leaching rate on the pH has been determined : the partial order related to $[\text{H}_3\text{O}^+]$ is in the 0.35 - 0.44 range while the apparent leaching rate is equal to about $1 \times 10^{-5} - 4 \times 10^{-5} \text{ g}/(\text{m}^2.\text{d})$.

Gamma ray irradiations have been achieved on TPD and on TUPD both in powder and in pellets forms. The paramagnetic signals observed on irradiated samples have been followed by EPR. The results obtained are interpreted in terms of three different kinds of radicals derived from phosphate and diphosphate ions. This assumption was partly confirmed by some additional thermal luminescence studies.

INTRODUCTION

Considering that phosphate matrices like apatites or monazites could be potential candidates for the immobilization of actinides coming from an advanced reprocessing or for the final disposal of the excess plutonium from dismantled nuclear weapons, the chemistry of uranium (IV) and thorium phosphates has been reexamined. Among the solids synthesized, the thorium phosphate-diphosphate $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ (TPD) was obtained through several ways of synthesis (using wet and dry chemistry methods) then characterized. The *ab initio* structure determination on powder and single crystal led to an orthorhombic unit cell (space group $Pcam$, $Z = 2$) with $a = 12.8646(9) \text{ \AA}$, $b = 10.4374(8) \text{ \AA}$ and $c = 7.0676(5) \text{ \AA}$ ($V = 949.0(1) \text{ \AA}^3$) (1).

This material is very resistant to aqueous corrosion (2). Thus, it was specially tailored for the ^{239}Pu immobilization and for the radiogenic ^{235}U . Nevertheless, we were also interested in the incorporation of the tetravalent neptunium (^{237}Np) or trivalent actinides like americium and

curium (^{241}Am , ^{244}Cm) for the long term storage. We studied the substitution of Th^{4+} by U^{4+} , Np^{4+} and Pu^{4+} on one hand and by Am^{3+} and Cm^{3+} on the other hand even if the substitution of thorium by trivalent actinides could be difficult because of the great difference between ionic radii. On the contrary, for tetravalent actinides it should be possible to get solid solutions with U^{4+} , Np^{4+} and Pu^{4+} because their ionic radii are close to the thorium one ($[8]r_{\text{Th}} = 1.05\text{\AA}$, $[8]r_{\text{U}} = 1.00\text{\AA}$, $[8]r_{\text{Np}} = 0.98\text{\AA}$ and $[8]r_{\text{Pu}} = 0.96\text{\AA}$) in the eightfold coordination number.

SYNTHESIS AND CHARACTERIZATION

$\text{Th}_{4-x}\text{M}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$ solid solutions ($\text{M}^{(\text{IV})} = \text{U, Np, Pu}$)

In our previous work concerning the $\text{ThO}_2 - \text{P}_2\text{O}_5$ system, we showed that for a mole ratio $r = \text{Th}/\text{PO}_4$ in the range $0.5 < r < 1$, only the thorium phosphate-diphosphate ($r = 2/3$) is well defined at high temperature. For all other ratios, the system obtained was polyphase [1]. For this reason, we performed all the syntheses considering a mole ratio $r = (\text{Th}+\text{M})/\text{PO}_4$ equal to $2/3$. Solid solutions of thorium-neptunium (IV) phosphate-diphosphate $\text{Th}_{4-x}\text{Np}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$ (TNPD) and thorium-plutonium (IV) phosphate-diphosphate $\text{Th}_{4-x}\text{Pu}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$ (TPPD) were synthesized for several x values from a mixture of thorium, tetravalent neptunium (or tetravalent plutonium) nitrate and concentrated phosphoric acid solutions. For thorium-uranium (IV) phosphate-diphosphate solid solutions (TUPD), solutions were prepared in hydrochloric acid in order to avoid the oxidization of U^{4+} into UO_2^{2+} . The mixtures were slowly evaporated between 100°C and 200°C , ground then heated in alumina nacelles at 300°C for 2 hours and at 1000°C for 14 hours in air (for TNPD and TPPD solid solutions) or in inert atmosphere (for TUPD solid solutions). Some details concerning these syntheses were already reported (3, 4).

The solids were characterized by X-ray powder diffraction. Silicon metal (JCPDS file number 27-1402) was added as internal reference in order to calibrate the angular positions of the diffraction lines. As the structure of TPD is well known, we studied the deformation of the lattice when thorium is partly replaced by a tetravalent smaller actinide ($\text{M}^{(\text{IV})} = \text{U, Np, Pu}$). For each solid solution $\text{Th}_{4-x}\text{M}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$, the variations of the unit cell parameters in terms of x are linear for a large x range values. They are presented in Table I. It was also possible to determine the maximum substitution of thorium (x_{max}) by each other tetravalent actinide and the corresponding Maximum Weight Loading (MWL). Both are gathered in Table I.

Table I. Unit cell parameters variations, x_{max} and MWL values for $\text{Th}_{4-x}\text{M}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$

	U	Np	Pu
a (Å)	12.871(6)-0.053(3) x	12.857(6)-0.069(7) x	12.864(1)-0.085(1) x
b (Å)	10.431(7)-0.030(3) x	10.437(2)-0.049(2) x	10.438(1)-0.072(1) x
c (Å)	7.069(4)-0.026(2) x	7.065(3)-0.037(3) x	7.067(2)-0.042(2) x
V (Å ³)	949.0(6)-10.0(4) x	947.9(9)-14.4(9) x	949.0(1)-19.0(1) x
x_{max}	3.00	2.09	1.63
MWL (Weight %)	47.6	33.2	26.1

 $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ doped with ^{241}Am or ^{244}Cm

The thorium phosphate-diphosphate loaded with trivalent americium ^{241}Am or curium ^{244}Cm was also synthesized in order to get informations about their immobilization in the TPD structure. Both of them need to be studied, since they appeared as separated minor actinides in the future advanced reprocessing of used nuclear fuels. Nevertheless, according to their relatively short half lives, the specific activity of these nuclides are so high that solid solutions can not be considered and only doped materials are realistic at the lab scale.

The conditions of preparation were quite similar than for previous solid solutions. Thorium nitrate and americium (or curium) solutions were first mixed with concentrated phosphoric acid then slowly evaporated. After grinding, the residues were heated in porcelain crucibles at 400°C for 2 hours then at 1050°C for 14 hours. All the details concerning the synthesis are shown in Table II.

Table II. Synthesis of $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ doped with ^{241}Am or ^{244}Cm

Solid	Activity (MBq)	Specific activity (MBq/g)	Weight loading	Yield of synthesis
$\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7 :$ ^{241}Am	1.8	7.2	$5.7 \times 10^{-3} \%$	97-100 %
$\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7 :$ ^{244}Cm	1.4	5.7	$1.9 \times 10^{-4} \%$	98-100 %

SINTERING

The sintering of TPD was performed from the dried residue prepared after the slow evaporation step of the mixture containing thorium nitrate and concentrated phosphoric acid. The particles size was around 10 - 40 μm while the specific area was about 5.5 m^2/g . This powder was shaped into pellets form via a room temperature pressing at 100 - 800 MPa. It was thermally

treated in air at 400°C for 2 hours then at 1250°C for 10 hours with an heating rate equal to 2°C/min. This heating treatment was repeated three times for several initial pressures in order to study the variation of the density obtained when the initial pressure or the heating time of this sintering process increases. All the results are presented in Figure 1.

All the densities measured correspond to 87-93% of the values calculated from crystallographic data which indicates that the TPD is very easy to sinter. The sintering is better when the dried residue is pressed between 300 and 800 MPa. In these conditions, the heating time has no influence on the density measured for the pellets. On the contrary, when the residue is first pressed between 100 and 200 MPa, the density is lower after the first 10 hours (87-90%) and increases when the heating treatment is repeated (91-93% after 30 hours at 1250°C).

As the TPD exhibits good properties of sintering, we attempted to synthesize pellets of TUPD solid solutions (with $x = 1.0$). For these materials, the conditions of synthesis were slightly different in order to avoid the oxidization of U^{4+} . The initial mixture was composed of powders of $UClPO_4 \cdot 4H_2O$ and $U(HPO_4)_2 \cdot xH_2O$ obtained in hydrochloric medium and $Th_4(PO_4)_4(HPO_4)_2 \cdot yH_2O$ synthesized in nitric medium. Pellets were obtained after grinding, pressing at room temperature at 500 MPa then heating at 1250°C in inert atmosphere. The density measured was equal to 91-92% of the calculated value ($d_{calc} = 5.26$ considering $M = 1488$ g/mol, $V = 939$ Å³ and $Z = 2$). Moreover, the sintering process is not dependent on the heating time (91% after 10 hours and 92% after 30 hours).

Table III. TPD pellets density in terms of the heating time and of the initial pressure

Pressure (MPa)	Heating time (1250°C)		
	10 hours	20 hours	30 hours
100	87.6±1.0	91.0±1.0	89.7±1.0
200	90.3±1.0	92.8±1.0	90.9±1.0
300	91.9±1.0	91.7±1.0	91.5±1.0
400	91.6±1.0	91.6±1.0	92.0±1.0
500	91.5±1.0	92.0±1.0	93.0±1.0
600	91.8±1.0	93.1±1.0	91.6±1.0
700	91.9±1.0	92.0±1.0	91.7±1.0
800	91.7±1.0	92.7±1.0	91.6±1.0

For technical reasons, in our conditions, the size of the sintered material can not exceeds the order of cubic centimeter in volume. Its shape depends on the geometrical form used for the pressing step. Two different types of final objects are represented on the following picture.



Figure 2. Sintered samples of TPD (the scale is given in centimeters).

LEACHING TESTS

Th₄(PO₄)₄P₂O₇ doped with ²⁴¹Am or ²⁴⁴Cm

Leaching tests were performed either for TUPD, TNPD, TPPD solid solutions or for TPD doped with ²⁴¹Am or ²⁴⁴Cm. For convenient reasons, it was simpler to investigate doped materials rather than solid solutions. Thus, most of the leaching results were obtained from the dissolution studies of americium and curium doped compounds. Samples of 100-200 mg of powder were put into 5-10 mL of distilled water (or acidic solutions) under agitation at room temperature or at 90°C for several months.

Several authors, mainly geologists, already studied thermodynamic and kinetic constraints on the reaction taking place between minerals and aqueous solutions (5, 6) They suggested that the rate-limiting step in the hydrolytic process can be described in terms of the transition state theory. This way of doing is valid until the appearance of a second solid phase in the system.

For pH-dependent dissolutions, the general dissolution rate of the solid can be expressed in terms of the hydronium ion activity $a_{\text{H}_3\text{O}^+}$:

$$R_H = k' \times |a_{\text{H}_3\text{O}^+}|^{-n} \times (1 - \exp(-A / \sigma RT)) \quad (1)$$

where :

k' is the apparent dissolution rate constant (depending on the effective area but not on pH) ;

n , the reaction coefficient of the H_3O^+ ions;

A , the chemical affinity of the reaction ;

σ , the average stoichiometric number (5).

Far from equilibrium where the chemical affinity term is negligible, the dissolution rate of the solid can be simplified as (5) :

$$R_H = k = k' \times |a_{H_3O^+}|^{-n} \quad (2)$$

The results presented obtained for TPD doped with ^{244}Cm are in good agreement with eq. 2. Indeed, for each solution, the total amount of dissolved matrix is linear after 90 days of contact between the solid and the solution. It is then possible to determine the corresponding leaching rate dissolution constants values k from the linear regression of experimental data. The values obtained in distilled water and in perchloric acid solutions 10^{-4}M - 10^{-1}M are gathered in Table III.

Table III. Leaching rate constants of TPD doped with ^{244}Cm

Medium	Distilled water	10^{-4}M HClO_4	10^{-3}M HClO_4	10^{-2}M HClO_4	10^{-1}M HClO_4
$k \text{ (g / (m}^2\text{.d))}$	NS*	$2.8(5) \times 10^{-9}$	$2.2(2) \times 10^{-7}$	$5.3(2) \times 10^{-6}$	$1.3(1) \times 10^{-5}$

* NS : leaching rate too small to be significant after 450 days of leaching

It appears from Table III that the logarithm of the leaching rate constant decreases linearly with $[\text{H}_3\text{O}^+]$ from HClO_4 10^{-1}M to 10^{-3}M . The linear regression of experimental data leads to :

$$\log(R_H) = 0.395(3) \times \log([\text{H}_3\text{O}^+]) - 4.487(6) \quad (3)$$

which corresponds to $n = -0.395(3)$ and $k' = 3.25(5) \times 10^{-5} \text{ g / (m}^2\text{.d)}$.

Some values quite similar were obtained for TPD doped with ^{241}Am and leached in nitric acid : $n = -0.35$ and $k' = 1.2(5) \times 10^{-5} \text{ g / (m}^2\text{.d)}$.

We observed that the ^{241}Am activity released in the solution strongly decreases in HNO_3 10^{-4}M (resp. in HClO_4 10^{-4}M for TPD doped with ^{244}Cm). It becomes constant as a function of the leaching time in distilled water (the corresponding leaching rate constant was too small to be significant). It could be due to the precipitation of the amorphous $\text{AmPO}_4 \cdot x \text{H}_2\text{O}$ (and by analogy of the amorphous $\text{CmPO}_4 \cdot x \text{H}_2\text{O}$). This solid was already mentioned in the literature. It appeared as the solubility-controlling solid for leaching of phosphate matrices when the leaching time exceeds 86 days (7). It was produced either by over- and undersaturation at room temperature.

The thermodynamic equilibrium constant for the reaction :



was calculated to be $K_S = 10^{-24.79 \pm 0.18}$ (7).

In HNO_3 10^{-4}M , the americium and phosphate concentrations were found to be $[\text{Am}^{3+}] = 4.9 \times 10^{-10}\text{M}$ and $C_{\text{PO}_4} = 10^{-6}\text{M}$ (i.e. $[\text{PO}_4^{3-}] = 3 \times 10^{-17}\text{M}$). In these conditions, the calculated solubility product is equal to $K_S = 1.5 \times 10^{-26}$ which is in good agreement with the value reported in the literature (7).

$\text{Th}_{4-x}\text{Pu}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$ solid solutions

Some leaching tests were also performed on TPPD solid solutions in distilled water and in french granitic mineral water for several x values (0.4 and 1.0) at room temperature. The results obtained in distilled water are presented in Figure 3.

For both solid solutions, the results obtained are quite similar, which indicates that the leaching rate of the matrix is not dependent on the plutonium amount loaded in TPD in the condition to get solid solutions (i.e. $x \leq 1.67$). At present, we did not investigate the behavior of polyphase systems obtained for higher x values.

For $\text{Th}_3\text{Pu}(\text{PO}_4)_4\text{P}_2\text{O}_7$ and $\text{Th}_{3.6}\text{Pu}_{0.4}(\text{PO}_4)_4\text{P}_2\text{O}_7$, the leaching rates become constant after 150-200 days of contact between the solid and the solution : the values obtained by linear regression are equal to $(2.6 \pm 0.1) \times 10^{-6} \text{ g}/(\text{m}^2 \cdot \text{d})$ and $(2.4 \pm 0.1) \times 10^{-6} \text{ g}/(\text{m}^2 \cdot \text{d})$, respectively. In the french granitic mineral water Volvic, the leaching rate is thirty times lower $((7.4 \pm 0.1) \times 10^{-8} \text{ g}/(\text{m}^2 \cdot \text{d}))$ between 75 and 200 days of contact then slightly increases after 200 days.

All these results confirm the very low solubility of the pure TPD already reported (2). Indeed, for leaching tests performed for $\text{Th}_{3.6}\text{Pu}_{0.4}(\text{PO}_4)_4\text{P}_2\text{O}_7$ (10 mole % of plutonium in the solid, specific area equal to $2.3 \text{ m}^2/\text{g}$) in distilled water, the matrix dissolved is equal to $1.03 \text{ mg}/\text{m}^2$ after one year of contact between the solid and the solution. Considering the dissolution rate as constant of time after 200 days, 1 mg of plutonium will be released in the leachate in about 18 years (for a contact area equal to 1 m^2). This value is better than those reported for other ceramics like zircons, apatites or synroc (8).

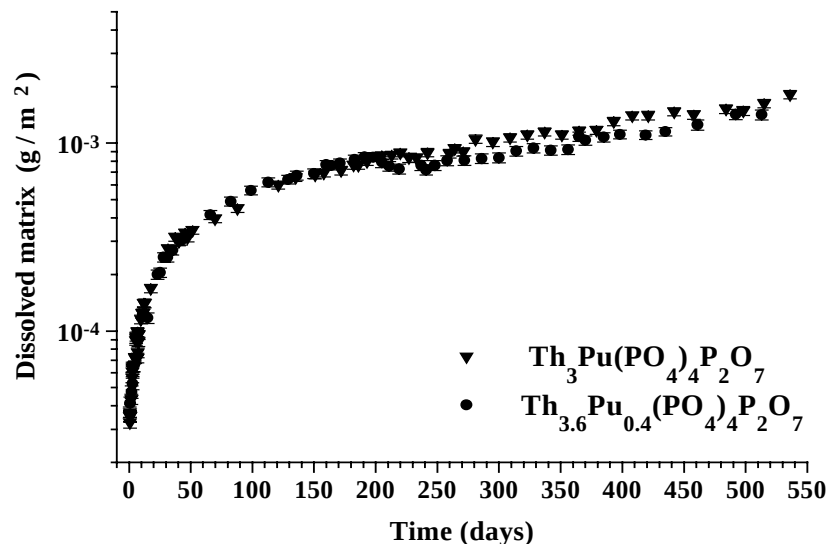


Figure 3. Leaching tests of TPPD in distilled water at room temperature.

Th_{4-x}U_x(PO₄)₄P₂O₇ solid solutions

In order to increase the dissolution rate and to bring to the fore the precipitation of other phases by saturation in the solution, leaching tests of TUPD ($x = 1.0$ and 3.0) were performed in nitric acid (10^{-4}M - 10^{-1}M) at 90°C (in these conditions, U^{4+} is rapidly oxidized into uranyl ion UO_2^{2+}). During the leaching tests, the uranium amount released in solution increases then reaches a plateau which corresponds to about 1-1.5% of the initial uranium amount in the solid (figure 4).

The initial green colored solid solution turns into yellow colored powder (characteristic of uranyl ions). The stabilization of the uranium activity measured in the solution is due to a precipitation process.

The solids obtained after leaching tests were analyzed by several techniques like X-ray powder diffraction, UV-visible spectroscopy and electron microprobe analysis. The characteristic bands of the uranyl ions (UO_2^{2+}) were observed in the UV-visible spectrum between 350 and 450 nm while the mains bands of tetravalent uranium were absent. The major part of the tetravalent uranium was then oxidized leading to the formation of an uranyl compound. The X-ray powder diffraction pattern of the crystallized solid was different from that of solid solutions TUPD. The interrogation of the ICDD PDF-2 database (9) by constraining the search to uranium phosphates showed a very good accordance with the X-ray powder diffraction of the uranyl phosphate tetrahydrate : $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4 \text{H}_2\text{O}$ (JCPDS Files number 13-39 and 37-0369). From the Electron Probe Microanalysis (EPMA), the solid is a two phase system. The first one is an uranium phosphate phase which chemical analysis is reported in Table IV and can be identified as

$(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4 \text{H}_2\text{O}$. The second one is a thorium-uranyl phosphate (weight percent : ThO_2 - 25(2) %, UO_2 - 38(3) %, P_2O_5 - 17(1) %) not yet identified. Experiments are under progress.

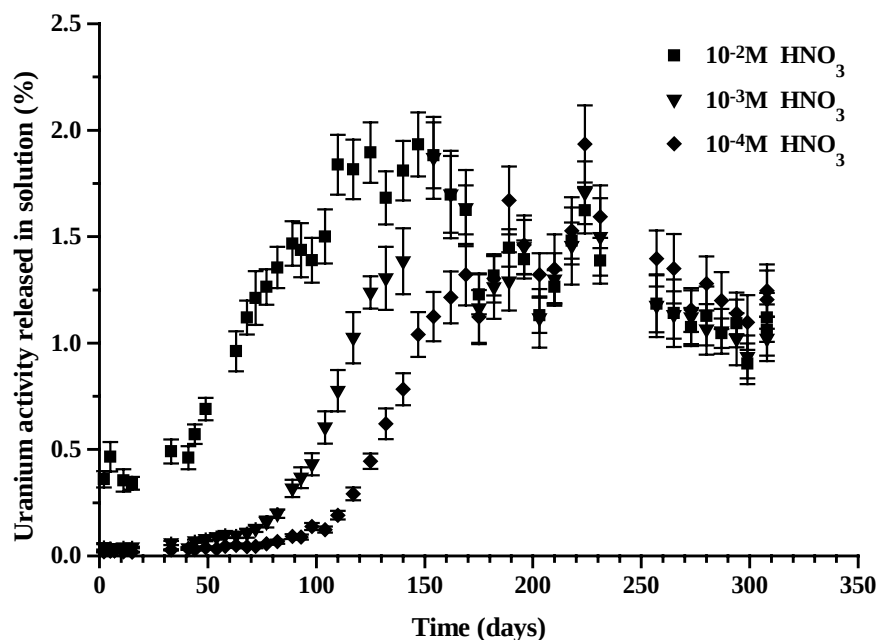


Figure 4. Leaching tests of TUPD in nitric acid at 90°C.

Table IV. Results of EMA analysis of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4 \text{H}_2\text{O}$

	Weight percent	
	exp.	calc.
U	64.3 ± 0.9	66.6
P	6.1 ± 0.2	5.8
O	27.9 ± 0.7	26.9
Th	1.7 ± 0.7	0
mole ratio		
PO_4/U	0.68 ± 0.02	0.67
$\text{H}_2\text{O}/\text{U}^*$	1.36 ± 0.06	1.33

* calculated by difference

For TUPD solid solutions, the uranium and phosphate concentrations measured in the solution during the leaching tests when the equilibrium is reached are equal to $[UO_2^{2+}] = 8.4 \times 10^{-4}M$ and $C_{PO_4} = 3.3 \times 10^{-4}M$ (i.e. $[PO_4^{3-}] = 5.4 \times 10^{-18}M$ considering $pH=1.6$ obtained at equilibrium). The associated solubility product $K_S = [UO_2^{2+}]^3[PO_4^{3-}]^2$ is then equal to 1.5×10^{-44} which is in good agreement with the value reported by several authors ($K_S = 10^{-45.45 \pm 0.16}$ for $I = 0.1 M$) (10).

RADIATION DEFECTS

One of the most important requirements for a radioactive waste form for a long term storage is to be resistant to the radiation damages. Our goal being the immobilization of actinides we must first check what happens during a short period just after the synthesis of the compound containing a large amount of activity. Thus, the X-ray patterns of a solid solution (TPPD) made with 25 weight percent of plutonium and stored during 2 years was done, the diagram does not reveal any difference with the same analysis realised on a fresh prepared compound. The calculated number of alpha particles corresponds to about 2.6×10^{16} desintegrations and $3.0 \times 10^{16}\beta^-$ desintegrations per gram of TPPD solid solution. In such experiment, it is known that the recoil atoms associated to the alpha emission could greatly affect the crystal structure, however, no amorphisation was observed. In the same objective, sintered pellets of pure TPD were irradiated with α particles of 1.6 MeV provided by an accelerator. The beam intensity and the irradiation time were calculated to give the same amount of α particles per gram than for TPPD solid solution ($x = 1$). In these conditions, we verified that TPD was still crystallised. These types of tests are not enough to definitely decide about the radioresistance of the material.

They were complete by γ ray irradiation studies. For this series of experiments TPD was on powder form. It was irradiated with a cesium 137 source at a dose of 3×10^5 gray. Then, the sample was analysed by EPR and Thermal Luminescence (TL) techniques. The main features are:

- the paramagnetic signal observed is made of a central component, a singulet line, interpreted as a peroxyde radical already seen in some irradiated phosphates (11),
- on both sides of the central part, an other intense and independent signal is present. It is due to the hyperfine coupling between radicals and the nuclear spin of phosphorus. This doublet was assumed to be related to the radical PO_3^{2-} (12). The 700 Gauss coupling between the two lines is in good agreement with the existence of the proposed radical.

- at low temperature irradiation (about 100 K) a signal attributed to the radical PO_4^{2-} is observed. When we increase the temperature of the sample, it disappears and gives rise to the previous doublet.

The values of the annealing temperature of the peaks, obtained by thermal luminescence, are in direct relation with the informations given by EPR. Furthermore, several checks made on pure TPD seems to indicate that the peaks observed by thermal luminescence are obtained at the same temperatures for a γ -ray irradiated sample as for a non irradiated one. This means that this technique is so sensitive that the defects produced *in situ* in TPD by natural thorium activity after

2 months is enough to be detected by TL. This also suggests that these damages created by α particles and recoil atoms leads to defects of the same nature as those generated by γ rays. No defects, leading to an EPR signal, exist for temperatures over 350 °C.

From a general point of view, we can conclude that the resistance to radiations of TPD seems very close to what is found for other phosphate compounds like monazites (naturally loaded with thorium and uranium) which are still crystallised, while some silicates in the same conditions are metamictised (13).

CONCLUSION

The thorium phosphate-diphosphate (TPD) appears as a good host-matrix for tetravalent actinides for the main following reasons :

- the study of the substitution of thorium by uranium, neptunium and plutonium in the TPD structure was performed with success. In the $\text{ThO}_2 - \text{MO}_2 - \text{P}_2\text{O}_5$ systems, solid solutions $\text{Th}_{4-x}\text{M}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$ can be synthesized up to $x = 3.00$, 2.09 and 1.67 for U^{4+} , Np^{4+} and Pu^{4+} , respectively. Considering the ionic radius of the tetravalent protactinium in the eightfold coordination number ($[8]r_{\text{Pa}} = 1.01\text{\AA}$) and the literature concerning phosphates of tetravalent protactinium, it could be possible to synthesize solid solutions $\text{Th}_{4-x}\text{Pa}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$ for $x \leq 3.75$.
- the TPD is very easy to prepare whatever the chemical way of synthesis (using dry or wet chemistry methods), the thorium salt and the phosphating reagent.
- the TPD is very easy to sinter after a room temperature pressing between 300 and 800 MPa then a heating treatment at 1250°C for 10 hours. The sintering of TUPD solid solutions from a mixture containing $\text{UClPO}_4 \cdot 4 \text{H}_2\text{O}$, $\text{U}(\text{HPO}_4)_2 \cdot x \text{H}_2\text{O}$ and $\text{Th}_4(\text{PO}_4)_4(\text{HPO}_4)_2 \cdot y \text{H}_2\text{O}$ was also obtained. Those of TPPD and TNPD solid solutions will be performed soon.
- leaching tests of TPD, PUPD or TPPD performed in distilled water, french granitic mineral water and acidic media showed that this material is very resistant to aqueous corrosion. The partial order related to $[\text{H}_3\text{O}^+]$ and the apparent dissolution rate constant are equal to 0.35 - 0.44 and 1×10^{-5} - $4 \times 10^{-5} \text{ g / (m}^2\cdot\text{d)}$, respectively. Moreover, leaching tests of TUPD in oxidizing conditions showed that the uranium concentration in the solution is controlled by the precipitation of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4 \text{H}_2\text{O}$.
- the TPD is resistant to α particles and γ -ray at high level doses. The defects induced by these irradiations were identified by EPR associated with Thermal Luminescence studies. It was shown that the defect nature is the same whatever the way of they are produced, that is to say, by external γ irradiation or *in situ* through the self irradiation brought in few months by the natural thorium radioactivity.

The immobilization of small amounts of trivalent actinides in the TPD structure was also investigated. Even if the substitution of thorium by trivalent actinides like ^{241}Am or ^{244}Cm was not obtained because of the great difference of ionic radii, the americium (or curium) concentration measured in the solution is very low, according to the precipitation of the americium (or curium) phosphate $\text{AmPO}_4 \cdot x \text{H}_2\text{O}$.

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