Influence of the pH on the dissolution of TPD and associated solid solutions

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Abstract

The dissolution of thorium phosphate diphosphate (TPD) doped or not with trivalent actinides and that of associated solid solutions with tetravalent plutonium was studied from a kinetic point of view as a function of the acidity or the basicity of the leachate. From the evolution of the normalized mass losses, the dissolution rates were determined. For all the solids considered, the values were found between 1.2×10^{-5} and 4.4×10^{-9} g m^{-2} d^{-1} which confirms the very good durability of TPD to aqueous corrosion. The expression of the dissolution rate was given in acidic and in basic media (10^{-1}–10^{-4} M HNO$_3$ or HClO$_4$ and 10^{-1}–10^{-4} M NaOH). The partial orders related to the proton and hydroxide ion concentrations were found to be equal to $n = 0.31$–0.40 and to $m = 0.37$, respectively. The associated dissolution rate constant at pH $= 0$ and pH $= 14$ were found to $k'_{298 \text{ K},0.1 \text{ M}} = 1.2 \times 10^{-5}$ to 2.4×10^{-5} g m^{-2} d^{-1} and to $k''_{298 \text{ K},0.1 \text{ M}}$, $(7.8 \pm 1.9) \times 10^{-5}$ g m^{-2} d^{-1}, respectively. In these conditions, the dissolution rate value extrapolated in neutral medium was evaluated to 2.4×10^{-7} to 3.6×10^{-7} g m^{-2} d^{-1} at room temperature and to 5.0×10^{-6} to 7.5×10^{-6} g m^{-2} d^{-1} at 90 °C which remains very low by comparison to the other ceramics studied for the same applications.
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1. Introduction

In the framework of the nuclear waste storage, phosphate matrices such as monazites [1–7], apatites [8–10], NZP [11–13], zirconium phosphates [14] or thorium phosphates [15,16] were already studied considering several properties of interest. In this context, we completely reexamined the chemistry of uranium and thorium phosphates in order to propose a new material highly resistant to aqueous corrosion. Hence, the thorium phosphate diphosphate Th$_4$(PO$_4$)$_4$P$_2$O$_7$ (namely TPD) was synthesized then characterized for the immobilization of actinides [15,17]. Among its interesting properties, we can report its very low dissolution rate and its capacity to incorporate large amounts of tetra-

valent actinides. Indeed, the replacement of Th^{4+} by large amounts of tetravalent cations like U^{4+}, Np^{4+} or Pu^{4+} in the TPD structure was successfully obtained [18–20] leading to the formation of solid solutions of the formula Th$_{(4-x)}$M$_x$(PO$_4$)$_4$P$_2$O$_7$ where M corresponds to the tetravalent actinide. These solid solutions were called TUPD for U^{4+}, TNpPD for Np^{4+} and TPuPD for Pu^{4+}. We also proved that the immobilization of trivalent actinides, like ^{241}Am or ^{244}Cm, in the TPD structure was possible only in very small quantities [21].

One of the main factors which could affect the safety of the nuclear waste storage in geological repository is the groundwater infiltration leading to the contact between the matrix and a given solution. In this context, we examined the capability of TPD samples, doped or not with radionuclides, and of the associated solid solutions to resist to aqueous corrosion then to avoid the migration of radionuclides to the biosphere. We report here the results of the leaching tests performed on TPD doped with Am^{3+} or Cm^{3+} and on TPuPD solid

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solutions. This paper is dedicated to the dissolution of these compounds from a kinetic point of view. The dissolution rates were determined for each acidic and basic media. We especially focused our attention on the influence of the pH on the dissolution rate. From these results, the extrapolation of the dissolution rate in neutral medium is given. The second part of this paper is dedicated to the thermodynamic aspect of the dissolution of TPD and to the identification of some thermodynamic constants associated to the thermodynamic equilibria occurring during the dissolution.

2. Experimental

2.1. Chemicals and apparatus

All the chemicals used during the synthesis and the leachate analyses were of 'pro-analysis' quality. They were from Merck, Prolabo and Fluka. The thorium chloride solution and the thorium nitrate pentahydrate salt were from Rhône Poulenc (La Rochelle, France). The [241]Am and [244]Cm solutions were radiochemically purified in the Nuclear Physics Institute of Orsay before their use for the sample preparation.

The high temperature treatment was performed in an ADAMEL FR20 furnace in alumina boats or crucibles up to 1050 °C with heating rates of 2–5 °C min^{-1}. X-ray powder diffraction diagrams were collected with a Philips PW 1050/70 diffractometer using Cu K$_\alpha$ rays ($\lambda = 1.5418$ Å) or a Jobin Yvon CGR using Cu K$_{\alpha 1}$ ray ($\lambda = 1.5406$ Å).

High density polyethylene containers were chosen for making the leaching experiments at room temperature. We checked that, in the conditions of leaching tests, less than 1% of the total dissolved elements is adsorbed onto the surface of the containers.

2.2. Synthesis

In our previous publications, we already reported several ways of preparation of the TPD based on wet and dry chemical methods [15,16]. This compound was synthesized after heating at high temperature (1100–1350 °C) in air or under inert conditions considering an initial mole ratio $r = Th/PO_4$ equal to 2/3 [15,16,22]. After heating, the solid was always well crystallized, homogenous and single phase as already shown from EPMA experiments [23].

Some of the samples used for this study were solid solutions of TPuPD (two kinds of solids were prepared with 6.4 and 16.1 wt% of [239]Pu in the solid). We also prepared samples of TPD doped with Am^{3+} or Cm^{3+} in similar conditions. These solids were obtained from a mixture of concentrated thorium nitrate (1.5–2 M), nitrate solution containing the given actinide and concentrated phosphoric acid (5 M). The mixture was slowly evaporated between 100 and 200 °C, ground in ethanol then heated first at 400 °C for 2 h then up to 1050 °C for 14 h in air, in alumina nacelles (heating rate of 3–5 °C min^{-1}). The solids obtained were analyzed using XRD in order to check the absence of secondary phases and the degree of crystallinity of the compound. The details concerning the specific activity of the solid synthesized are gathered in Table 1.

2.3. Leaching tests procedure and analysis of the leachate

Prior to making leaching experiments, all the samples were washed in order to avoid any perturbation due to the presence of crystal defects, minor phases or small particles which could produce, as instance, large amounts of colloids during the first days of leaching tests. This washing step was performed at 25 °C for 10–25 days in 10^{-1}–10^{-4} M HNO$_3$, HClO$_4$ or in NaOH.

For each dissolution curve, the leaching tests were achieved by mixing 200 mg of powder with 10 ml of solution. The samples were kept under agitation during all the dissolution tests (from few months to several years). In order to have a better understanding of the kinetic law of the dissolution process and to increase the dissolution rates, several leaching tests were performed in acidic media (10^{-1}–10^{-4} M HNO$_3$) or in basic media (10^{-1}–10^{-4} M NaOH). For all the experiments, the ionic strength was kept constant ($I = 0.1$ M) by addition of NaClO$_4$ or NaNO$_3$.

Table 1
Specific activities of TPD samples doped with [241]Am or [244]Cm

Solid	Total activity (MBq)	Specific activity (MBq g^{-1})	Mole loading (%)
TPD: [244]Cm	1.4 to 8.5	5.7 to 33.9	0.29×10^{-3} to 1.72×10^{-3}
TPD: [241]Am	1.8 to 9.3	7.2 to 37.2	0.88×10^{-2} to 4.50×10^{-2}
Th$_{3.6}$Pu$_{0.4}$P$_6$O$_{23}$	33.1 (α) 39.6 (β^-)	1.7×10^2 (α) 2.0×10^2 (β^-)	10
Th$_3$PuP$_6$O$_{23}$	82.5 (α) 98.7 (β^-)	4.1×10^2 (α) 4.9×10^2 (β^-)	25

Before each measurement, the liquid and solid phases were separated by centrifugation at 2500 rpm for 15–30 min then at 13 000 rpm for 15–30 min. The activity of actinide released in the leachate was measured by photon electron rejecting alpha liquid scintillation (PER-ALS) spectrometry using 1% of the total sample volume and considering the optimal conditions of extraction for each actinide measured [24,25]. This small volume was renewed by fresh solution and we considered that, in these conditions, the system solution-solid was not modified. The phosphorus concentrations were determined by ICP-OES using an Ultima apparatus from Jobin Yvon. For these determinations, the value considered was an average of at least three measures.

3. Theoretical section

In our previous works, we already reported the main notions required to have a good description of the TPD dissolution [26,27]. A summary of these expressions is given here.

3.1. Definition and expression of the normalized mass loss and dissolution rate

The leachability of the element i from a mineral can be described by its normalized mass loss, $N_L (i)$ $(\mathrm{g\,m^{-2}})$, which is defined by the relation [26–28]:

$$N_L(i) = \frac{\Delta m_{i\ \mathrm{sol}}}{f_i S}, \tag{1}$$

where $\Delta m_{i\ \mathrm{sol}}$ is the total amount of the element i released into the solution (g), S is the solid area (m²) and f_i is the mass ratio of i in the solid. For a congruent dissolution (all the elements are dissolved with the same dissolution rate and do not form any neoformed phases in the back-end of the dissolution process), the mass of matrix dissolved can be calculated directly from the concentration of the element measured in the leachate. Thus, the expression of the dissolution rate can be deduced from the evolution of the normalized mass loss. Using the approach described by Lasaga [28], the dissolution rate of the solid, R_L $(\mathrm{g\,m^{-2}\,d^{-1}})$ can be written as

$$R_L = \frac{1}{S}\frac{dm}{dt} = \frac{1}{f_i S}\frac{dm_i}{dt} = \frac{dN_L(i)}{dt}, \tag{2}$$

when the dissolution is congruent. From literature, it appears that the dissolution rate (i.e., the slope obtained when plotting the normalized mass loss versus the leaching time) is constant for several minerals [29–33]. In acidic medium, the dissolution rate R_L is usually noted R_H in acidic media and R_{OH} in basic media. In the case of unwashed minerals, parabolic rate laws were often ob-

served because of the heterogeneity in the surface properties (various phases, various particle sizes, crystal defects). As already discussed, we avoided this phenomenon by washing the solid prior to perform the leaching tests. For each solid considered, the actinide release during this washing step is reported in Table 2. We verified that this release was low for tetravalent plutonium as it was expected from the preparation of solid solutions, but also for the trivalent actinides considered (americium and curium). By making a lot of leaching experiments, we checked that this release was not reproducible and mainly dependent on the chemical conditions of preparation even for well crystallized and single phase compounds. This phenomenon was also observed for many kinds of solids such as oxides, phosphates, silicates, ... It is mainly due to the difficulty to obtain experimentally pure stoichiometric compound as close as possible to that given by the chemical formula.

3.1.1. Influence of the proton concentration on the dissolution rate

Several authors investigated the dissolution reactions between minerals and aqueous solutions from a kinetic point of view [34–37]. The dependence of R_H on the pH was experimentally demonstrated as follows:

$$R_H = k_T'(\gamma_{H_3O^+}[H_3O^+])^n = k_{T,I}'[H_3O^+]^n. \tag{3}$$

In this expression, $k_{T,I}'$ is expressed in $\mathrm{g\,m^{-2}\,d^{-1}}$ and represents the apparent dissolution rate constant for pH < 7, n is the partial order related to the proton concentration and $\gamma_{H_3O^+}$ corresponds to the proton activity coefficient. $k_{T,I}'$ is independent of the pH (its value corresponds to pH = 0) but is dependent on the temperature, the medium and the ionic strength.

For most of the minerals, the experimental n values are usually in the range $0 < n < 1$ as reported in previous published works [37–40]. Several explanations based on the transition state theory [28,36] or on the coordination chemistry involving surface proton concentration [34,35,37] were given. Furthermore, the n value depends on the kinetic mechanism but does not correspond to the

Table 2
Actinide release during the washing step (10^{-1} M HNO₃ or HClO₄, $\theta = 25$ °C)

Solid	Washing time (days)	$N_L(\mathrm{An})$ $(\mathrm{g\,m^{-2}})$	Activity release (%)
TPD: ²⁴⁴Cm	10	1.2×10^{-2}	2.6
TPD: ²⁴¹Am	25	4×10^{-3}	0.9
Th₃.₆Pu₀.₄P₆O₂₃	9	1×10^{-4}	8.7×10^{-2}
Th₃PuP₆O₂₃	15	6×10^{-4}	1.0×10^{-1}

number of protons involved in the global reaction of dissolution.

3.1.2. Influence of the hydroxide ions concentration on the dissolution rate

Many authors also studied the influence of pH on the dissolution rates in basic media. A relation similar to that obtained in acidic media was thus established related to the hydroxide ions concentration:

$$R_{OH} = k''_T \times (a_{OH^-})^m = k''_{T,I}[OH^-]^m, \tag{4}$$

where $k''_{T,I}$ represents the apparent dissolution rate constant; a_{OH^-} is the hydroxide ion activity and m corresponds to the partial order related to the hydroxide ions concentration. $k''_{T,I}$ is independent of pH (it corresponds to the dissolution rate at pH = 14) but dependent on the temperature, the medium and the ionic strength I. For most of the minerals, the m values reported in the literature were found between 0 and 1 [33,34].

4. Results and discussion

4.1. Kinetic study of the TPD dissolution

4.1.1. Influence of the proton concentration on the dissolution rate

4.1.1.1. Dissolution of TPD and associated solid solutions in acidic media. We first performed experiments at 25 °C on pure TPD samples in 10^{-1}–10^{-4} M HNO_3. In this series of experiments, the phosphate and thorium ion concentrations were determined by ICP-OES. For leaching tests performed in 10^{-3} and 10^{-4} M HNO_3, the

concentrations were always in the range or lower than the detection limit of the analytical method considered. The results obtained in 10^{-1}–10^{-2} M HNO_3 are given in Fig. 1.

Although it was expected from Eqs. (1) and (2), we did not observe a significant increase of the normalized mass loss calculated from thorium or phosphate ions concentrations with the leaching time. In these conditions, these data did not allow to determine the dissolution rates of TPD. As reported in a previous publication [26], the almost constant values obtained were assigned to the rapid saturation of the leachate by the precipitation of secondary phase(s) containing thorium and phosphorus ions. The final neoformed phase was identified as $Th_2(PO_4)_2(HPO_4), xH_2O$ [26] by dissolving pure TPD in 5 M HNO_3 at 90 °C. Its complete characterization is now under progress from a crystallographic point of view in order to check if the solid is single phase and contains hydrogenphosphate or consists of a mixture of several compounds with very small grains size (30 nm $< \varnothing < 5$ μm). Moreover, the first observation of TPD leached in 10^{-1} M HNO_3 for 423 days by transmission electron microscopy pointed out the existence of an amorphous layer at the surface of TPD. Although the characterization of the layer was difficult to realize, we checked that the mole ratio $Th/PO_4 = 2/3$ determined was consistent with the proposed formula. Since the normalized mass loss calculated from the thorium release, $N_L(Th)$, is almost the same than that determined from the phosphorus amount in the leachate, $N_L(P)$, (i.e., $Th/PO_4 = 2/3$ in solution), the TPD dissolution appeared incongruent (precipitation of neoformed phase) but stoichiometric ($N_L(Th) = N_L(P)$) in these operating conditions. In these
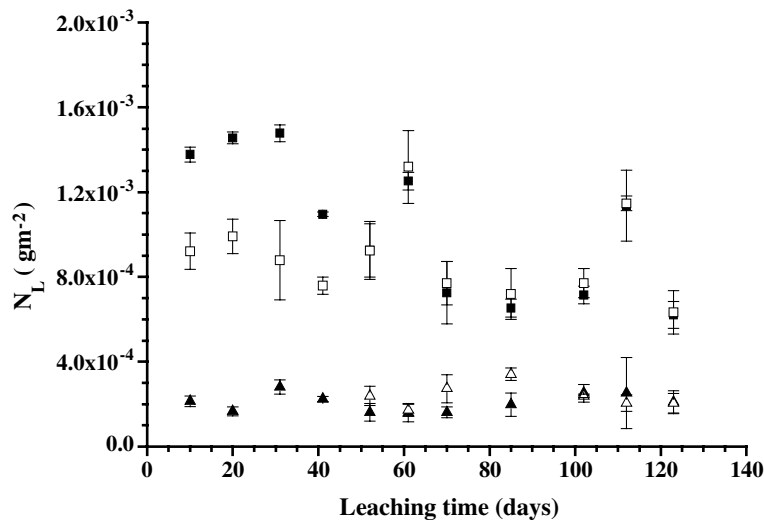

Fig. 1. Evolution of $N_L(Th)$ (solid symbols) and $N_L(P)$ (open symbols) in HNO_3 10^{-1} M (■/□) and 10^{-2} M (▲/△) (25 °C, $I = 0.1$ M).

conditions, we followed the TPD dissolution by using radiotracers such as [241]Am and [244]Cm radionuclides which do not precipitate with phosphate ions in this pH range.

4.1.1.2. Dissolution of TPD doped with trivalent actinides in acidic media. Owing to the precipitation of thorium during the TPD dissolution tests in acidic media, we examined the behavior of the solids doped with trivalent actinides and determined the corresponding dissolution rates. This study was developed in 10^{-1}–10^{-4} M HNO$_3$ for samples doped with [241]Am or in 10^{-1}–10^{-4} M HClO$_4$

for the solids doped with [244]Cm. For these solids, the evolution of the normalized mass losses was studied up to 800–900 days of leaching time (Figs. 2 and 3). For both actinides and for pH $\leqslant$ 3, we observed that the normalized mass loss increased linearly with the leaching time in the first part of the dissolution curves. Thus, it was possible to determine the corresponding dissolution rates, R_H, by linear regression of the experimental data. We observed that the normalized mass loss increases with the acidity of the leachate (Table 3) as expected from literature [34,37]. All the R_H values were found between 1.2×10^{-5} and 4.4×10^{-9} g m^{-2} d^{-1} which
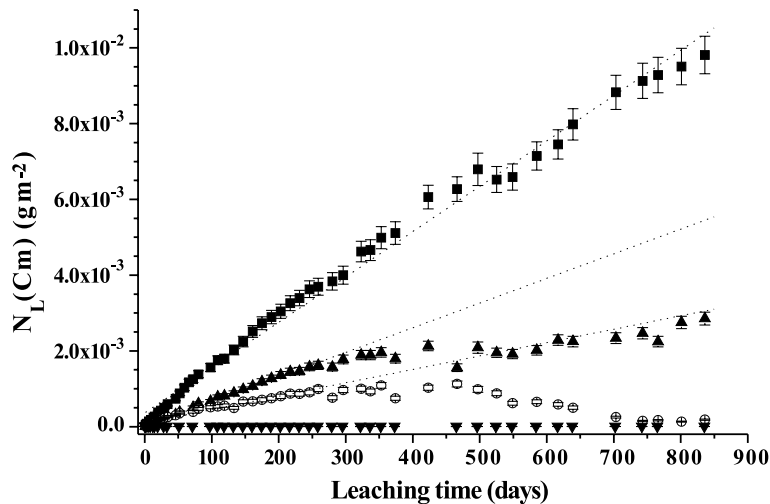

Fig. 2. Evolution of N_L(Cm) for TPD doped with [244]Cm leached in 10^{-1} M (■); 10^{-2} M (▲); 10^{-3} M (○) and 10^{-4} M (▼) HClO$_4$ ($\theta = 25$ °C, $I = 0.1$ M).
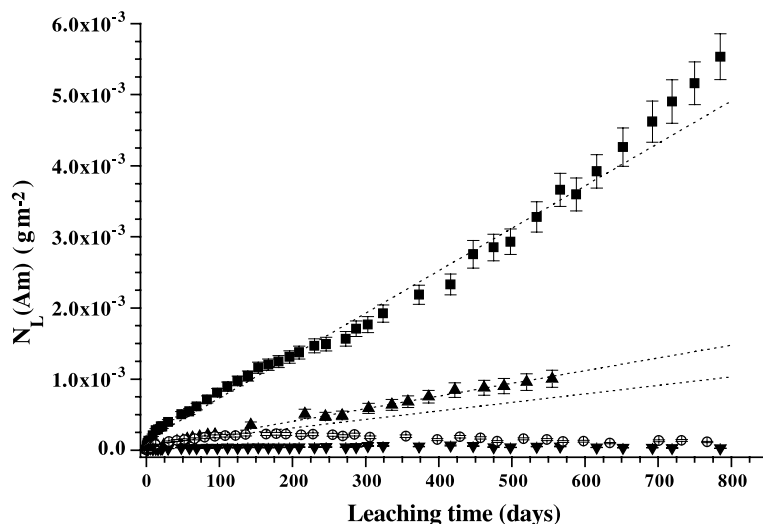

Fig. 3. Evolution of N_L(Am) for TPD doped with [241]Am leached in 10^{-1} M (■); 10^{-2} M (▲); 10^{-3} M (○) and 10^{-4} M (▼) HNO$_3$ ($\theta = 25$ °C, $I = 0.1$ M).

Table 3
Dissolution rates of TPD: An^{3+}, R_H, in acidic medium ($\theta = 25$ °C; $I = 0.1$ M)

$[H_3O^+]$	Dissolution rate R_H ($g\,m^{-2}\,d^{-1}$)[a]	
	TPD: ^{244}Cm	TPD: ^{241}Am
10^{-1} M[b]	$(1.2 \pm 0.1) \times 10^{-5}$	$(5.9 \pm 0.1) \times 10^{-6}$
10^{-2} M[b]	$(6.0 \pm 0.2) \times 10^{-6}$	$(1.84 \pm 0.04) \times 10^{-6}$
10^{-3} M[b]	$(2.9 \pm 0.2) \times 10^{-6}$	$(1.18 \pm 0.04) \times 10^{-6}$
10^{-4} M[b]	$(4.4 \pm 0.6) \times 10^{-9c}$	$(6.5 \pm 0.6) \times 10^{-8c}$
n	0.31 ± 0.01	0.35 ± 0.04
$k'_{298\ K,0.1\ M}$ ($g\,m^{-2}\,d^{-1}$)	$(2.4 \pm 0.1) \times 10^{-5}$	$(1.2 \pm 0.3) \times 10^{-5}$

[a] Calculated on actinide release $N_L(An^{3+})$.

[b] Leaching tests performed in $HClO_4$ for curium and in HNO_3 for americium.

[c] Dissolution rates not significant due to the rapid saturation of the leachate.

confirms the very good durability of TPD to aqueous corrosion. Moreover, for both kinds of solids, we observed the linear decrease of $\log(R_H)$ as a function of $\log([H_3O^+])$ which is consistent with Eq. (3). The corresponding values of the partial order related to the proton concentration, n, as well as the dissolution rate constant (at pH $= 0$), $k'_{298\ K,0.1\ M}$, were found to be equal to $n = 0.31 \pm 0.01$ and $k'_{298\ K,0.1\ M} = (2.4 \pm 0.1) \times 10^{-5}$ $g\,m^{-2}\,d^{-1}$ for solids doped with ^{244}Cm and to $n = 0.35 \pm 0.04$ and $k'_{298\ K,0.1\ M} = (1.2 \pm 0.3) \times 10^{-5}$ $g\,m^{-2}\,d^{-1}$ for that doped with ^{241}Am. The n values are in good agreement with that reported for several minerals [34,37,41] and very close to that calculated in basic media as it will be mentioned in the following sections, which is also consistent with literature [33,34,42].

All the dissolution rates determined in 10^{-4} M $HClO_4$, 10^{-4} M HNO_3 or in distilled water were not significant due to the rapid saturation of the leachate (Fig. 4). In these conditions, the saturation of the leachate could be probably due to the precipitation of actinide phosphate hydrates (amorphous form or crystallized such as rhabdophane [43,44]) in the back – end of the TPD dissolution. This saturation was observed when the leaching tests of the samples doped with trivalent actinides were longer than 200–400 days in 10^{-3} M and 10^{-2} M $HClO_4$ or HNO_3. Indeed, in these media, a strong decrease of the normalized mass loss was observed in the second part of the dissolution curves for pH $\leqslant 3$ which confirmed that the concentration of trivalent actinides was controlled in the leachate by thermodynamic equilibria. Owing to the speciation of the phosphate species and to the release of ions in these media, the solubility product was reached for leaching times longer than in 10^{-4} M $HClO_4$ or HNO_3.

4.1.1.3. Dissolution of TUPD or TPuPD solid solutions in acidic media. In our previous published paper, we already reported the behavior of tetravalent actinides like uranium when leaching TUPD solid solutions in 10^{-1}–10^{-4} M HNO_3 at 90 °C. The partial order related to the proton concentration and the apparent dissolution rate constant at pH $= 0$ were found to 0.40 ± 0.02 and to $k'_{363\ K,0.1\ M} = (2.8 \pm 0.7) \times 10^{-4}$ $g\,m^{-2}\,d^{-1}$. Both values are consistent with that determined for TPD doped with trivalent actinides at room temperature.
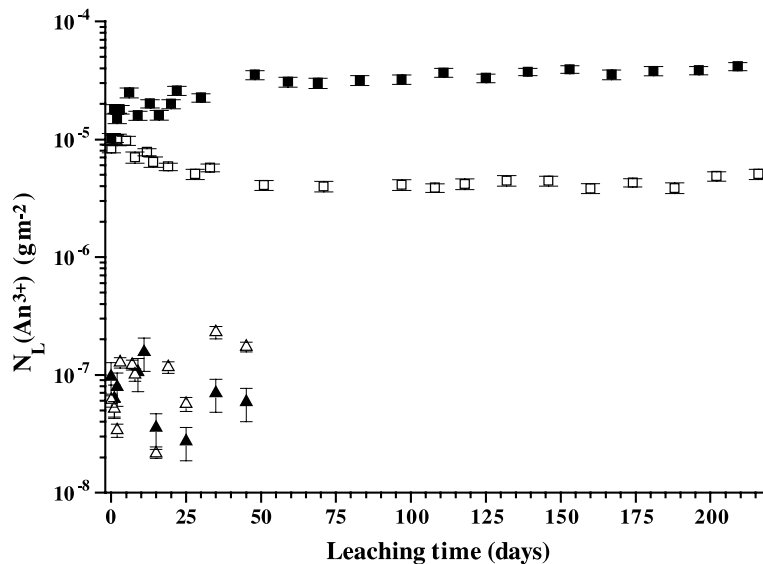

Fig. 4. Evolution of N_L (An^{3+}) for TPD doped with An^{3+} leached in 10^{-4} M $HClO_4$ or HNO_3 (■: ^{241}Am; □: ^{244}Cm) or in distilled water (▲: ^{241}Am; △: ^{244}Cm) ($\theta = 25$ °C, $I = 0.1$ M).

Leaching tests were also performed for TPuPD solid solutions in order to compare the results obtained with that of pure TPD or TPD doped with trivalent actinides. Two kinds of thorium–plutonium (IV) phosphate diphosphate solid solutions (TPuPD): $Th_{3.6}Pu_{0.4}(PO_4)_4P_2O_7$ (10 mol.% i.e., 6.4 wt% of ^{239}Pu in the solid) and $Th_3Pu(PO_4)_4P_2O_7$ (25 mol.% i.e., 16.1 wt% of ^{239}Pu in the solid) were leached in distilled water at room temperature. The linear increase of the normalized mass loss as a function of the leaching time was also observed for these solids. In these conditions, the dissolution rates reached $(2.4 \pm 0.1) \times 10^{-6}$ and $(2.6 \pm 0.1) \times 10^{-6}$ $g\,m^{-2}\,d^{-1}$, respectively while the pH measured at equilibrium decreased to about 4.0 due to radiolytic effects. These values also revealed that the total amount of plutonium in the solid did not play any role on the TPD dissolution. For each solid, we observed the saturation of the leachate after 700 days of leaching time. It could be due to the neoformation of a plutonium phosphate phase.

Several leaching tests of $Th_{3.6}Pu_{0.4}(PO_4)_4P_2O_7$ were also performed in acidic media (10^{-1}–10^{-4} M HNO$_3$). The evolution of the normalized mass loss is not linear probably because of the rapid precipitation of tetravalent plutonium with phosphate ions. Furthermore, all the normalized mass losses are comparable for the pH studied. The linear regression of the experimental data for leaching times between 150 and 350 days led to the dissolution rates and to the $k'_{T,I}$ and n values reported in Table 4. The first results concerning these experiments showed that the n value (0.13) is lower than that determined for pure TPD (0.31–0.35) or for TUPD solid solutions (0.40). This low n value suggested that the saturation of the leachate was probably reached. This point of view was confirmed by the apparition of a plateau for leaching times higher than 350 days in these

acidic media. In these conditions, all the dissolution rates correspond to apparent rates since they are perturbed by the precipitation of neoformed phases. In order to prove this saturation, the solid leached in 10^{-1} M HNO$_3$, was washed for 1 hour in 1 M HNO$_3$ at room temperature. In these conditions, the average value of the dissolution rate increased from 5.8×10^{-6} up to $(9.4 \pm 0.3) \times 10^{-6}$ $g\,m^{-2}\,d^{-1}$ which clearly confirms that a significant part of the plutonium was precipitated in neoformed phases in these operating conditions. A complementary study, based on leaching tests in dynamic conditions, is now under progress to avoid this problem and to give accurate dissolution rate values.

4.1.2. Influence of the hydroxide ions concentration on the dissolution rate

4.1.2.1. TPD dissolution in basic media. Several leaching tests were also performed in basic media (10^{-1}–10^{-4} M NaOH) and under inert atmosphere (argon) in order to avoid any influence of carbonate ions in the solutions. Although, the thorium concentration in the leachate was found to be lower than the detection limit of the apparatus, the normalized mass loss calculated from the phosphate amount in the leachate, $N_L(P)$, increased linearly with the leaching time (Fig. 5). This linear increase showed the absence of precipitation for phosphate ions in these experimental conditions. Taking into account the values obtained for $N_L(P)$ and $N_L(Th)$, the mole ratio $Th/PO_4 = 2/3$ of the solid is not conserved in the leachate which clearly shows that the TPD dissolution becomes incongruent in these media. Moreover, thorium ions were certainly precipitated as a thorium hydroxide $Th(OH)_4$ [45] or $ThO(OH)_2$ as suggested by literature and by the available thermodynamic data.

As phosphate ions do not precipitate with thorium ions, the dissolution rates were determined for each

Table 4
Dissolution rates of TPuPD, R_H, in acidic medium ($\theta = 25\ °C$, $I = 0.1$ M)

Leachate	Dissolution rate R_H $(g\,m^{-2}\,d^{-1})$[a]	
	$Th_{3.6}Pu_{0.4}(PO_4)_4P_2O_7$	$Th_3Pu(PO_4)_4P_2O_7$
10^{-1} M HNO$_3$	$(5.8 \pm 0.3) \times 10^{-6}$	ND
10^{-2} M HNO$_3$	$(4.3 \pm 0.4) \times 10^{-6}$	ND
10^{-3} M HNO$_3$	$(3.5 \pm 0.2) \times 10^{-6}$	ND
10^{-4} M HNO$_3$	$(2.4 \pm 0.1) \times 10^{-6}$	ND
Distilled water[b]	$(2.4 \pm 0.1) \times 10^{-6}$	$(2.6 \pm 0.1) \times 10^{-6}$
Mineral water[c]	ND	$(4.8 \pm 0.3) \times 10^{-8}$ (pH = 7.0)
		$(1.5 \pm 0.1) \times 10^{-6}$ (pH = 4.5)
n	0.13 ± 0.02	0.40 ± 0.03
$k'_{298\ K, 0.1\ M}$ $(g\,m^{-2}\,d^{-1})$	$(7.8 \pm 0.9) \times 10^{-6}$	$(1.2 \pm 0.3) \times 10^{-5}$

ND: Not determined.
[a] Calculated on plutonium release $N_L(Pu)$.
[b] pH equal to 3.9 at equilibrium due to radiolytic effects.
[c] pH equal to 7 during the first 200 days of leaching then to 4.5 after 450 days.
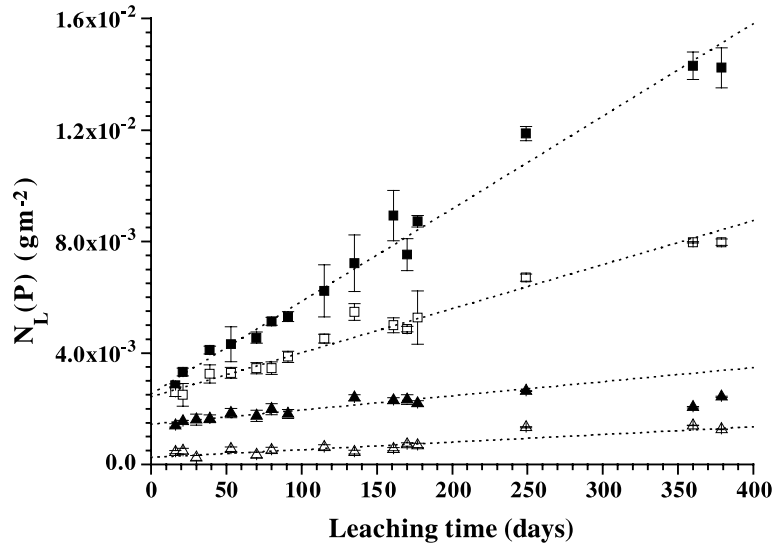
Fig. 5. Evolution of $N_L(P)$ in 10^{-1} M (■), 10^{-2} M (□), 10^{-3} M (▲) and 10^{-4} M (△) NaOH (25 °C, $I = 0.1$ M).

Table 5
Dissolution rates of TPD, R_{OH}, in basic medium ($\theta = 25$ °C, $I = 0.1$ M)

Leaching solution	Dissolution rate: R_{OH} $(g\,m^{-2}\,d^{-1})$[a]
10^{-4} M NaOH	$(2.8 \pm 0.4) \times 10^{-6}$
10^{-3} M NaOH	$(4.9 \pm 0.2) \times 10^{-6}$
10^{-2} M NaOH	$(1.5 \pm 0.1) \times 10^{-5}$
10^{-1} M NaOH	$(3.3 \pm 0.2) \times 10^{-5}$
m	0.37 ± 0.03
$k''_{298\ K,0,1\ M}$ $(g\,m^{-2}\,d^{-1})$	$(7.8 \pm 1.9) \times 10^{-5}$

[a] Calculated on phosphorus release $N_L(P)$.

medium from the evolution of $N_L(P)$ (Table 5). According to Eq. (4) and to the regression of the experimental data when plotting $\log(R_{OH})$ versus $\log([OH^-])$, the partial order related to the hydroxide ion concentrations, m, was found to be equal to 0.37 ± 0.03 while the corresponding apparent dissolution rate constant at pH = 14, $k''_{298\ K,0,1\ M}$, was $(7.8 \pm 1.9) \times 10^{-5}$ $g\,m^{-2}\,d^{-1}$. The m value is of the same order of magnitude to that obtained for n in acidic media and to that mentioned in literature for several minerals and materials [33,34,42]. Moreover, the low apparent dissolution rate constant measured in basic media, $k''_{T,I}$, confirms the very good chemical durability of TPD already shown in acidic media.

4.1.3. Extrapolation of the dissolution rate of TPD in neutral medium

If we do not consider the problems occurring when leaching solid solutions of TPuPD which were probably due to the rapid precipitation of secondary phase(s) as

already discussed, the partial orders related to the protons or hydroxide ion concentrations were found between 0.3 and 0.4 for leaching tests performed between pH = 1 and pH = 4, and between pH = 10 and pH = 13. From these results (Fig. 6), we extrapolated the dissolution rate when leaching TPD in neutral medium taking into account the contribution of protons and hydroxide ions during the TPD dissolution process:

$$R_L = R_H + R_{OH} = k'_{T,I}[H_3O^+]^n + k''_{T,I}[OH^-]^m. \qquad (5)$$

The calculated dissolution rate at pH = 7 was found between 2.4×10^{-7} and 3.6×10^{-7} $g\,m^{-2}\,d^{-1}$ at room temperature. As the apparent activation energy of the reaction of the TPD dissolution was already evaluated to $E_A = (42 \pm 3)$ kJ mol^{-1} [26], this value was found between 5×10^{-6} and 7.5×10^{-6} $g\,m^{-2}\,d^{-1}$ at 363 K which remains very low by comparison to the other ceramics studied in the same objective (Table 6) [46–51].

We attempted to verify the behavior of TPD and associated solid solutions in neutral media by leaching thorium–plutonium (IV) phosphate diphosphate solid solutions in the French mineral water Volvic™ (pH = 7.0, $\theta = 25$ °C) (Fig. 7). During the first 300 days of leaching, the dissolution rate was found to $(4.8 \pm 0.3) \times 10^{-8}$ $g\,m^{-2}\,d^{-1}$ while the pH of the solution remained equal to 7. This value is lower to that extrapolated at pH = 7.0 (2.4×10^{-7} to 3.6×10^{-7} $g\,m^{-2}\,d^{-1}$). That was probably due to the presence of several ions such as calcium (2.5×10^{-4} M), magnesium (2.5×10^{-4} M), sulfate (7.2×10^{-5} M), or hydrogencarbonate (1.1×10^{-3} M) which concentrations could be sufficient to decrease the dissolution rate of TPuPD solid solutions by interacting at the surface of the solid as it was already
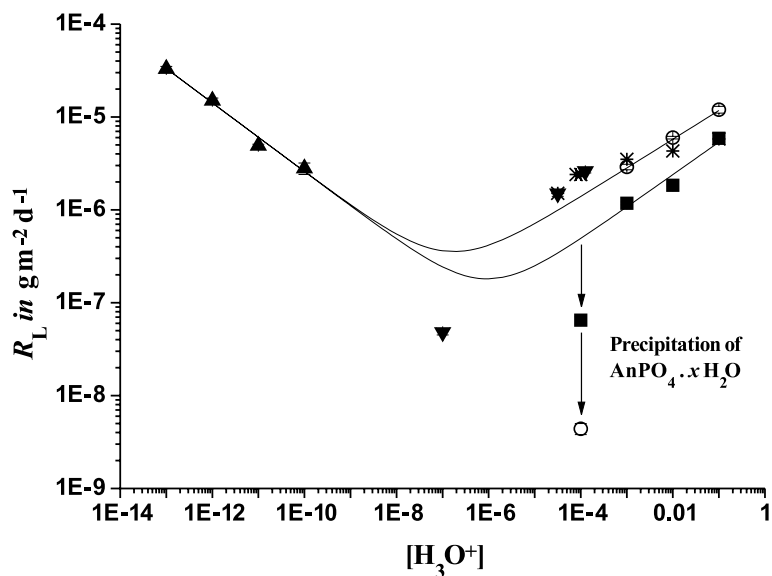
Fig. 6. Variation of $\log(R_L)$ versus $\log[H_3O^+]$ for pure TPD (▲), TPD doped with [241]Am (■) or [244]Cm (○), TPuPD solid solutions ($x = 0.4$: ✳ and $x = 1.0$: ▼) (25 °C, $I = 0.1$ M).

Table 6
Dissolution rates of several matrices in neutral media ($\theta = 25$ °C)

Matrix	Dissolution rate ($g\,m^{-2}\,d^{-1}$)	Leaching temperature °C
Monazite (LaPO$_4$) [46]	1.2×10^{-6a}	90
TPD (this work)	3×10^{-7}	25
Apatite [47]	5×10^{-6}	90
	2×10^{-3}	25
Zircon [48]	4.6×10^{-5}	90
Zirconolite [49]	10^{-4} then 10^{-5}	90
Pyrochlore [50]	10^{-5}–10^{-3}	90
Synroc [51]	10^{-4}–10^{-3}	70

[a] The precipitation of LaPO$_4$, xH$_2$O could be already observed in the operating conditions.

shown when leaching pure UO$_2$ crystals [52]. This point is now under study. For higher leaching times, the pH of the leachate decreases slowly down to 4.5 owing to radiolytic effects leading to the increase of the dissolution rate value: $(1.51 \pm 0.08) \times 10^{-6}$ $g\,m^{-2}\,d^{-1}$ which is in good agreement with that determined in 10^{-4} M HNO$_3$.

According to all the results already reported, the n values are consistent for the different actinides considered. The partial order related to the proton or hydroxide ions and the apparent rate constants are close whatever the radionuclide studied (U, Pu, Am, Cm). Moreover, the retention properties of TPD regarding to all these radionuclides are very good even in acidic or basic media. On this basis and considering the R_H values extrapolated in neutral medium, the leaching time required to observe the release of 1 mg of plutonium in the leachate when leaching 1 m^2 of Th$_{3.6}$Pu$_{0.4}$(PO$_4$)$_4$P$_2$O$_7$ should exceed 210 years at room temperature and 10 years at 363 K in the absence of neoformed phases. This time could be significantly increased by the formation of secondary phases in the back – end of the dissolution process which precipitation is almost guaranteed.

4.2. Thermodynamic study of the TPD dissolution: determination of the solubility products of the neoformed phases

As we showed in the previous section, the concentrations of the species present in solution are controlled by the kinetic of dissolution of the TPD in the first part of the leaching curves. Nevertheless, in a second step, they seem to be controlled by the establishment of thermodynamic equilibrium associated to the precipitation of neoformed phases.

4.2.1. Neoformation of Th$_2$(PO$_4$)$_2$(HPO$_4$), xH$_2$O
In a previous publication [26], we identified the secondary phase precipitated during the TPD dissolution in very acidic medium (5 M HNO$_3$) as Th$_2$(PO$_4$)$_2$(HPO$_4$), xH$_2$O (TPHP). In this medium, the solubility product was not estimated owing to the probable coexistence of both amorphous and crystallized TPHP (which differ from the numbers of water molecules, this amount degrading the global crystallization state of the solid).
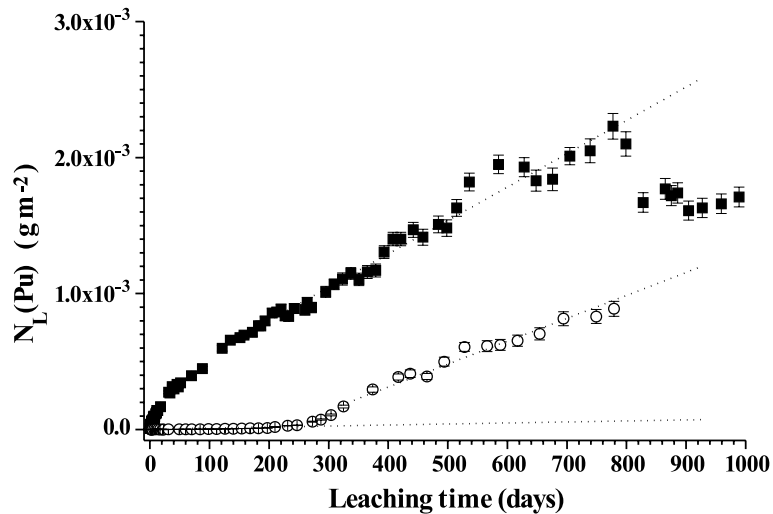
Fig. 7. Evolution of N_L(Pu) for $Th_3Pu(PO_4)_4P_2O_7$ in distilled water (■) or in Volvic™ French mineral water (○).

For leaching experiments achieved at 25 °C in 10^{-1}–10^{-4} M HNO_3, we determined the concentrations product $[Th^{4+}]^2[PO_4^{3-}]^2[HPO_4^{2-}]$ associated to the precipitation of TPHP. The concentrations were determined taking into account the speciation of phosphate and thorium using the program CHESS while the activity coefficient were estimated considering the specific interaction theory [53,54]. The values of the conventional solubility product, calculated in several media, were consistent and led to the mean value $K_{s,0}^{\circ*} \approx 10^{-67}$ which confirms the very low solubility of this solid. A detailed study on this point is now under progress. The main results (crystal structure determination, preparation of the solid by over and undersaturation conditions, ...) will be published soon.

4.2.2. Neoformation of trivalent actinide phosphate hydrates

During the leaching tests of TPD samples doped with ^{244}Cm in 10^{-2}–10^{-3} M HNO_3, the increase of the normalized mass loss is not linear after 300 days of leaching time (Fig. 2). The same observation can be done for samples of TPD doped with ^{241}Am after 150 days of leaching in 10^{-3} M and in 10^{-4} M HNO_3 (Figs. 3 and 4). As already mentioned, these observations indicated the precipitation of neoformed phase containing the trivalent actinide. Moreover, taking into account the species present in solution, an hydrated trivalent actinide phosphate, of formula $AnPO_4$, xH_2O could be formed. Nevertheless, owing to the very small amount of solid obtained (the high specific activity of both ^{241}Am or ^{244}Cm constraining to work with small amounts of radionuclides), its complete characterization by conventional techniques remained impossible. For this reason,

we identified this phase from the comparison of its solubility product with that mentioned in literature [43,44].

We calculated the solubility product of $CmPO_4$, xH_2O and $AmPO_4$, xH_2O from the concentrations of trivalent actinides determined by PERALS spectrometry. Phosphate ions concentrations were estimated from the dissolution rates of pure TPD in the same leaching conditions. Therefore, the calculation of the solubility product took into account the precipitation of $Th_2(PO_4)_2(HPO_4)$, xH_2O as already mentioned in our published works [26]. The notion of conventional solubility product was used here because americium phosphate hydrate could be partially amorphous in our experimental conditions [44]. The concentrations of free ions An^{3+} and PO_4^{3-} were calculated taking into account the speciation of species and using the program CHESS [53]. Furthermore we used the specific interaction theory [54] to extrapolate the conventional solubility product at a zero ionic strength from the data collected at ionic strength equal to 10^{-1} M:

$$K_{s,0}^{\circ*} = a_{An^{3+}} \times a_{PO_4^{3-}}$$
$$= [An^{3+}] \times \gamma_{An^{3+}} \times [PO_4^{3-}] \times \gamma_{PO_4^{3-}}. \quad (6)$$

As presented in Table 7, the conventional solubility products are in rather good agreement with those reported by Rai et al. [44] for the hydrated americium phosphate. In fact, the three orders of magnitude observed can be due to the uncertainties associated to the americium and phosphate ion concentrations, to the values of the specific interaction coefficients considered and to the degree of crystallinity of the solid neoformed. No thermodynamic data are available for curium compound

Table 7
Conventional solubility product values of $AmPO_4, xH_2O$ or $CmPO_4, xH_2O$ ($\theta = 25$ °C)

Sample	Medium	$\log[An^{3+}][PO_4^{3-}]$ ($I = 10^{-1}$ M)	$\log K_{s,0}^{\circ *}$
TPD: ^{241}Am	10^{-3} M HNO_3	-25.9 ± 0.1	-27.9 ± 0.1
TPD: ^{241}Am	10^{-4} M HNO_3	-24.9 ± 0.1	-26.9 ± 0.1
Mean value of $\log(K_{s,0}^{\circ *})$ ($AmPO_4, xH_2O$)		-27.4 ± 0.5	
TPD: ^{244}Cm	10^{-2} M $HClO_4$	-27.6 ± 0.1	-29.6 ± 0.1
TPD: ^{244}Cm	10^{-3} M $HClO_4$	-26.8 ± 0.2	-28.8 ± 0.2
TPD: ^{244}Cm	10^{-4} M $HClO_4$	-27.4 ± 0.1	-29.3 ± 0.1
Mean value of $\log(K_{s,0}^{\circ *})$ ($CmPO_4, xH_2O$)		-29.2 ± 0.4	
$AmPO_4, xH_2O$	$I = 0$	–	-24.8 ± 0.6
$CePO_4, PrPO_4,$ $NdPO_4, SmPO_4$ hydrated	$I = 0$	–	-26.3 ± 0.2

but several authors obtained similar values studying the solubility of rare earth phosphates [43,44,55]. Moreover, some amounts of trivalent actinides could also be sorbed on to the surface of the neoformed $Th_2(PO_4)_2$-(HPO_4), xH_2O. This phenomenon is consistent with a precedent study which showed that ^{241}Am can be fixed significantly on amorphous $Th_2(PO_4)_2(HPO_4)$, xH_2O even in 10^{-3}–10^{-4} M HNO_3 [56]. Several experiments are now under progress to confirm the existence of such precipitates.

4.2.3. Neoformation of plutonium phosphate hydrates

In the previous part, we already mentioned that the establishment of thermodynamic equilibria did not allow to determine the dissolution rates with a good accuracy for TPuPD solid solutions. Indeed, for several kinds of leaching tests, we observed the stabilization (or the decrease) of the plutonium amount in the leachate which is not consistent with a pure kinetics of the dissolution process. When the saturation of the leachate is observed, tetravalent plutonium could be precipitated as a plutonium phosphate compound such as $Pu(HPO_4)_2$, xH_2O or $Pu_3(PO_4)_4$, xH_2O as suggested from the literature [57,58], identical to that reported for $Th_3(PO_4)_4$, xH_2O [59,60] or for $U_3(PO_4)_4$, xH_2O [61]. Nevertheless, due to several doubts existing about the real chemical formula of both compounds, the complete characterization of the solids precipitated are now under progress. The calculations of the corresponding solubility products will be performed after this characterization in order to estimate the capability of retention of the tetravalent actinides in the neoformed phases for a long term storage. Complementary experiments will be also performed by leaching TUPD solid solutions in anoxic conditions in order to avoid the oxidation of tetravalent uranium into uranyl ions during the dissolution process and to perform the leaching tests in accurate conditions

to simulate tetravalent plutonium by tetravalent uranium in an underground repository.

5. Conclusion

The dissolution of TPD doped or not with trivalent or tetravalent actinide was studied from a kinetic point of view as a function of the acidity or the basicity of the leachate. The influence of the amount of actinide was also studied. From the evolution of the normalized mass loss of an element present in the initial solid, the normalized dissolution rates were determined. These dissolution rates showed that TPD is very resistant to aqueous corrosion even in acidic media. The partial orders related to the protons in acidic media ($n = 0.31$–0.35) and to the hydroxide ions in basic media are quite similar ($m = 0.37$). Furthermore, the results obtained with the different actinides considered (different weight loading, chemical behavior and oxidation states, ...) were consistent. In some cases, we were able to point out that TPD dissolution was stoichiometric.

We also attempted to determine the solubility products of the neoformed phases which are associated to the saturation of the leachate. For all the actinides studied, these phases were hydrated phosphates solids of very low solubility products. For $AmPO_4, xH_2O$ and $CmPO_4$, xH_2O, the values were found to $\log(K_{s,0}^{\circ *}) = -27.4 \pm 0.5$ and $\log(K_{s,0}^{\circ *}) = -29.2 \pm 0.4$, respectively. They were consistent with that reported in the literature. In these conditions, the actinide concentration in the leachate remains very low even when the initial matrix is partly dissolved. Concerning the neoformed phase obtained when leaching pure TPD and solid solutions of TPuPD in 10^{-1}–10^{-4} M HNO_3, further experiments will be performed soon to have a better characterization of this

solid (thorium phosphate hydrogenphosphate or hydrated thorium phosphate diphosphate).

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