Investigation of $^{137}Cs^{+}$, $^{85}Sr^{2+}$ and $^{241}Am^{3+}$ ion exchange on thorium phosphate hydrogenphosphate and their immobilization in the thorium phosphate diphosphate

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Thorium phosphate diphosphate (TPD) has been proposed as a host matrix for the long-term storage of tetravalent actinides such as U(IV), Np(IV) and Pu(IV), which form solid solutions with TPD. Small amounts of di- or trivalent cations can also be immobilized in this matrix. Another method of loading of TPD, using the ion-exchange properties of thorium phosphate hydrogenphosphate (TPHP), a precursor of TPD, was applied to $^{137}Cs^{+}$, $^{85}Sr^{2+}$ and $^{241}Am^{3+}$. The adsorption of these cations on TPHP was studied in terms of pH in $NaClO_4$ and $NaNO_3$ media. The ion-exchange process on TPHP was found to be reversible for $^{85}Sr^{2+}$ and $^{241}Am^{3+}$. Doped TPHP obtained in this way was heated at 1050 °C until TPD was formed. Several leaching tests were performed in acidic media on TPD doped with radionuclides with ionic strength equal to 0.1 M. The average partial order related to the proton was found to be equal to 0.24 ± 0.10 and the normalized leaching rate constant was in the range of 3×10^{-6} to 2×10^{-5} g m^{-2} d^{-1}. These results are similar to those obtained for thorium plutonium(IV) phosphate diphosphate solid solutions. On the basis of the results obtained from the adsorption and leaching studies, this adsorption-immobilization process, based on the TPHP matrix, can be proposed for the decontamination of low level radioactive liquid wastes.

In the context of the long-term storage of radioactive waste, thorium phosphate diphosphate, $Th_4(PO_4)_4P_2O_7$ (TPD), has been proposed for the immobilization of tetravalent actinides such as uranium, neptunium or plutonium.[1,2] Indeed, this material is very resistant to aqueous corrosion and exhibits a high thermal stability.[3] Moreover, it can also be loaded *in situ* with trivalent actinides, then used as a host matrix for radioactive waste storage.[4]

Another method of loading involves the initial precipitation of a precursor of TPD. This solid was identified as thorium phosphate hydrogenphosphate (TPHP), whose formula is $Th_2(PO_4)_2(HPO_4)\cdot nH_2O$ with $n = 3$–7.[5] This amorphous ion exchanger was characterized by several physico-chemical techniques. Some of its properties are a high specific surface area, a good chemical stability and a high ion-exchange capacity. All these make it a particularly suitable product for the adsorption of several cations from solution. When heated at 800–1200 °C, TPHP transforms into well-crystallized TPD. TPD can also be obtained in a sintered form *via* uniaxial pressing at 200–800 MPa, then heating at 1200 °C for 10 h. Under these conditions the density of the pellets reaches 95–99% of the value calculated from XRD data.

The aim of this work was to perform, successively, the decontamination of waste solutions and the final immobilization of various radionuclides using the same thorium phosphate compound and a simple process. Hayashi *et al.*[6] have recently studied the same process for strontium immobilization in fibrous cerium(IV) bis(monohydrogenphosphate), obtained under hydrothermal conditions.

Adsorption and H^{+} ion exchange by mono-, di- and trivalent cations in tetravalent element hydrogenphosphates like $Zr(HPO_4)_2$,[7–9] $Ce(HPO_4)_2$[10,11] and $Th(HPO_4)_2$[12–15] have already been studied by several authors. Amorphous zirconium hydrogenphosphate[8,16] has been proposed for the treatment of radioactive waste containing $^{137}Cs^{+}$ and $^{90}Sr^{2+}$. Because of the presence of hydrogenphosphate sites in TPHP, we expected an analogous ion-exchange mechanism for TPHP.

The effect of pH on the uptake of cations was determined from the removal of $^{137}Cs^{+}$, $^{85}Sr^{2+}$ and $^{241}Am^{3+}$ in 0.1 M $NaNO_3$ and $NaClO_4$ solutions. After separation and calcination of TPHP at 1050 °C for 10 h, the powdered TPD loaded with radionuclides was obtained. In order to verify the resistance of this solid to aqueous corrosion, leaching tests of TPD samples doped with $^{85}Sr^{2+}$ and $^{241}Am^{3+}$ were performed in several acidic solutions at room temperature.

Experimental

Thorium nitrate, $Th(NO_3)_4$, solution ($C_{Th} = 1$ M) from Rhone-Poulenc was used for the synthesis of TPHP. Other chemicals of high purity (>99.5%) were from Fluka-Aldrich. The total initial concentration of cation was equal to about 10^{-8} M for caesium and strontium and to 10^{-10} M for americium (including all isotopes).

The TPHP synthesis and characterization was extensively reported in our previously published work.[5] It is precipitated by mixing diammonium hydrogenphosphate and thorium nitrate solutions in the molar ratio $r = PO_4 : Th = 3 : 2$. The optimum conditions required to get the final solid are the following: (1) initial pH value in the 8.5–9.5 range; (2) final pH equal to about 6; (3) concentration of the reactants equal to 0.5 M.

The specific surface area of the dried powdered samples (120 °C) was determined in nitrogen using a Coulter SA 3100 apparatus.

The ion-exchange properties of TPHP were studied by a batch process. High density polyethylene (HDPE) containers

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purchased from Nalgene were used to minimize the adsorption of the radionuclides studied onto the container surfaces. Even in the case of high loading, the adsorption of cations onto the surface was negligible (lower than 1% of the measured activity).

The TPHP "solubility" was determined by measuring the thorium released into the solution, for several perchloric acid solutions (10^{-1}–10^{-6} M), keeping the ionic strength I constant at 0.1 M (by addition of sodium perchlorate). The ratio V/m, where V is the volume of the solution (mL) and m is the mass of the TPHP sample (g), was fixed to 50 mL g^{-1}. Samples were stirred at room temperature for 1, 7, 15 and 30 days.

Ion exchange of the three radionuclides studied ($^{137}Cs^{+}$, $^{85}Sr^{2+}$, $^{241}Am^{3+}$) onto TPHP was carried out by a batchwise operation. In the first step, 0.2 g of TPHP was mixed with 10 mL of 10^{-1}–10^{-6} M $HClO_4$ or HNO_3 solutions ($V/m = 50$ mL g^{-1}). The ionic strength was kept constant ($I = 0.1$ M) by addition of sodium perchlorate or nitrate. In order to obtained a V/m ratio equal to 250 mL g^{-1}, we kept the volume of the solution constant (10 mL) and decreased the weight of TPHP powder (0.04 g). Samples were stirred for 24 h to reach solid–solution equilibrium before radionuclide addition. The supernatant was then separated by centrifugation for 30 min at 3500 rpm and the remaining radioactivity in the solution was measured.

For each solution used, the concentrations of thorium and americium were determined using a photon electron rejecting alpha liquid scintillation (PERALS) spectrometer purchased from Novelec (Ortec), after a liquid–liquid extraction step as already described.[17,18] The total concentrations of strontium and caesium in the solutions were determined by measuring the $^{137}Cs^{+}$ and $^{85}Sr^{2+}$ activities with a gamma spectrometry using a pure germanium crystal detector under reproducible conditions.

In order to obtain TPD loaded with radionuclides, samples were heated in air in a Pyrox MDB15 furnace in alumina crucibles with a heating rate equal to 5 °C min^{-1}. The samples were slowly evaporated between 120 and 200 °C, then heated at 1050 °C for 10 h.

Leaching tests were performed in 10^{-1}–10^{-6} M $HClO_4$ solutions at room temperature, keeping the ionic strength I constant at 0.1 M (provided by addition of sodium perchlorate). Prior to making leaching measurements, all the samples were washed for 50 days in order to remove superficial crystal imperfections, defaults, minor phases (non-stoichiometry) or very small grain size, which are usually produced during the synthesis and can lead to perturbations. After this preliminary washing step, leaching investigations of the TPD doped with radionuclides were carried out. Samples consisting of 0.17 g of powder were put into 10 mL of 10^{-1}–10^{-6} M perchloric acid under permanent stirring at room temperature for several months at constant ionic strength ($I = 0.1$ M). Before each measurement, liquid and solid phases were separated by centrifugation at 13 000 rpm. Then, only 1–2% of the total volume of the leachate (100–200 μL) was taken off in order to avoid any perturbation of the solution–solid system. This volume was renewed with a fresh solution. Under these conditions, the leaching flux was equal to 3–6 × 10^{-2} mL m^{-2} d^{-1}, which can be considered very low, corresponding to quasi-static experiments. After each separation, the radionuclide concentration in the leachate was determined.

Ion-exchange model applied

The uptake percentage of cations was calculated using the following equation:

$$\%\ \text{removal} = \frac{A_\text{i} - A_\text{f}}{A_\text{i}} \times 100 \qquad (1)$$

where A_i is the initial and A_f the final radionuclide activity measured in the solution.

The exchange experiments were performed for several pH values at room temperature, then the distribution coefficients, K_d, were calculated using the following equation:[19]

$$K_\text{d} = \frac{(A_\text{i} - A_\text{f}) \times V}{A_\text{f} \times m} \qquad (2)$$

where V is the volume of the solution used (mL) and m is the mass of the TPHP sample (g). The distribution coefficient is thus expressed in mL g^{-1}.

In the case of the exchange reaction of mono-, di- or trivalent cations with hydrogen ions of the hydrogenphosphate sites, the ion-exchange model indicates that the variation of log K_d *vs.* the pH is linear. The calculated slope for the log $K_\text{d} = f$ (pH) function represents the charge of the studied cation, according to H. Hayashi and co-workers.[10,11]

Leaching definitions

Normalized leaching. Some authors have already attempted to explain the dissolution kinetics by invoking transition state theory[20] or through a concept based on the coordination chemistry.[21] These authors agreed that the dissolution rate of most solids is controlled by surface reactions at the solid–solution interface with the decomposition of an activated complex.[22] A rigorous application of the rate law determined from transition state theory is only possible for elementary reactions, which makes this rate law difficult to apply to overall dissolution reactions. Thus, we were especially interested in the approach developed by Lasaga,[23] in which all the parameters are macroscopic.

The leachability of an element i from a solid can be described by its normalized leaching, $N_\text{L}(i)$ (g m^{-2}), which is defined by the relation:

$$N_\text{L}(i) = \frac{\Delta m_{i,\,\text{sol}}}{f_i \times S} = \frac{m_i}{f_i \times S} \qquad (3)$$

where m_i is the total amount of the element i measured in the solution (g), S corresponds to the surface area of the solid (m^2) and $\Delta m_{i,\,\text{sol}}$ corresponds to the mass variation of i in the solid:

$$\Delta m_{i,\,\text{sol}} = m_{i,\,\text{sol},\,0} - m_{i,\,\text{sol},\,t} \qquad (4)$$

where $m_{i,\,\text{sol},\,0}$ is the initial mass of i in the solid and $m_{i,\,\text{sol},\,t}$ is the mass of i in the solid after a leaching time equal to t. f_i is the mass ratio of i in the solid, which is defined as follows:

$$f_i = \frac{m_{i,\,\text{sol},\,0}}{m_{\text{sol},\,0}} \qquad (5)$$

where $m_{\text{sol},\,0}$ represents the initial total mass of the solid.

Dependence of the normalized leaching on the leaching time. The normalized leaching rate of a solid R_L (g m^{-2} d^{-1}) can be obtained from the evolution of the normalized leaching.[23] It can be calculated from the equation:

$$R_\text{L} = \frac{\text{d}m}{\text{d}t} \times \frac{1}{S} \qquad (6)$$

where dm/dt represents the derivative of the dissolved mass of the solid (g d^{-1}) as a function of the leaching time.

Furthermore, if the dissolution process is congruent (stoichiometric dissolution and absence of neoformed phases), dm/dt can be defined from the mass change of one of the elements i of the solid considering the following equation:

$$\frac{\text{d}m}{\text{d}t} = \frac{1}{f_i} \times \frac{\text{d}m_i}{\text{d}t} \qquad (7)$$

Thus, for a congruent dissolution, the normalized leaching rate becomes:

$$R_L = \frac{1}{f_i \times S} \times \frac{dm_i}{dt} = \frac{dN_L(i)}{dt} \qquad (8)$$

where dm/dt corresponds to the derivative of eqn. (3).

In acidic media, the normalized leaching rate R_L is usually denoted as R_H, while in basic media it is denoted as R_{OH}. In this paper, we will only use the R_H notation because all the leaching tests were performed in acidic media. For each acidic solution, the linear regression obtained from the evolution of $N_L(i)$ allows the determination of the normalized leaching rate R_H according to eqn. (8).

Influence of the proton concentration on the normalized leaching rate. Several chemical kinetics investigations of dissolution reactions between solids and aqueous solutions have already been published.[24–27] These studies showed that the normalized leaching rate of most of the solids increased with proton activity for pH < 7. Chou and Wollast[24] studied the dissolution kinetics of albite at room temperature under a wide range of experimental conditions including pH, and showed that in acidic media the normalized leaching rate can be written as:

$$R_H = k'_T \times a^n_{H_3O^+} \qquad (9)$$

where k'_T corresponds to the apparent normalized leaching rate constant (g m^{-2} d^{-1}), which is dependent on temperature according to the Arrhenius law, $a_{H_3O^+}$ refers to the proton activity and n is the partial order related to the H_3O^+ ions.

For most of the solids, the partial order related to the proton activity, n, was found to be between 0 and 1.[24–27] We must note that even if this order depends on the dissolution mechanism, it does not correspond to the number of protons involved in the dissolution reaction. Eqn. (9) invokes the proton activity, nevertheless, in most cases it is easier to use the proton concentration, leading to:

$$R_H = k'_T \times (\gamma_{H_3O^+} \times [H_3O^+])^n = k'_{T,I} \times [H_3O^+]^n \qquad (10)$$

with $k'_{T,I} = k'_T \times \gamma^n_{H_3O^+}$, where $\gamma_{H_3O^+}$ corresponds to the proton activity coefficient and $k'_{T,I}$ represents the apparent normalized leaching rate constant for proton dissolution defined for pH < 7, independent of the pH, but dependent on the temperature and on the ionic strength I. $k'_{T,I}$ and n are then obtained from the variation of log R_H *vs.* log [H_3O^+]:

$$\log R_H = \log k'_{T,I} + n \log[H_3O^+] \qquad (11)$$

where the slope of the straight line corresponds to the partial order n while the intercept is equal to log $k'_{T,I}$.

Results and discussion

The specific surface area measured for TPHP dried at 120 °C was 150 ± 5 m^2 g^{-1}.[5] When heated at 800–1200 °C, it transforms to well-crystallized TPD according to the reaction:

$$2Th_2(PO_4)_2(HPO_4)\cdot nH_2O \rightarrow Th_4(PO_4)_4P_2O_7 + (2n+1)H_2O\uparrow \qquad (12)$$

Simultaneously, the specific surface area decreases to about 2.3 ± 0.2 and 0.2–0.3 m^2 g^{-1} after heating at 1050 °C and at 1150–1250 °C, respectively. From TGA results the total weight loss when heating TPHP at 1050 °C is about 15%.[5]

The experimental "solubility" of TPHP in 0.1 M $NaClO_4$ is plotted in Fig. 1. As shown in this figure, equilibrium between the solid and the solution is reached after one day of contact. The TPHP solubility is then almost constant in the studied pH range ($C_{Th} \approx 10^{-6}$ M). For pH < 2, the formation of a gelatinous layer on the surface of the powder was observed.

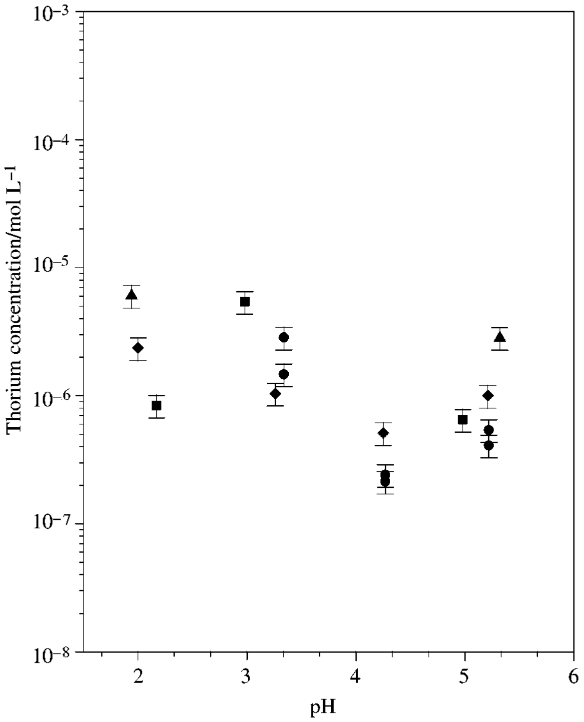

Fig. 1 "Solubility" of TPHP in 0.1 M $NaClO_4$ solution at room temperature for several pH values. Thorium concentration in solution after 1 (■), 7 (●), 15 (◆) and 30 days (▲).

The characterization of this new phase is now under process using transmission electron microscopy. In order to avoid possible effects from this layer on the cation exchange, the experiments were conducted at pH > 2.

The average of the experimental total exchange capacity (TEC) in NaOH, NaCl and $NaNO_3$ solutions is equal to 1.2 meq g^{-1}. This is in good agreement with the value calculated from the TPHP formula (1.19 ± 0.05 meq g^{-1}).[5] After heating at 1050 °C, the product obtained after this cation exchange was identified as dithorium sodium phosphate, $Th_2Na(PO_4)_3$, mentioned by several authors in the literature (JCPDS file no. 16-812).[28–30] The exchange reaction can be written as:

$$Th_2(PO_4)_2(HPO_4)\cdot nH_2O + Na^+ + OH^- \rightarrow Th_2Na(PO_4)_3 + (n+1)H_2O\uparrow \qquad (13)$$

An electron probe microanalysis confirmed that the molar ratio $PO_4 : Th$ remains at 3 : 2 in the final compound obtained. An analogous process was also observed for caesium ions.[5]

From the speciation curves it was calculated that under the experimental conditions 20% of the strontium is complexed as $SrNO_3{}^+$ while 30% americium is in the $AmNO_3{}^{2+}$ form. The concentrations of MOH^{n+} forms are negligible.

The study of the kinetics showed that 6 h were necessary to reach the caesium exchange equilibrium for 2 ⩽ pH ⩽ 6 in 0.1 M $NaNO_3$ and $NaClO_4$ solutions. For strontium and americium it was reached within a few minutes. Nevertheless, we chose a contact time of 24 h for all experiments to be sure that the global equilibrium between the solid, the solution and the cations was reached.

The variation of the uptake percentage of $^{137}Cs^+$ (Fig. 2), $^{85}Sr^{2+}$ and $^{241}Am^{3+}$ (Fig. 3) as a function of the pH in 0.1 M $NaNO_3$ and $NaClO_4$ solutions are presented for a V/m ratio equal to 250 mL g^{-1}. On one hand, the acidity of the solution containing the radionuclides has a strong influence on the TPHP selectivity for caesium, strontium and americium, which was demonstrated by the decrease in the uptake values in acidic solutions. On the other hand, comparison between the results obtained in $NaClO_4$ or in $NaNO_3$ solutions indi-

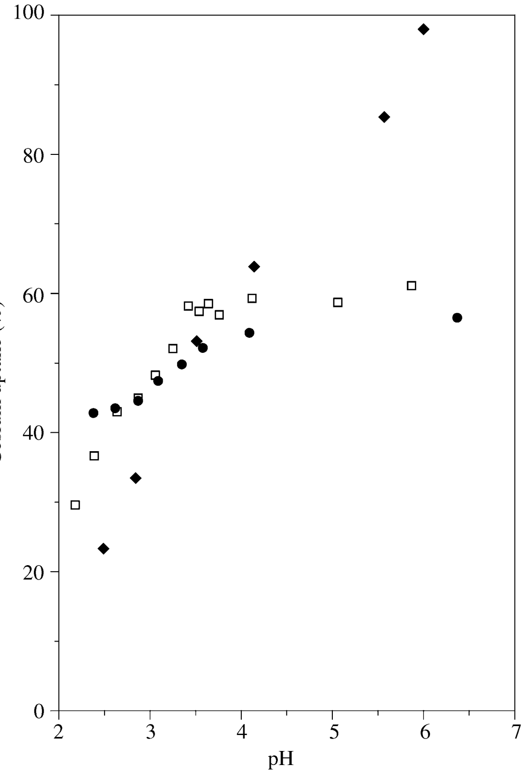

Fig. 2 Effect of pH on the caesium ion uptake on TPHP for $V/m = 250$ mL g^{-1} in 0.1 M $NaNO_3$ (□), 0.1 M $NaClO_4$ (●) and in distilled water (◆).

cates that the anionic species has no influence on the cation exchange. The caesium uptake became constant and reached 60% (Fig. 2) for $4 \leqslant pH \leqslant 6$, resulting from the competition with Na^+ ion exchange. Indeed, the caesium uptake reached 100% in distilled water (equilibrium at pH 6). Zamin *et al.*[8] observed the same phenomena on a $Zr(HPO_4)_2$ ion exchanger.

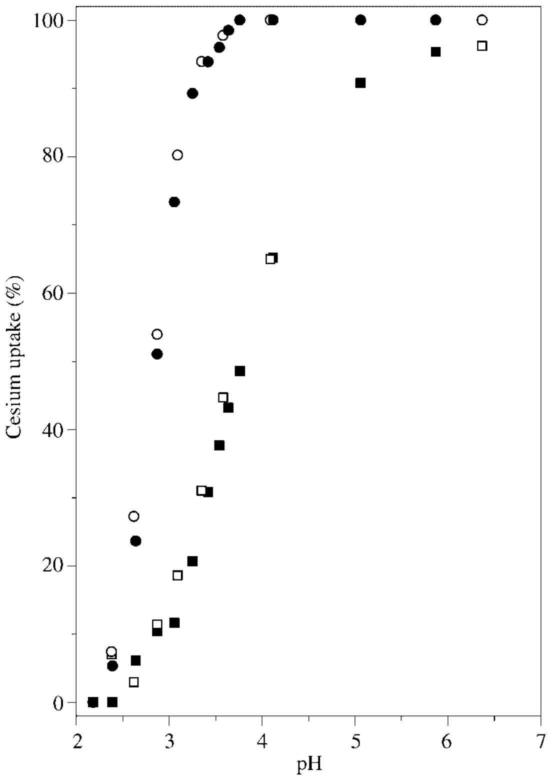

Fig. 3 Effect of pH on the americium (○, ●) and strontium (□, ■) ion uptake on TPHP for $V/m = 250$ mL g^{-1} in 0.1 M $NaNO_3$ (full symbols) or in 0.1 M $NaClO_4$ (open symbols) solutions.

The influence of the V/m ratio on the uptake percentage was also studied in the case of strontium and americium ions. In accordance with the ion-exchange model [eqn. (2)] the variation of the V/m ratio does not change the log K_d values (Fig. 4). Moreover, the ion-exchange model indicates that the slope should be equal to 2 for strontium (Sr^{2+}) and to 3 for americium (Am^{3+}) ions, but we observed an experimental slope equal to 1.1 and 2.1, respectively. This could be explained by the sodium (Na^+) influence on the ion exchange. In fact, the concentration of sodium ions is very high in comparison to the concentrations of the investigated cations (lower than 10^{-8} M).

The desorption of Sr^{2+} and Am^{3+} ions previously fixed onto TPHP was also studied in order to observe the reversibility of the uptake process (Fig. 5). The results indicate that the ion-exchange process is reversible for the studied cations, which is in accord with the ion-exchange model.

The presence of a high sodium concentration in the solution containing radionuclides led to a two-phase solid system after heating at high temperature. It is usually composed of TPD and dithorium sodium phosphate, as already mentioned. In order to obtain a single phase, which is required to obtain accurate results during the leaching tests, it was necessary to modify the ion-exchange procedure.

For this reason, the radionuclides were stirred with 0.2 g of TPHP in the presence of 10 mL of 10^{-4} M $HClO_4$ solution without addition of any salt. The initial concentrations were about 10^{-7} M for strontium and 10^{-8} M for americium. In these conditions the uptake of $^{85}Sr^{2+}$ and $^{241}Am^{3+}$ onto TPHP reached 100%. After separating the solid from the solution, the TPHP containing radionuclides was first heated at 400 °C for 2 h, then up to 1050 °C for 10 h with a heating rate equal to 5 °C min^{-1}. In this way, we finally obtained TPD doped with ^{85}Sr or ^{241}Am. The mass ratio f_i of the element i in the solids [eqn. (5)], and the initial specific activity are summarized in Table 1.

The evolution of the normalized leaching of ^{85}Sr and ^{241}Am is reported in Fig. 6 and 7, respectively. For $1 \leqslant pH \leqslant 4$, the normalized leaching increases linearly with the leaching time after about 45 days of contact between the solid and the solution. Moreover, decreasing pH induces an

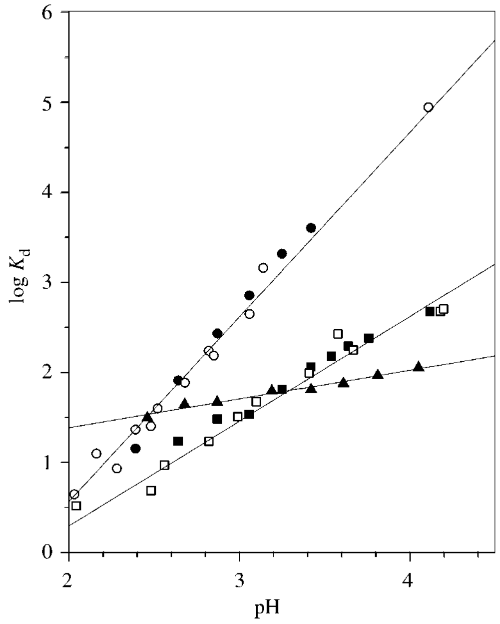

Fig. 4 Variation of log K_d for caesium (▲), strontium (□, ■) and americium (○, ●) ions as a function of pH in 0.1 M $NaNO_3$ solution for $V/m = 250$ mL g^{-1} (full symbols) of for 50 mL g^{-1} (open symbols).

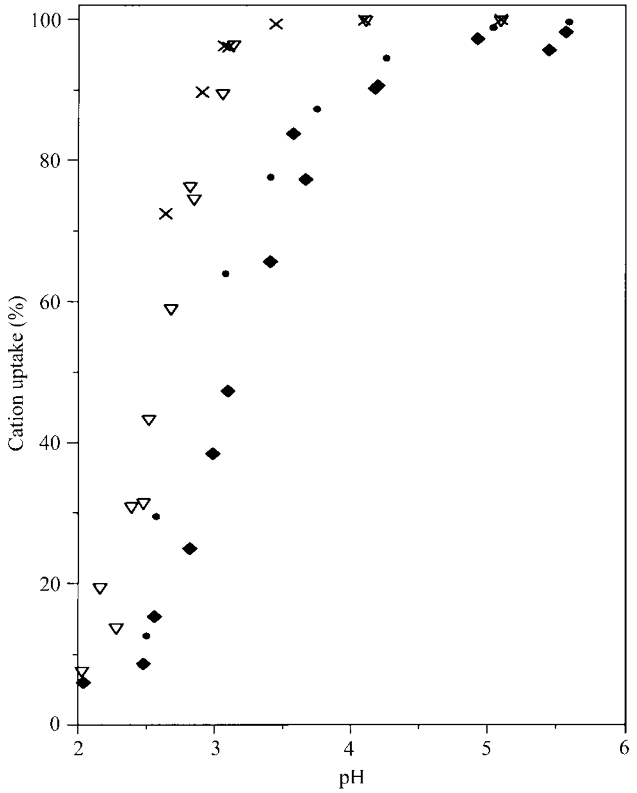

Fig. 5 Effect of pH on the uptake of americium (▽) and strontium (◆) and desorption of americium (×) and strontium (●) ions on TPHP for $V/m = 50$ mL g^{-1} in 0.1 M $NaNO_3$ solution.

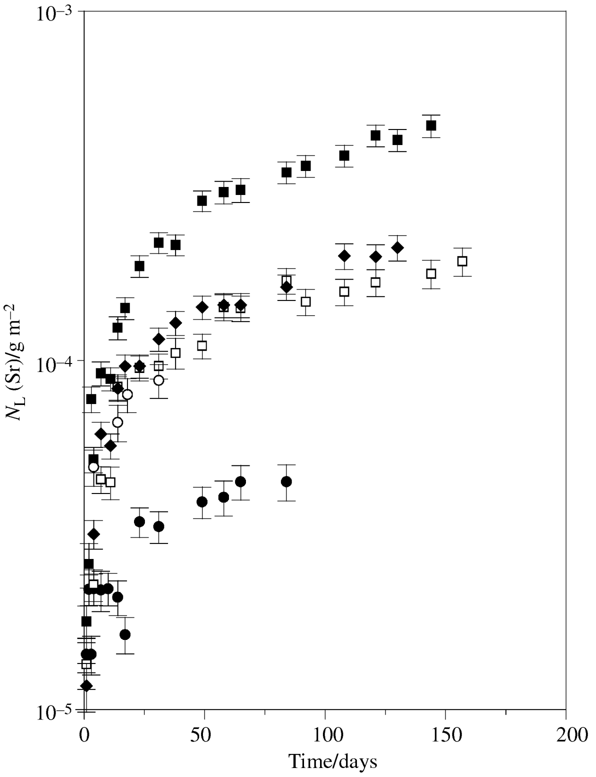

Fig. 6 Evolution of N_L(Sr) for TPD samples doped with ^{85}Sr in 10^{-1} (■), 10^{-2} (○), 10^{-3} (◆), 10^{-4} M (□) perchloric acid and in distilled water (●) at room temperature.

increase of the radionuclide release in the leachate, which is consistent with eqn. (9).

The results obtained were compared with previous leaching tests performed on TPD doped *in situ* with ^{241}Am and on thorium plutonium(IV) phosphate diphosphate (TPPD) solid solutions. The solid solution $Th_{3.6}Pu_{0.4}(PO_4)_4P_2O_7$ was prepared from a mixture of thorium nitrate, tetravalent plutonium nitrate and concentrated phosphoric acid solutions as reported previously.[1] The preparation of the thorium phosphate diphosphate loaded *in situ* with ^{241}Am was similar.[4] The temperature (100 °C) and heating time (14 h) were the same for all the samples.

All the R_H values obtained by linear regression are reported in Table 2 and are presented in Fig. 8. They are compared with other results obtained for the TPPD solid solution in Fig. 8. We observe from Fig. 8 that log R_H decreases linearly with log $[H_3O^+]$ between 10^{-1}–10^{-6} M $HClO_4$ for TPD doped with strontium, between 10^{-1}–10^{-4} M $HClO_4$ for TPPD and between 10^{-1}–10^{-3} M $HClO_4$ for TPD doped with americium. All these observations are in very good agreement with eqn. (10) and allowed the determination of the $k'_{T,I}$ and n values by linear regression of the experimental data. These values, as well as those reported for TPD doped *in situ* with ^{241}Am, are summarized in Table 2.[31,32] The average partial order related to the proton concentration was found to be about 0.24 ± 0.10 at room temperature and for $I = 0.1$ M in perchloric acid. The corresponding apparent leaching rate, $k'_{298\,K,0.1\,M}$, varied between 2×10^{-5} and 3×10^{-6} g m^{-2} d^{-1}. These values are lower than those reported for several matrices such as zircon,[33] zirconolite,[33] Synroc,[34] monazites[35] or apatites[36] proposed for the immobilization of radionuclides.

We already mentioned that log R_H decreases linearly for $1 \leqslant pH \leqslant 3$ for TPD doped with ^{241}Am. It becomes constant as a function of the leaching time in 10^{-4} M $HClO_4$ and in 0.1 M $NaClO_4$ solution (Fig. 7). For log $[H_3O^+] < 3$, the

Table 1 Specific activity of TPD samples doped with radionuclides

Solid	Specific activity/MBq g^{-1}	f_i(wt%)
$Th_4(PO_4)_4P_2O_7$: ^{85}Sr	17.6	1.5×10^{-6}
$Th_4(PO_4)_4P_2O_7$: ^{241}Am	8.8	7×10^{-5}

Table 2 Leaching rate constants R_H, $k'_{T,I}$ and n values obtained for TPD and thorium plutonium(IV) phosphate diphosphate (TPPD) solid solutions

	TPD : ^{241}Am			
pH	Ion exchange[a]	*in situ*[b]	TPPD[32]	TPD : ^{85}Sr[a]
R_H/g m^{-2} d^{-1}				
1	$7.8(5) \times 10^{-7}$	$5.9(1) \times 10^{-6}$	$1.4(1) \times 10^{-5}$	$2.0(2) \times 10^{-6}$
2	$3.6(2) \times 10^{-7}$	$1.84(4) \times 10^{-6}$	$9.1(8) \times 10^{-6}$	$1.5(3) \times 10^{-6}$
3	$2.9(3) \times 10^{-7}$	$1.18(4) \times 10^{-6}$	$8.0(7) \times 10^{-6}$	$9.2(6) \times 10^{-7}$
4	$1.3(8) \times 10^{-8}$	$6.5(6) \times 10^{-8}$	$5.7(6) \times 10^{-6}$	$6.5(5) \times 10^{-7}$
6	NS[c]	NS[c]	$2.5(1) \times 10^{-6}$	$2.4(5) \times 10^{-7}$
n	0.24 ± 0.08	0.35 ± 0.04	0.21 ± 0.06	0.17 ± 0.01
$k'_{298\,K,0.1\,M}$/g m^{-2} d^{-1}	$1.3(1) \times 10^{-6}$	$1.2(3) \times 10^{-5}$	$2.0(9) \times 10^{-5}$	$3.1(1) \times 10^{-6}$

[a] Doped TPD obtained from TPHP by ion exchange. [b] TPD doped *in situ*.[31] [c] Leaching rate too small to be significant even after 300 days.[31]

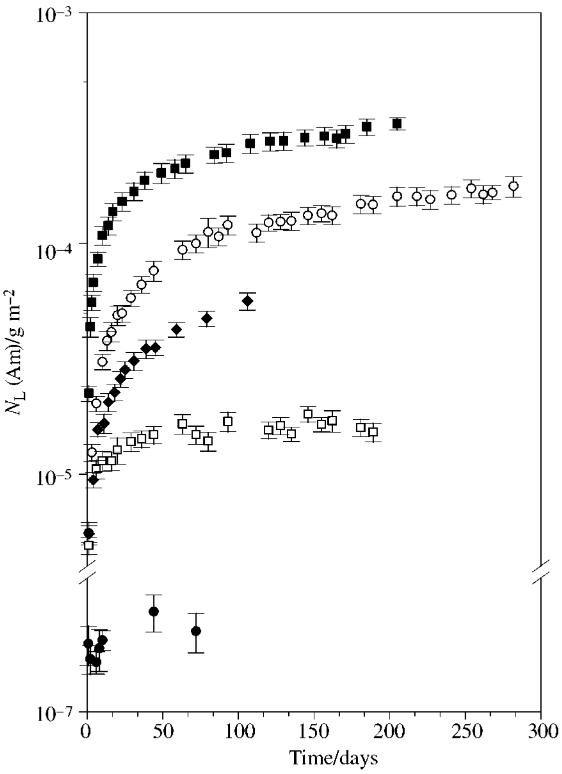

Fig. 7 Evolution of N_L(Am) for TPD samples doped with ^{241}Am in 10^{-1} (■), 10^{-2} (○), 10^{-3} (◆), 10^{-4} M (□) perchloric acid and in distilled water (●) at room temperature.

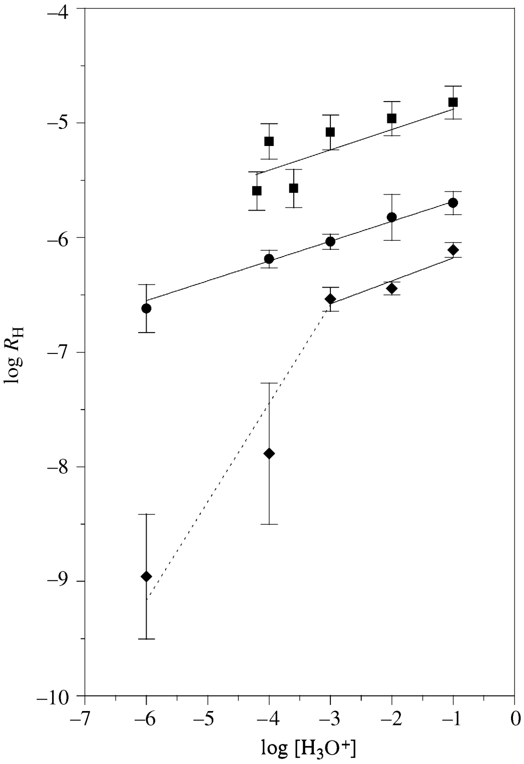

Fig. 8 Comparison of log R_H obtained for TPD doped with ^{85}Sr (●), TPD doped with ^{241}Am (◆) and TPPD solid solutions (■) as a function of log [H$_3$O$^+$].

activity released in solution decreases more sharply (Fig. 8). Under these conditions, the corresponding normalized leaching rate is not significant for TPD dissolution. This phenomenon was explained by the precipitation/adsorption of an americium phosphate hydrate of very low solubility.[37] A complete study of $AmPO_4 \cdot xH_2O$ showed that this solid can be prepared in over- and under-saturation conditions at room temperature[37] and was thought to be the solubility-controlling solid for phosphate matrices after 86 days of leaching time, according to the following equilibrium:

$$AmPO_4 \cdot xH_2O \leftrightharpoons Am^{3+} + PO_4{}^{3-} + xH_2O \qquad (14)$$

$AmPO_4 \cdot xH_2O$ is considered to be amorphous by comparison with the study of Rai *et al.*[37] The logarithm of the conventional equilibrium constant $K_{s,0}^{\ominus *}$ was calculated, assuming that the activity of the amorphous phase is equal to one, and found to be log $K_{s,0}^{\ominus *} = -24.8 \pm 0.2$. We must know the variation of $K_s^{\ominus *}$ as a function of the ionic strength I, in order to compare our results to the value obtained for $AmPO_4 \cdot xH_2O$ and for the analogous rare earth phosphate hydrates mentioned in the literature.[38,39] For these solids, log $K_s^{\ominus *}$ was found to vary between −24.8 and −26.2 (Table 3).

The variation of log $K_s^{\ominus *}$ with the ionic strength (at 20 °C) was determined considering the specific-ion interaction theory (SIT)[40] and the review of Silva *et al.*[41] concerning the chemical thermodynamics of americium. Considering m_x, the molality (mol kg^{-1}) of the ion X, we obtain:

$$\log K_s^{\ominus *} = \log K_{s,0}^{\ominus *} + \log \gamma_{Am^{3+}} + \log \gamma_{PO_4{}^{3-}} \qquad (15)$$

where:

$$\log \gamma_{Am^{3+}} = -z^2_{Am^{3+}} \times D + \varepsilon_{Am^{3+},\,ClO_4^-} \times m_{ClO_4^-} \qquad (16)$$

$$\log \gamma_{PO_4{}^{3-}} = -z_{PO_4{}^{3-}} \times D + \varepsilon_{PO_4{}^{3-},\,Na^+} \times m_{Na^+} \qquad (17)$$

$$D = \frac{0.509\sqrt{I}}{1 + 1.5\sqrt{I}} \qquad (18)$$

D is the Debye–Huckel term and ε is the ion interaction coefficient. For this calculation we took $\varepsilon_{Am^{3+},\,ClO_4^-} = 0.49$ and $\varepsilon_{PO_4{}^{3-},\,Na^+} = -0.39$, as reported in the literature.[41]

Fourest and co-workers[42,43] have studied TPD dissolution by determining the values of the thorium concentration in solution for $1 \leqslant pH \leqslant 12$. Because TPD dissolution is stoichiometric,[32] the total phosphate ion concentrations were determined from this study with respect to the TPD stoichiometric ratio. The phosphate and americium concentrations obtained from the leaching studies at pH 4 and 6 (with $I = 0.1$ M) are reported in Table 4, as well as the corresponding log $K_{s,0}^{\ominus *}$ values determined from eqn. (15). The average value of log $K_{s,0}^{\ominus *}$ is equal to about −28, which is in rather good agreement with the results obtained for rare earth phosphate hydrates, considering the inaccurate value of the total phosphate concentration. Thus, the observation that activity released in the solution quickly decreases for concentrations of $HClO_4$ lower than 10^{-3} M can be attributed to the precipitation of the americium phosphate hydrate as an amorphous solid. Under these conditions, the evolution of the normalized leaching does not allow the determination of the normalized leaching rate. In fact, the dissolution process, which is a kinetic process, is masked by the precipitation of the amer-

Table 3 Log $K_{s,0}^{\ominus *}$ of rare earth phosphate hydrates

	log($K_{s,0}^{\ominus *}$)
YPO_4	−24.76 ± 0.14
$LaPO_4$	−26.15 ± 0.52
$PrPO_4$	−26.06 ± 0.18
$NdPO_4$	−25.95 ± 0.06
$SmPO_4$	−25.99 ± 0.05
$EuPO_4$	−25.75 ± 0.27
$GdPO_4$	−25.39 ± 0.23
$TbPO_4$	−25.07 ± 0.03
$DyPO_4$	−25.15 ± 0.07
$HoPO_4$	−25.57 ± 0.46
$ErPO_4$	−25.78 ± 0.45
$TmPO_4$	−26.05 ± 0.06
$YbPO_4$	−26.17 ± 0.01
$LuPO_4$	−25.39 ± 0.03

Table 4 Determination of log $K^{*}_{s,0}$ for amorphous americium phosphate hydrate in equilibrium with its constituent ions in $NaClO_4$ + $HClO_4$ solution: $T = 25\,°C$, $I = 0.1$ M $NaClO_4$

	pH 4	pH 6
C_{PO_4}/mol l^{-1}	6×10^{-7}	2×10^{-8}
$[PO_4{}^{3-}]$ mol l^{-1}	2×10^{-17}	1.2×10^{-14}
$[Am^{3+}]$ mol l^{-1}	1.1×10^{-10}	2.4×10^{-12}
log $K^{\ominus *}_{s,0}$	−28.6	−27.5

icium phosphate hydrate, which is thermodynamically controlled. So in these media (pH ⩾ 4), trivalent americium does not appear to be a good tracer for the study of TPD dissolution.

Conclusions

The ion exchange of $^{137}Cs^{+}$, $^{85}Sr^{2+}$ and $^{241}Am^{3+}$ radionuclides onto thorium phosphate hydrogenphosphate (TPHP) was studied as a function of the pH in 0.1 M $NaNO_3$ and $NaClO_4$ solutions. Between pH 4 and 6, the caesium uptake reaches only 60%, due to the competition with Na^{+} ion exchange. By studying the caesium uptake in distilled water, we obtained 100% uptake for pH values higher than 6. The uptake of strontium and americium reaches 100% for a V/m ratio equal to 250 mL g^{-1} for pH ⩾ 6 and pH ⩾ 4, respectively. For these two cations, the V/m ratio and medium have no influence on the distribution coefficient, K_d. The ion-exchange process was found to be reversible indicating that the ideality of the ion exchange is probably fulfilled.

This new method of loading TPD, using the ion-exchange properties of TPHP, appears to be a promising one for the decontamination of low level liquid radioactive waste. After heating at 1050–1250 °C, the TPD loaded with radionuclides could be obtained either in powdered or sintered form. The final immobilization of small amounts of actinides incorporated in this way in TPD was proven. Indeed, the normalized leaching rates are similar to those observed for thorium plutonium(IV) phosphate diphosphate solid solutions and TPD doped *in situ* with radionuclides. The average partial order related to the proton concentration was found to be 0.24 ± 0.10 and the average apparent normalized leaching rate constant, $k'_{298\,K,0.1\,M}$, was found to lie between 2×10^{-5} and 3×10^{-6} g m^{-2} d^{-1} at room temperature for an ionic strength equal to 0.1 M. Furthermore, the normalized leaching rate can be calculated by applying these data in water at pH 7. It can be evaluated to lie between 4×10^{-7} and 2×10^{-8} g m^{-2} d^{-1}, which appears lower than the values reported for other materials devoted to the same objective. We must also note that this value was calculated only taking into account a kinetic process. Moreover, we must consider the precipitation of neoformed phosphate phases when the saturation of the solution is reached, which are of very low solubility and should delay the migration of the radionuclides into the biosphere under static conditions. The complete study of these phases is now under progress and will be published separately.

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