

# Behavior of thorium–uranium (IV) phosphate–diphosphate sintered samples during leaching tests. Part I – Kinetic study

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## Abstract

The dissolution of  $\beta$ -TUPD sintered samples was examined in various conditions of pH, temperature, concentrations of anions in the leachate and leaching flow rates. All the normalized dissolution rates were in the range  $10^{-7}$  to  $10^{-4}$   $\text{g m}^{-2} \text{day}^{-1}$  even in very aggressive media, showing the good resistance of these ceramics to aqueous alteration. The first part of this paper describes several parameters exhibiting a significant influence on the normalized dissolution rate of the pellets prepared. Both the partial order relative to the proton concentration ( $n = 0.39\text{--}0.41$ ) and the apparent activation energy ( $E_{\text{app}} = 49 \text{ kJ mol}^{-1}$ ) were found in good agreement with the data reported for powdered samples showing that the sintering process does not degrade the chemical durability of the ceramics. Moreover, due to the high thermodynamical constant of complexation of phosphate species for tetravalent uranium and thorium, the influence of other ligands such as nitrate, chloride or sulphate on the normalized dissolution rates was limited. Near the equilibrium, the increasing of the leaching time, the temperature or the leachate acidity led to the thorium precipitation at the surface of the pellets either in static or in dynamic conditions. Consequently, the dissolution became clearly incongruent and controlled by saturation processes which are described in the second part of this paper.

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## 1. Introduction

In order to answer to several points mentioned in the French law relative to the radioactive waste management and, as instance, to the immobilization

of actinides and fission products in the field of an underground repository [1], a French research group called NOMADE was constituted. One of the aim of the study was to examine several ceramics for the final disposal of minor actinides (Np, Am, Cm) or plutonium excess with weight loadings up to 10 wt%, exhibiting good sintering properties, low normalized dissolution rates during dissolution and good resistance to irradiation [2]. In this context, the chemistry of uranium and thorium

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phosphates was completely reexamined considering some interesting properties of these materials for such an application [3–7].

Based on the previous properties, four matrices were selected [8]. Zirconolite ( $\text{CaZrTi}_2\text{O}_7$ ) [2], britholites  $\text{Ca}_{10-x}\text{Nd}_x(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{F}_2$  [9], monazites  $\text{M}^{\text{III}}\text{PO}_4$ /brabantites  $\text{N}^{\text{II}}\text{M}^{\text{IV}}(\text{PO}_4)_2$  solid solutions [10–13] and Thorium Phosphate-Diphosphate,  $\beta\text{-Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$  ( $\beta\text{-TPD}$ ) [4] with derivative  $\beta\text{-TPD}$ /monazite composites were chosen [14]. In this objective,  $\beta\text{-TPD}$  was first prepared for the efficient and specific conditioning of large amounts of tetravalent actinides (up to 47.6 wt% for uranium) [15–17], leading to the formation of associated solid solutions  $\beta\text{-Th}_{4-x}\text{U}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$  ( $\beta\text{-TUPD}$ ),  $\beta\text{-Th}_{4-x}\text{Np}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$  ( $\beta\text{-TNpPD}$ ) and  $\beta\text{-Th}_{4-x}\text{Pu}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$  ( $\beta\text{-TPuPD}$ ) and small amounts of trivalent actinides (<0.5 wt%) [18].

One of the main damages which could affect the host matrix consists of the infiltrations of underground water which could induce the release of the radionuclides then their migration to the biosphere. In this context, the chemical durability of these materials was extensively examined. All the leaching tests devoted to the study of the chemical durability of the powdered materials already led to conclude to the high resistance of  $\beta\text{-TPD}$  (and associated solid solutions) to aqueous alteration. In this field, the dissolution of  $\beta\text{-TPD}$ , doped or not with trivalent actinides such as  $^{241}\text{Am}$  or  $^{244}\text{Cm}$ , and of associated  $\beta\text{-TPuPD}$  solid solutions was examined from a kinetic point of view as a function of the pH [19], the temperature and the concentration of phosphate ions of the leachate [20,21]. Some preliminary results on the dissolution of  $\beta\text{-TUPD}$  powdered samples were also discussed [21].

$\beta\text{-TPD}$  and associated  $\beta\text{-TUPD}$  solid solutions were prepared as sintered pellets (with a relative density of 90–99% of that calculated from crystallographic data) using a two-step procedure based on a room-temperature uniaxial pressing at 200–800 MPa then a heat treatment at 1250 °C for 5–30 h, depending on the chemical way of preparation considered [22,23]. More recently, the homogeneity of the final ceramics was significantly improved by using a new way of preparation based on the precipitation of initial low-temperature crystallized precursors,  $\text{Th}_2(\text{PO}_4)_2(\text{HPO}_4)\cdot\text{H}_2\text{O}$  (Thorium Phosphate–HydrogenPhosphate Hydrate, TPHPH) [24] and  $\text{Th}_{2-x/2}\text{U}_{x/2}(\text{PO}_4)_2(\text{HPO}_4)\cdot\text{H}_2\text{O}$  (TUPHPH) solid solutions [25]. Their high reactivity allowed to prepare dense pellets for shorter times of calcina-

tion, with associated higher relative densities (92–99% of the calculated density) and better final homogeneity [23]. The associated very low solubility reported for these precursors ( $K_{\text{S},0} \approx 10^{-67}$ ) [18,19] allowed to consider the quantitative decontamination of low and high level radioactive liquid waste containing actinides (Th, U, Np, Pu) through a decontamination/precipitation – immobilization chemical process [26,27].

However, the sintering process developed could degrade significantly the chemical durability of the materials due to the formation, as instance, of minor phases (usually mainly localized at the surface of the samples) or poorly crystallized zones. The aim of this paper mainly concerns the better knowledge of the successive steps of the dissolution mechanism of  $\beta\text{-TUPD}$  sintered samples and the evaluation of the consequences of the sintering process on their chemical durability. The first part of this paper is focused on the kinetic aspect of the dissolution of  $\beta\text{-TUPD}$  solid solutions while the second one is essentially dedicated to the study of the saturation processes involved near the equilibrium then to the characterization of the neoformed phases.

## 2. Experimental

### 2.1. Preparation and characterization of the $\beta\text{-TUPD}$ sintered samples

$\beta\text{-TUPD}$  sintered samples with several  $x$  values were prepared by wet chemistry methods [23] from low-temperature crystallized precursors through a two-step procedure including an uniaxial pressing at room temperature (200–500 MPa) then a heat treatment for 10 h at 1250 °C under inert atmosphere to avoid the oxidation of uranium (IV) into uranyl ions [25]. Among these precursors, crystallized TUPHPH solid solutions were prepared by precipitation of a mixture containing tetravalent uranium chloride ( $C_{\text{U}} = 1.1\text{--}1.5$  M), thorium chloride ( $C_{\text{Th}} = 0.7\text{--}1.0$  M) concentrated solutions and 5 M phosphoric acid [25].

The samples were extensively characterized by Electron Probe MicroAnalyses (EPMA) using a Cameca SX 50 apparatus with an acceleration voltage of 15 kV and a current of 10 nA considering  $\text{SmPO}_4$  ( $K_{\alpha}$  ray of phosphorus),  $\text{ThO}_2$  ( $M_{\alpha}$  ray of thorium) and  $\text{UO}_2$  ( $M_{\beta}$  ray of uranium) as calibration standards. The counting time was fixed to 10–30 s while the size of the spot was evaluated to

1  $\mu\text{m}$ . The elementary wt% and associated mole ratios of the unleached  $\beta$ -TUPD sintered samples confirmed the improved homogeneity and the purity of the phases obtained. Moreover, they revealed a rather good agreement between the composition determined and that expected [23].

The XRD diagrams were collected with a Brüker D8 Advanced Roentgen diffractometer system using  $\text{CuK}_\alpha$  rays ( $\lambda = 1.5418 \text{ \AA}$ ). The precise peak positions were determined using the fitting program EVA, available in the software package Diffrac-AT V 3.0 [28]. For all the solids studied, the unit cell parameters refined using the U-Fit program [29] were consistent with that expected for  $\beta$ -TUPD solid solutions [15].

In order to perform an accurate correction of the effective surface in contact with the solutions, the specific surface area of each sample was determined using the B.E.T. method (nitrogen or krypton adsorption) with a COULTER SA 3100 apparatus. The samples were dried for 10 h at 100 °C prior to these experiments.

## 2.2. Leaching tests procedure and analysis of the leachate

Since the dissolution rates of  $\beta$ -TPD (and  $\beta$ -TUPD) are very low, several experiments were carried out in corrosive media at constant temperature for several months in order to accelerate the dissolution process and to study the nature of the dissolution.

Static batch experiments were performed on sintered samples using high density polyethylene (HDPE) containers below 343 K while polytetrafluoroethylene (PTFE) vials were chosen for the leaching experiments achieved above 363 K. In these conditions, less than 1% of the total dissolved elements is adsorbed onto the surface of the containers. For each dissolution test, 100–200 mg of sintered  $\beta$ -TUPD were put in contact with 5–25 mL of acidic solution for several days to few months. At regular intervals, both phases were separated by centrifugation at 13000 rpm. A small part of the leachate (usually 100–200  $\mu\text{L}$ ) was removed then analyzed. Since only 1–2% of the leachate was renewed (which corresponds to a leaching flow equal to  $6.0 \times 10^{-2} \text{ mL m}^{-2} \text{ day}^{-1}$ ), it was possible to consider that the system composed by the solid and the solution was not modified by this take off.

Due to the low renewing of the leachate, this first kind of leaching tests often led to saturation condi-

tions thus to the precipitation of neoformed phases. In order to avoid these problems which can alter the determination of the real normalized dissolution rates values, some experiments were performed using dynamic conditions in open PTFE flow reactors set in aluminium baths for temperatures ranging from room temperature to 363 K. The reactors used were comparable to that reported in literature [30]. The reactive fluids were deionized water or acidic media. All the inlet solutions, free of thorium, uranium and phosphate, were placed in glass bottles and injected with a rate of 1–2  $\text{mL h}^{-1}$  into reactors through a 10  $\mu\text{m}$  filter using a peristaltic pump. The uranium and/or thorium concentrations were determined in the outlet solutions by Inductively Coupled Plasma-Mass Spectroscopy ICP-MS (Fisons Plasma Quad) or  $\alpha$ -liquid scintillation technique (PERALS: Photon Electron Rejecting Alpha Liquid Scintillation Spectrometry) [31]. For the ICP-MS experiments, 1 ppb of terbium and bismuth were added to the samples as internal standards.

A slightly higher release was initially observed because of the surface heterogeneity of unwashed minerals (minor phases, non-stoichiometry at the surface, etc.). This problem was avoided by making a preliminary washing step at 298 K for several days in  $10^{-1}$  to  $10^{-4} \text{ M HNO}_3$ . Moreover, on the basis of the corrosive medium used, the surface irregularities were rapidly eliminated and, by this way, no significant increase was noted at the beginning of the dissolution curves.

## 3. Theoretical section

### 3.1. Expression of the normalized leaching and of the normalized leaching (or dissolution) rate

The leachability of the element  $i$  from a material is usually described by its normalized leaching,  $N_L(i)$  ( $\text{g m}^{-2}$ ), [20,21] defined by the relation:

$$N_L(i) = \frac{m_i}{f_i \times S} \quad (1)$$

where  $m_i$  is the total amount of  $i$  measured in solution (g),  $S$  is the corresponding solid area ( $\text{m}^2$ ) in contact with the solution and  $f_i$  is the mass ratio of the element  $i$  in the solid.

The expression of the normalized dissolution rate,  $R_L$  (expressed in  $\text{g m}^{-2} \text{ day}^{-1}$  and usually noted  $R_H$  in acidic media), can be deduced from

the evolution of the normalized leaching [32], as follows:

$$R_L(i) = \frac{1}{f_i \times S} \times \frac{dm_i}{dt} = \frac{dN_L(i)}{dt}. \quad (2)$$

Far from equilibrium, the normalized dissolution rate was found to be constant for several minerals [33–37]. On the contrary, near the equilibrium, parabolic evolution of the normalized dissolution can be observed due to the diffusion of the elements through a protective layer formed onto the surface of the samples (this aspect will be developed in the second part of this paper). Consequently, a decrease of the associated normalized dissolution rate is usually observed [38].

### 3.2. Description and nature of the dissolution

The dissolution of ceramics such as  $\beta$ -TUPD solid solutions can be schematically described as reported in Fig. 1. In the case of unwashed materials, initial perturbations, leading to a higher increase of the normalized leaching, can be observed as already described [20,21]. They were avoided by making a rapid washing of the solids.

The second part of the curve, driven by kinetics, allows the direct determination of the normalized dissolution rates by determining the slope of the linear evolution of the normalized leaching versus time. Finally, the third part, which corresponds to

the significant deceleration of the reaction of dissolution can be associated to diffusion processes and to the precipitation of neoformed phases (mainly driven by thermodynamics).

As already described, the study of the dissolution of a material can be described by the release of several constitutive elements in the leachate. Depending on the ratio between the normalized dissolution rates determined for each element, it is possible to qualify the dissolution as congruent (all the elements being released in the leachate with the same normalized dissolution rates) or incongruent (if one element is significantly retained in the phases formed onto the surface of the sample). On the basis of the results obtained for two elements  $i$  and  $j$ , the dissolution can be considered to be congruent for normalized dissolution rate ratios  $r = R_L(i)/R_L(j)$  between 0.5 and 2. On the contrary, for  $r$  values lower than 0.2 or higher than 5, the element  $i$  or  $j$ , respectively, can be considered to be significantly retained in the phases of degradation of the initial solid and thus the dissolution can be qualified as incongruent.

We have here focused our study on the comparison of the behavior of both actinides which exhibit different behaviors due to main differences in their redox properties (uranium being easily oxidized into uranyl thus released in the leachate in several media considered contrary to thorium which often forms neoformed phases due to its tetravalent oxidation state).

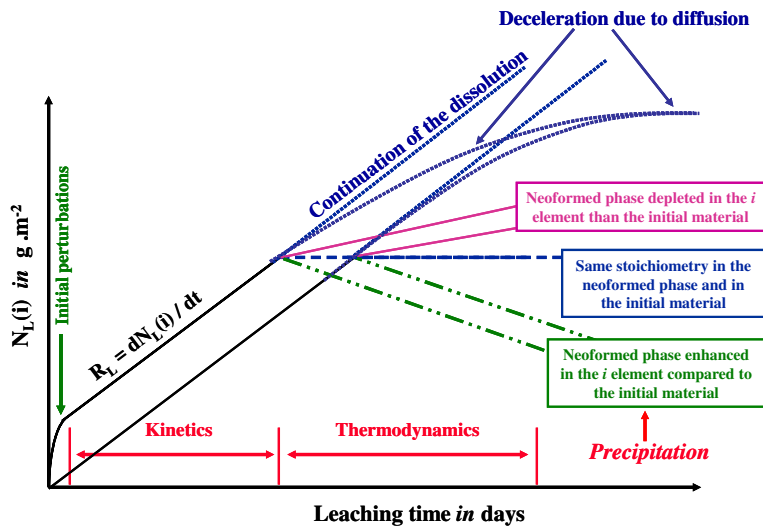


Fig. 1. Schematic representation of the dissolution of a material such as  $\beta$ -TUPD solid solutions.

### 3.3. Dependence of the normalized dissolution rate on pH or temperature

Several authors investigated the dissolution reactions between minerals and aqueous solutions from a kinetic point of view [20,21,32,39–45]. They showed that the proton concentration strongly contributes to the dissolution of the materials in acidic media, as follows:

$$R_H = k'_T(a_{H_3O^+})^n = k'_{T,I}(\gamma_{H_3O^+}[H_3O^+])^n = k'_{T,I}[H_3O^+]^n, \quad (3)$$

where  $k'_T$  and  $k'_{T,I}$  correspond to the apparent normalized dissolution rate constants dependent on temperature ( $\text{g m}^{-2} \text{day}^{-1}$ ),  $a_{H_3O^+}$  refers to the protons activity,  $\gamma_{H_3O^+}$  corresponds to the proton activity coefficient and  $n$  is the partial order related to the  $H_3O^+$  ions concentration. For most of the materials and minerals, the experimental  $n$  values are usually in the range  $0 < n < 1$  [20,42–45].

In several previous works concerning the leaching tests performed on powdered samples of pure  $\beta$ -TPD and associated solid solutions [20,21], the normalized dissolution rate was found to be dependent on temperature according to the simple Arrhenius law [46], i.e.,

$$R_H = k e^{(-\frac{E_{app}}{RT})}, \quad (4)$$

where  $k$  is the normalized dissolution rate constant ( $\text{g m}^{-2} \text{day}^{-1}$ ) independent of the temperature and  $E_{app}$  is the apparent activation energy of the material dissolution ( $\text{kJ mol}^{-1}$ ).

## 4. Results and discussion

### 4.1. Nature of the dissolution of sintered samples of $\beta$ -TUPD solid solutions

The first aim of the study was focused on the nature of the dissolution of  $\beta$ -TUPD sintered samples. As already described, the presence of two actinides (uranium and thorium) exhibiting different redox properties can induce the congruence or incongruence during the dissolution process. In this objective, several leaching tests were performed in various acidic media. The evolutions of the normalized leachings  $N_L(U)$  and  $N_L(Th)$  in  $10^{-1}$  M  $HNO_3$ ,  $10^{-1}$  M  $HCl$  and  $10^{-1}$  M  $H_2SO_4$  at 298 K are presented in Fig. 2 while several results obtained for higher pH values and temperatures are presented in Fig. 3. The associated thorium and uranium con-

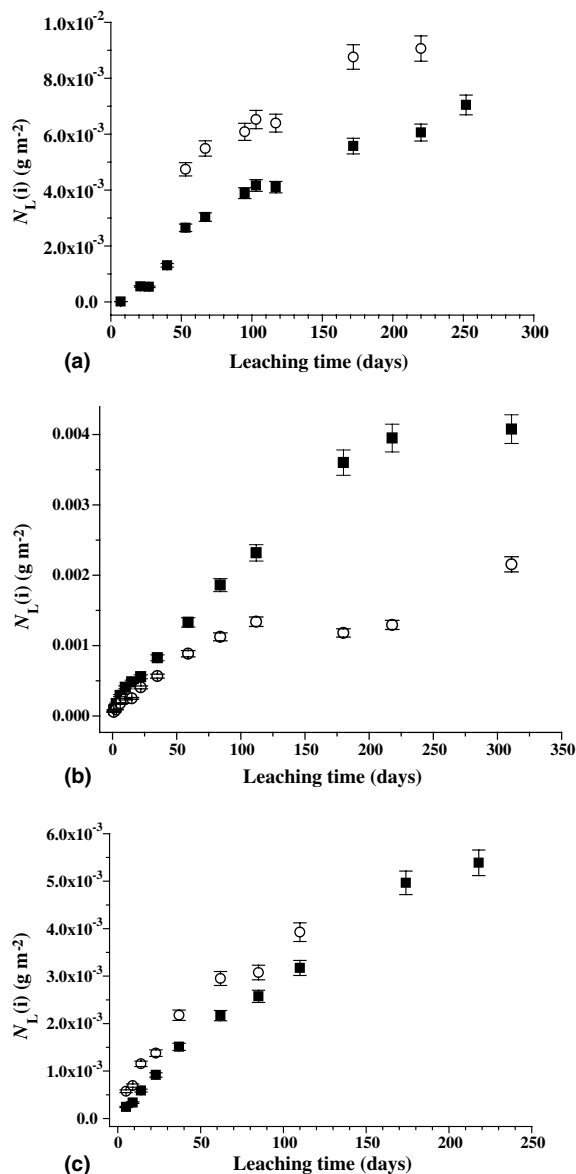


Fig. 2. Evolution of  $N_L(U)$  (■) and  $N_L(Th)$  (○) during the dissolution of  $\beta$ -TUPD sintered samples in  $10^{-1}$  M  $HNO_3$  (a),  $10^{-1}$  M  $HCl$  (b) and  $10^{-1}$  M  $H_2SO_4$  (c) at 298 K.

centrations determined in the leachate are gathered in Table 1.

From these results, the chemical durability of the solids, thus the behavior of both actinides, depends significantly on the pH of the leachate. Whatever the medium considered, the releases of uranium and thorium are almost the same during the first 150 days of leaching at  $\text{pH} = 1$  and for  $298 \text{ K} < T < 363 \text{ K}$  showing the congruence of the dissolution (Table 2 and Fig. 4). From the evolution

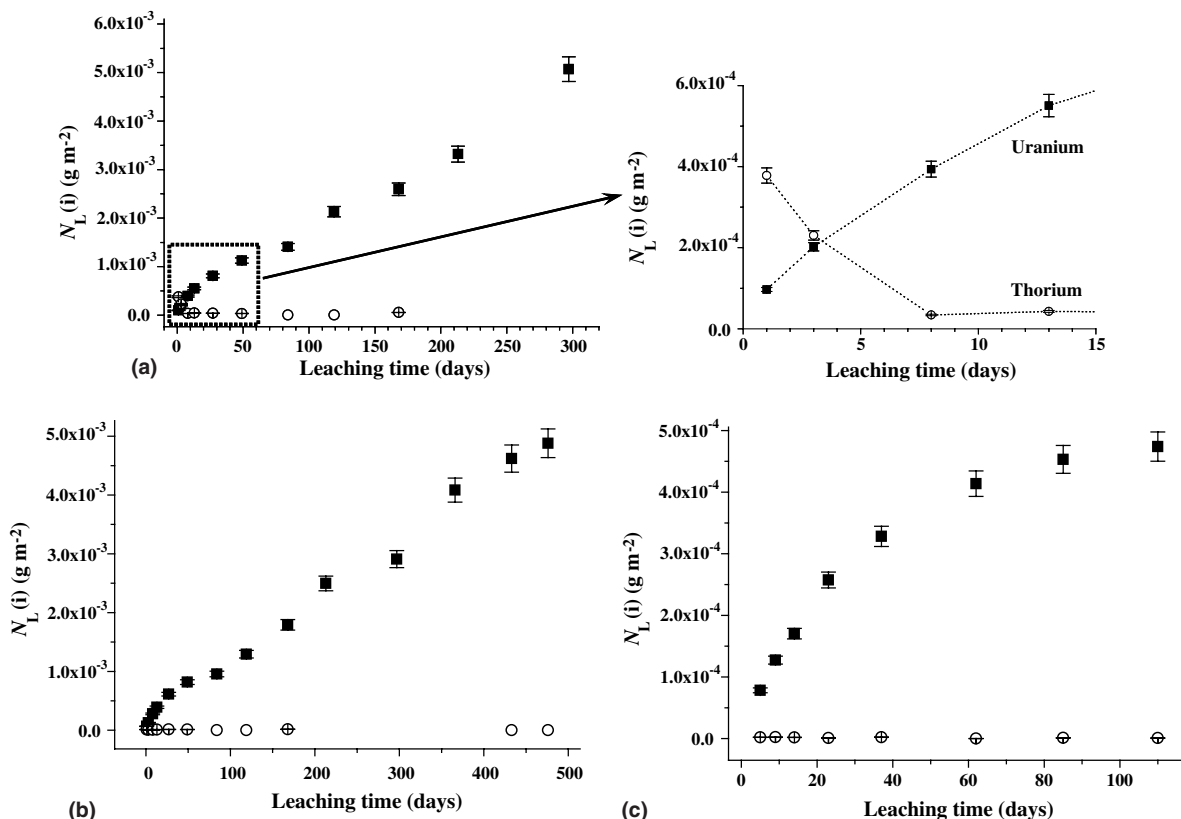


Fig. 3. Evolution of  $N_L(\text{U})$  (■) and  $N_L(\text{Th})$  (○) during the dissolution of  $\beta$ -TUPD sintered samples in  $10^{-2}$  M  $\text{HNO}_3$  and  $T = 323$  K (a),  $10^{-3}$  M  $\text{HNO}_3$  and  $T = 323$  K (b) and  $10^{-3}$  M  $\text{H}_2\text{SO}_4$  and  $T = 298$  K (c).

of the normalized leachings  $N_L(\text{U})$  and  $N_L(\text{Th})$ , the determination of both  $R_L(\text{U})$  and  $R_L(\text{Th})$  values led to the results gathered in Table 2. It is worth to note that for all the media considered, the normalized dissolution rates remain very low which confirms the good chemical durability of the pellets prepared. The fluctuations of the  $r = R_L(\text{U})/R_L(\text{Th})$  values were evaluated for each series of leaching tests (Table 2 and Fig. 4). In the media considered, they remain low, confirming the congruence of the dissolution during the first days of leaching.

This observation contrasts significantly with the results obtained for  $\text{pH} \geq 2$ . Indeed, whatever the leaching conditions and the operating temperature (Table 3), the normalized dissolution rates  $R_L(\text{Th})$  decrease drastically from  $10^{-5}$   $\text{g m}^{-2} \text{day}^{-1}$  down to  $10^{-8}$   $\text{g m}^{-2} \text{day}^{-1}$  while the  $R_L(\text{U})$  values are divided by a factor of 2–3 for each pH-unit. This observation can be correlated to the rapid precipitation of the tetravalent thorium at the surface of the pellets (or to its retention in the alteration layer formed onto the surface of the samples) while ura-

nium, oxidized in the uranyl form, is released with the normalized dissolution rate of the material. Indeed, its precipitation as the uranyl phosphate pentahydrate  $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$  occurs for higher concentrations thus for longer leaching times [21]. It is important to note that the Th-precipitation is enhanced either by the increase of the pH or temperature or by extending the leaching time. In these conditions, the dissolution becomes clearly incongruent as confirmed by the increase of the  $r$  values (from 1 to 10–1000: Table 3 and Fig. 4). On this basis, only uranium was considered to perform the accurate determination of the normalized dissolution rate of  $\beta$ -TUPD sintered samples.

This different behavior in less acidic media can be explained by the nature of the neoformed thorium phase. Indeed, we proved that thorium is quantitatively precipitated as the thorium phosphate-hydrogenphosphate hydrate (TPHPH), as described in the second part of this paper, which solubility product directly depends on the concentration of free phosphate and hydrogenphosphate ions in the

Table 1  
Uranium and thorium concentrations determined in the leachate for several initial conditions (L.D.: limit of detection)

Medium		Leaching time (days)											
		7	21	27	40	53	67	95	103	117	172	220	252
$10^{-1}$ M HNO <sub>3</sub>													
$x = 2$	$C_U$ (M)	$1.3 \times 10^{-8}$	$6.0 \times 10^{-7}$	$5.9 \times 10^{-7}$	$1.4 \times 10^{-6}$	$2.9 \times 10^{-6}$	$3.3 \times 10^{-6}$	$4.2 \times 10^{-6}$	$4.5 \times 10^{-6}$	$4.5 \times 10^{-6}$	$6.1 \times 10^{-6}$	$6.6 \times 10^{-6}$	$7.7 \times 10^{-6}$
$T = 298$ K	$C_{Th}$ (M)	–	–	–	–	$1.5 \times 10^{-5}$	$1.8 \times 10^{-5}$	$1.9 \times 10^{-5}$	$2.1 \times 10^{-5}$	$2.0 \times 10^{-5}$	$2.8 \times 10^{-5}$	$2.9 \times 10^{-5}$	–
$10^{-1}$ M HCl		<b>1</b>	<b>6</b>	<b>10</b>	<b>15</b>	<b>22</b>	<b>35</b>	<b>59</b>	<b>84</b>	<b>112</b>	<b>180</b>	<b>218</b>	<b>311</b>
$x = 1.2$	$C_U$ (M)	$9.1 \times 10^{-8}$	$3.1 \times 10^{-7}$	$4.3 \times 10^{-7}$	$5.1 \times 10^{-7}$	$5.9 \times 10^{-7}$	$8.8 \times 10^{-7}$	$1.4 \times 10^{-6}$	$2.0 \times 10^{-6}$	$2.5 \times 10^{-6}$	$3.8 \times 10^{-6}$	$4.2 \times 10^{-6}$	$4.3 \times 10^{-6}$
$T = 298$ K	$C_{Th}$ (M)	$1.8 \times 10^{-7}$	$5.7 \times 10^{-7}$	$7.6 \times 10^{-7}$	$8.0 \times 10^{-7}$	$1.3 \times 10^{-6}$	$1.8 \times 10^{-6}$	$2.8 \times 10^{-6}$	$3.6 \times 10^{-6}$	$4.3 \times 10^{-6}$	$3.8 \times 10^{-6}$	$4.1 \times 10^{-6}$	$6.9 \times 10^{-6}$
$10^{-1}$ M H <sub>2</sub> SO <sub>4</sub>		<b>5</b>	<b>9</b>	<b>14</b>	<b>23</b>	<b>37</b>	<b>62</b>	<b>85</b>	<b>110</b>	<b>174</b>	<b>218</b>		
$x = 1.6$	$C_U$ (M)	$1.8 \times 10^{-5}$	$2.4 \times 10^{-5}$	$4.3 \times 10^{-5}$	$6.7 \times 10^{-5}$	$1.1 \times 10^{-4}$	$1.6 \times 10^{-4}$	$1.9 \times 10^{-4}$	$2.3 \times 10^{-4}$	$3.6 \times 10^{-4}$	$3.9 \times 10^{-4}$		
$T = 298$ K	$C_{Th}$ (M)	$6.3 \times 10^{-5}$	$7.6 \times 10^{-5}$	$1.3 \times 10^{-4}$	$1.5 \times 10^{-4}$	$2.4 \times 10^{-4}$	$3.2 \times 10^{-4}$	$3.4 \times 10^{-4}$	$4.3 \times 10^{-4}$	–	–		
$10^{-3}$ M HNO <sub>3</sub>		<b>1</b>	<b>8</b>	<b>13</b>	<b>27</b>	<b>49</b>	<b>84</b>	<b>119</b>	<b>168</b>	<b>213</b>	<b>297</b>	<b>433</b>	<b>476</b>
$x = 2$	$C_U$ (M)	$1.2 \times 10^{-7}$	$5.0 \times 10^{-7}$	$7.1 \times 10^{-7}$	$1.1 \times 10^{-6}$	$1.5 \times 10^{-6}$	$1.7 \times 10^{-6}$	$2.3 \times 10^{-6}$	$3.2 \times 10^{-6}$	$4.5 \times 10^{-6}$	$5.3 \times 10^{-6}$	$8.4 \times 10^{-6}$	$8.8 \times 10^{-6}$
$T = 323$ K	$C_{Th}$ (M)	$6.0 \times 10^{-8}$	$4.3 \times 10^{-8}$	$6.0 \times 10^{-8}$	$7.3 \times 10^{-8}$	$6.5 \times 10^{-8}$	<L.D.	<L.D.	$8.7 \times 10^{-8}$	<L.D.	<L.D.	<L.D.	<L.D.
$10^{-3}$ M HCl		<b>1</b>	<b>6</b>	<b>8</b>	<b>12</b>	<b>15</b>	<b>21</b>	<b>25</b>					
$x = 1.6$	$C_U$ (M)	$6.1 \times 10^{-7}$	$5.4 \times 10^{-7}$	$3.1 \times 10^{-7}$	$4.2 \times 10^{-7}$	$3.8 \times 10^{-7}$	$3.0 \times 10^{-7}$	$3.2 \times 10^{-7}$					
$T = 363$ K	$C_{Th}$ (M)	$2.4 \times 10^{-7}$	$2.0 \times 10^{-7}$	$2.6 \times 10^{-8}$	$2.5 \times 10^{-8}$	$2.2 \times 10^{-8}$	$2.6 \times 10^{-8}$	$2.2 \times 10^{-8}$					
$10^{-3}$ M H <sub>2</sub> SO <sub>4</sub>		<b>5</b>	<b>9</b>	<b>14</b>	<b>23</b>	<b>37</b>	<b>62</b>	<b>85</b>	<b>110</b>				
$x = 1.6$	$C_U$ (M)	$2.9 \times 10^{-6}$	$4.7 \times 10^{-6}$	$6.2 \times 10^{-6}$	$9.4 \times 10^{-6}$	$1.2 \times 10^{-5}$	$1.5 \times 10^{-5}$	$1.7 \times 10^{-5}$	$1.7 \times 10^{-5}$				
$T = 298$ K	$C_{Th}$ (M)	$1.1 \times 10^{-7}$	$1.2 \times 10^{-7}$	$1.0 \times 10^{-7}$	$4.8 \times 10^{-8}$	$1.2 \times 10^{-7}$	$7.3 \times 10^{-9}$	$6.2 \times 10^{-8}$	$4.8 \times 10^{-8}$				
Bridges water		<b>1</b>	<b>5</b>	<b>11</b>	<b>20</b>	<b>50</b>	<b>113</b>	<b>157</b>	<b>198</b>	<b>239</b>	<b>287</b>	<b>363</b>	
$x = 1.6$	$C_U$ (M)	$8.3 \times 10^{-7}$	$3.1 \times 10^{-6}$	$7.8 \times 10^{-6}$	$1.2 \times 10^{-5}$	$2.9 \times 10^{-5}$	$6.2 \times 10^{-5}$	$6.3 \times 10^{-5}$	$7.4 \times 10^{-5}$	$6.7 \times 10^{-5}$	$9.9 \times 10^{-5}$	$9.2 \times 10^{-5}$	
$T = 298$ K	$C_{Th}$ (M)	<L.D.	$6.3 \times 10^{-8}$	$2.6 \times 10^{-8}$	$7.6 \times 10^{-8}$	$1.7 \times 10^{-7}$	–	–	$9.7 \times 10^{-6}$	$3.7 \times 10^{-6}$	$5.3 \times 10^{-6}$	$6.8 \times 10^{-6}$	

Table 2

Normalized dissolution rates  $R_L(\text{U})$  and  $R_L(\text{Th})$  of  $\beta$ -TUPD sintered samples at pH = 1 and for several leaching conditions

Medium	$T$ (K)	Mode	$R_L(i)$ ( $\text{g m}^{-2} \text{day}^{-1}$ )		$r = R_L(\text{U})/R_L(\text{Th})$
			Uranium	Thorium	
HNO <sub>3</sub>	298	Static	$(2.5 \pm 0.2) \times 10^{-5}$	$(2.4 \pm 0.1) \times 10^{-5}$	1.0
HCl	298	Static	$(1.9 \pm 0.2) \times 10^{-5}$	$(1.5 \pm 0.1) \times 10^{-5}$	1.3
H <sub>2</sub> SO <sub>4</sub>	298	Static	$(2.6 \pm 0.1) \times 10^{-5}$	$(2.8 \pm 0.3) \times 10^{-5}$	0.9
HNO <sub>3</sub>	323	Static	$(9.7 \pm 0.8) \times 10^{-5}$	$(1.0 \pm 0.1) \times 10^{-4}$	1.0
HCl	363	Dynamic	$(1.4 \pm 0.2) \times 10^{-4}$	$(1.0 \pm 0.1) \times 10^{-4}$	1.4

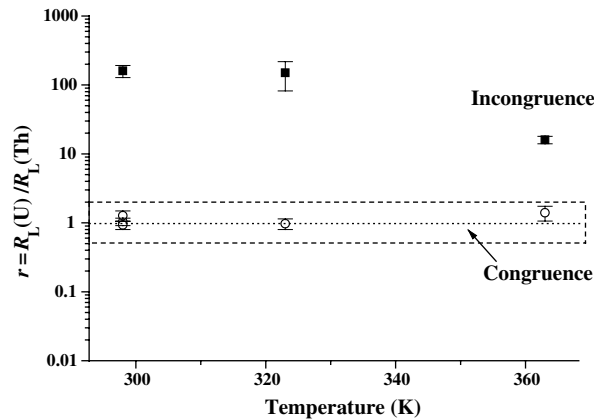


Fig. 4. Variation of the ratio  $R_L(\text{U})/R_L(\text{Th})$  at pH = 1 (open symbols) and pH = 3 (solid symbols) and for several temperatures of leaching tests. The congruence is delimited by the dash lines.

leachate. Even though the normalized dissolution rate is decreased by a factor of 2–3 (from a kinetic point of view) when increasing the pH value by one unit, the free phosphate and hydrogenphosphate ions concentrations are simultaneously increased by a factor of at least 1000 and 100, respectively (from thermodynamic considerations), due to the speciation of phosphate species in the solution. Consequently, the solubility product is reached more rapidly inducing the precipitation of TPHPH.

Table 3

Normalized dissolution rates  $R_L(\text{U})$  and  $R_L(\text{Th})$  of  $\beta$ -TUPD sintered samples for pH > 1 and for several leaching conditions

Medium	pH	$T$ (K)	Mode	$R_L(i)$ ( $\text{g m}^{-2} \text{day}^{-1}$ )		$r = R_L(\text{U})/R_L(\text{Th})$
				Uranium	Thorium	
H <sub>2</sub> SO <sub>4</sub>	3	298	Static	$(4.9 \pm 0.2) \times 10^{-6}$	$< 3.1 \times 10^{-8\text{a}}$	>160
HNO <sub>3</sub>	2	323	Static	$(3.7 \pm 0.2) \times 10^{-5}$	$< 3.3 \times 10^{-8\text{a}}$	>1000
HNO <sub>3</sub>	3	323	Static	$(2.1 \pm 0.1) \times 10^{-5}$	$< 1.4 \times 10^{-7\text{a}}$	>150
HNO <sub>3</sub>	4	323	Static	$(6.8 \pm 0.3) \times 10^{-6}$	$< 2.3 \times 10^{-7\text{a}}$	>30
HCl	3	363	Dynamic	$(3.3 \pm 0.1) \times 10^{-5}$	$(2.1 \pm 0.2) \times 10^{-6}$	16

<sup>a</sup> Normalized dissolution rate values affected by the Th-precipitation.

The consequence of Th-precipitation (in the TPHPH form) at the surface of the sintered samples is the significant decrease of the release of uranium from the solid to the leachate inducing a dissolution mechanism similar to that evidenced for glass matrices [47–49]. The release of the elements can be described in two steps as expected from the schematic representation reported in Fig. 1. The first one (occurring for smaller leaching times) corresponds to the direct release of the elements in solution from the raw material then, during the second step, diffusion mechanisms take place through the layer formed at the surface inducing a progressive decrease of the normalized dissolution rate  $R_L(\text{U})$ . This phenomenon is clearly evidenced by drawing the normalized leaching of uranium versus the square root of time (Fig. 5) [50].

In order to avoid these diffusion processes and the precipitation of neoformed phases, some experiments were also driven using dynamic conditions (Fig. 6). However, although we considered very high flow rates (1–2 mL h<sup>-1</sup>) to avoid the Th-precipitation, we observed the same behavior than using static experiments. Indeed, thorium and uranium are leached identically at pH = 1 confirming the congruence of the  $\beta$ -TUPD dissolution ( $r = 1.4$ ). On the contrary, the thorium is significantly precipitated when leaching in  $10^{-3}$  M HNO<sub>3</sub> leading to the strong decrease of the normalized dissolution rate  $R_L(\text{Th})$  down to  $(2.1 \pm 0.2) \times 10^{-6}$  g m<sup>-2</sup> day<sup>-1</sup>



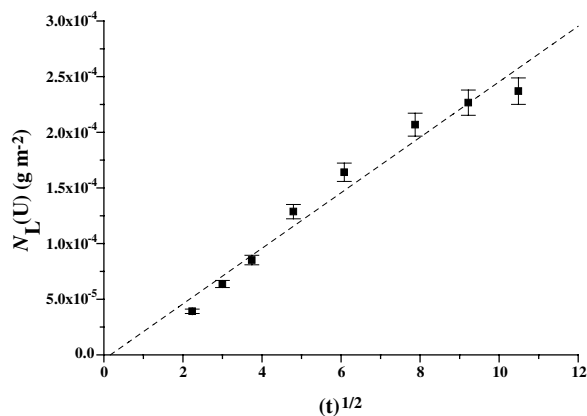


Fig. 5. Variation of the normalized leaching  $N_L(U)$  versus the square root of the leaching time ( $10^{-3}$  M  $\text{H}_2\text{SO}_4$ ,  $T = 298$  K) showing diffusion phenomena.

and to an associated  $r$  value of 16. Consequently, Th-precipitation can not be avoided and probably occurs onto the surface of the material.

#### 4.2. Influence of the pH on the normalized dissolution rate

On the basis of the previous results, only data obtained far from thermodynamic equilibrium were considered for the evaluation of the influence of the pH on the dissolution of  $\beta$ -TUPD samples. From the data obtained at each operating temperature,

the logarithm of the normalized dissolution rates  $R_L(\text{Th})$  and/or  $R_L(\text{U})$ , plotted in Fig. 7, always exhibit a linear variation versus the pH of the leachate. Taking into account Eq. (3), the regression of the experimental data led to partial orders relative to the proton concentration ( $n = 0.39\text{--}0.41$ ) and associated apparent normalized dissolution rates gathered in Table 4. At room temperature, both values appear consistent with that obtained on powdered samples of  $\beta$ -TPD doped with trivalent actinides,  $\beta$ -TUPD and  $\beta$ -TPuPD solid solutions [19–21] which confirms that the sintering procedure does not induce any modification of the resistance of the material to dissolution. Moreover, it is important to note that the  $n$  value seems to be independent of the temperature of the leaching tests ( $298 \text{ K} \leq T \leq 363 \text{ K}$ ) while the increase of the apparent normalized dissolution rate with temperature,  $k'_{T,L}$ , is in agreement with Eq. (4) (see next section).

#### 4.3. Influence of the temperature on the normalized dissolution rate

We already mentioned that the increase of temperature could favor the Th-precipitation for  $\text{pH} > 1$  and long leaching times. For this reason, the influence of temperature on the normalized dissolution rate of sintered  $\beta$ -TUPD samples was evaluated by making the leaching tests between 298 K

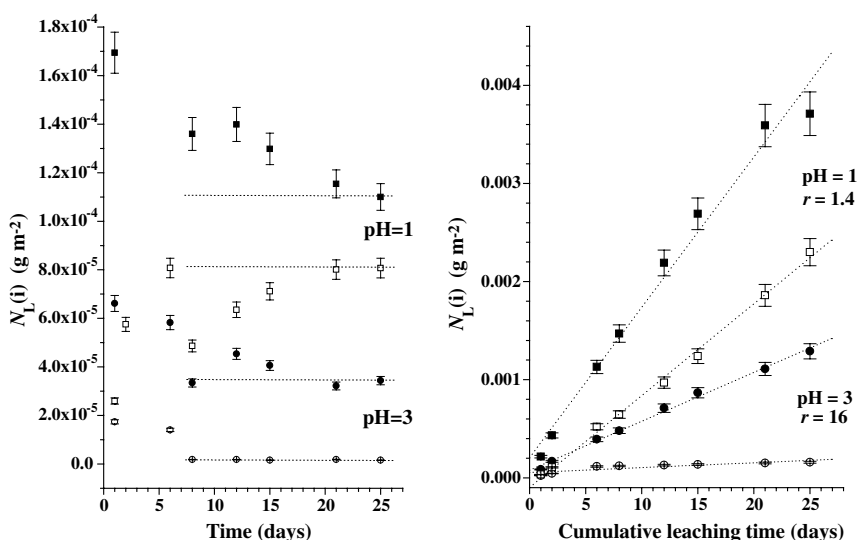


Fig. 6. Evolution of the normalized leaching  $N_L(\text{Th})$  (open symbol) and  $N_L(\text{U})$  (solid symbol) versus the leaching time and as a function of the cumulative leaching time in dynamic conditions ( $T = 363$  K) for the dissolution of  $\beta$ -TUPD sintered samples in  $10^{-1}$  M HCl ( $\blacksquare/\square$ ) and  $10^{-3}$  M HCl ( $\bullet/\circ$ ).

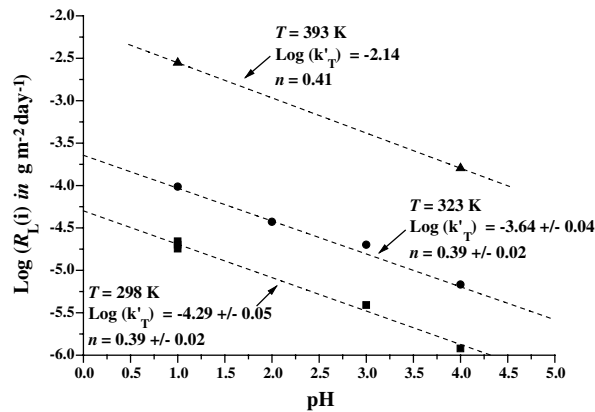


Fig. 7. Variation of  $\text{Log}(R_L(U))$  versus the pH value at  $T = 298 \text{ K}$  (■),  $T = 323 \text{ K}$  (●) and  $T = 393 \text{ K}$  (▲).

and 393 K and avoiding all the saturation processes. The normalized dissolution rates were determined in several media and at various temperatures then their variation versus the opposite temperature were drawn for several media (Fig. 8). The values of the apparent activation energy, determined from the linear regression of the results lead, in agreement with Eq. (4), to an activation energy of  $(49 \pm 4 \text{ kJ mol}^{-1})$ . These values appear consistent with that obtained for pure powdered  $\beta$ -TPD ( $42 \pm 3 \text{ kJ mol}^{-1}$ ) or thorium-plutonium (IV) phosphate–diphosphate solid solutions ( $\beta$ -TPuPD) ( $41 \pm 1 \text{ kJ mol}^{-1}$ ) [19,20,51], confirming the absence of degradation of the chemical durability of the ceramics consequently to the sintering process and to the use of TUPHPH as an initial low-temperature crystallized precursor. On the basis of these results, the dissolution mechanism seems to be similar for all the samples considered whatever their composition and their morphology.

Moreover, the  $E_{\text{app}}$  values are very close to that reported for several minerals and other phosphate matrices [52–56]. They could indicate the existence

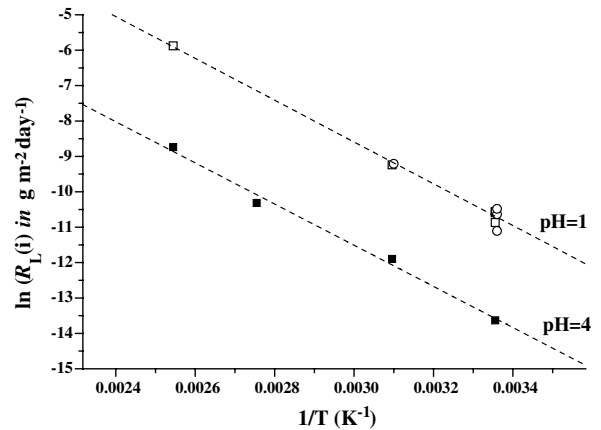


Fig. 8. Variation of  $\ln(R_L(\text{Th}))$  (○) and  $\ln(R_L(U))$  (□/■) versus the opposite temperature in  $10^{-1} \text{ M HNO}_3$  (open symbols) and in  $10^{-4} \text{ M HNO}_3$  (solid symbols).

of an activated complex which adsorption energy on the surface of the sample probably reduces the apparent activation energy.

#### 4.4. Influence of the complexing species present in the solution on the normalized dissolution rate

In order to study the influence of several ligands such as chloride, nitrate or sulphate on the normalized dissolution rates, the dissolution of sintered  $\beta$ -TUPD samples was examined in several acidic media (Table 2 and Fig. 2). As already discussed, the dissolution appears to be congruent at  $\text{pH} = 1$  and  $T = 298 \text{ K}$  for the three media considered. Moreover, the normalized dissolution rates  $R_L(\text{Th})$  and  $R_L(U)$  are spread from  $(1.5 \pm 0.1) \times 10^{-5} \text{ g m}^{-2} \text{ day}^{-1}$  to  $(2.8 \pm 0.3) \times 10^{-5} \text{ g m}^{-2} \text{ day}^{-1}$  and from  $(1.9 \pm 0.2) \times 10^{-5} \text{ g m}^{-2} \text{ day}^{-1}$  to  $(2.6 \pm 0.1) \times 10^{-5} \text{ g m}^{-2} \text{ day}^{-1}$ , respectively, indicating that they are not significantly affected by the presence of such ligands in the leaching solution. These results significantly contrast with the data obtained

Table 4

Apparent normalized dissolution rates and partial orders relative to the proton concentration of  $\beta$ -TUPD sintered samples

Solid	Form	$T$ (K)	$k'_{T,I}$ ( $\text{g m}^{-2} \text{ day}^{-1}$ )	$n$	Reference
$\beta$ -TUPD	Pellet	298	$(5.1 \pm 0.5) \times 10^{-5}$	$0.39 \pm 0.02$	This work
		323	$(2.3 \pm 0.3) \times 10^{-4}$	$0.39 \pm 0.02$	
		393	$7.2 \times 10^{-3}$	0.41	
$\beta$ -TPD: <sup>241</sup> Am	Powder	298	$(1.2 \pm 0.3) \times 10^{-5}$	$0.35 \pm 0.04$	[19]
$\beta$ -TPD: <sup>241</sup> Am		298	$(2.4 \pm 0.1) \times 10^{-5}$	$0.31 \pm 0.01$	
$\beta$ -TPuPD		298	$(1.2 \pm 0.3) \times 10^{-5}$	$0.40 \pm 0.03$	
$\beta$ -TUPD		363	$(2.8 \pm 0.7) \times 10^{-4}$	$0.40 \pm 0.02$	

Table 5  
Apparent activation energy of the reaction of dissolution of  $\beta$ -TUPD sintered samples

Solid	Form	Medium	$E_{app}$ (kJ mol <sup>-1</sup> )	Reference
$\beta$ -TUPD	Pellet	10 <sup>-1</sup> M HNO <sub>3</sub>	49 ± 2 (U)	This work
		10 <sup>-4</sup> M HNO <sub>3</sub>	49 ± 4 (Th) 48 ± 3 (U)	
$\beta$ -TPD	Powder	5 M HNO <sub>3</sub>	42 ± 3	[20]
$\beta$ -TPuPD		10 <sup>-1</sup> M HNO <sub>3</sub>	41 ± 1	[21]
$\beta$ -TUPD		10 <sup>-1</sup> M HNO <sub>3</sub>	40	

Table 6  
Thermodynamic constants of complexation of Th<sup>4+</sup>, U<sup>4+</sup> and UO<sub>2</sub><sup>2+</sup> by several ligands at room temperature

	log $\beta_1^a$					
	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HSO <sub>4</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	HPO <sub>4</sub> <sup>2-</sup>
Th <sup>4+</sup> [61,62]	0.67	0.25	3.3 ± 0.1	N.D.	N.D.	15.7
U <sup>4+</sup> [63]	1.47 ± 0.13	1.72 ± 0.13	3.8 ± 0.1	2.41 ± 0.05	N.D.	N.D.
UO <sub>2</sub> <sup>2+</sup> [63]	0.30 ± 0.15	0.17 ± 0.02	1.85 ± 0.10	0.88 ± 0.06	13.23 ± 0.15	7.24 ± 0.26

N.D.: Constant not determined.

<sup>a</sup> Constant of complexation defined for the thermodynamic equilibrium:  $M^{n+} + B^{m-} \rightleftharpoons MB^{(n-m)+}$ .

for several other ceramics such as oxides [57] for which the influence of complexing species in the leachate appears stronger (see Table 5).

On the basis of the thermodynamical constants of complexation of the ligands relative to thorium or tetravalent uranium,  $\beta_1$  (Table 6), this observation could appear rather surprising. However, the presence of phosphate ions in the material could explain this fact. Indeed, the phosphate derivative anions exhibit stronger  $\beta_1$  values than the other ligands used. Consequently, the complexation of actinides by the ligands added in the leachate (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HSO<sub>4</sub><sup>-</sup>) could be counterbalanced by that of phosphate species (PO<sub>4</sub><sup>3-</sup>, HPO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, ...) which could act as a 'protective ligands' for the dissolution of the material. In these conditions, the presence of 'phosphate consuming' cations, such as calcium or magnesium in the leachate could influence significantly the release of the actinides. This point was already suggested when studying the degradation of monazite then the mobility of actinides in highly saline brines [58,59]. As a confirmation of this effect, some experiments were driven in Brides<sup>TM</sup> French mineral water (main ions concentrations: [Cl<sup>-</sup>] = 2.9 × 10<sup>-2</sup> M, [HCO<sub>3</sub><sup>-</sup>] = 2.7 × 10<sup>-3</sup> M, [SO<sub>4</sub><sup>2-</sup>] = 2.6 × 10<sup>-2</sup> M, [Ca<sup>2+</sup>] = 1.4 × 10<sup>-2</sup> M, [Mg<sup>2+</sup>] = 4.8 × 10<sup>-3</sup> M). The associated normalized dissolution rate value,  $R_L(U)$ , reaches (1.1 ± 0.1) × 10<sup>-5</sup> g m<sup>-2</sup> day<sup>-1</sup> at room temperature (pH value equal to 6.5 at equilibrium) which appears

higher than that determined in distilled water at pH = 7 and  $T = 298$  K (typically estimated to 3 × 10<sup>-7</sup> g m<sup>-2</sup> day<sup>-1</sup>) [19] or in Volvic<sup>TM</sup> French mineral water (main ions concentrations: [Cl<sup>-</sup>] = 3.8 × 10<sup>-4</sup> M, [HCO<sub>3</sub><sup>-</sup>] = 1.2 × 10<sup>-3</sup> M, [SO<sub>4</sub><sup>2-</sup>] = 8.4 × 10<sup>-5</sup> M, [Ca<sup>2+</sup>] = 2.9 × 10<sup>-4</sup> M, [Mg<sup>2+</sup>] = 3.3 × 10<sup>-4</sup> M) when leaching Th<sub>3</sub><sup>239</sup>PuP<sub>6</sub>O<sub>23</sub> solid solutions ( $R_L(Pu) = (4.8 \pm 0.3) \times 10^{-8}$  g m<sup>-2</sup> day<sup>-1</sup> at pH = 7 and  $T = 298$  K) [19].

## 5. Conclusion

The dissolution of  $\beta$ -TUPD sintered samples examined in various leaching conditions (pH, temperature, concentrations of ligands or leaching flow rates) confirmed the high resistance of the ceramics prepared to alteration even in very aggressive media.

Far from equilibrium, the influence of several parameters driving the kinetics of dissolution of the ceramics was examined. All of them, such as the partial order relative to the proton concentration ( $n = 0.39$ – $0.41$ ) or the apparent activation energy ( $E_{app} = 49$  kJ mol<sup>-1</sup>) are not influenced by the sintering process developed. Furthermore, the influence of several ligands such as nitrate, chloride or sulphate on the normalized dissolution rates was found to be limited, probably due to the strong thermodynamic constants of complexation of phosphate species relative to actinides.

Even though the saturation processes are delayed when using dynamic conditions (high leaching flow rates), they are always observed by increasing the leaching time, the temperature or the leachate acidity. In these conditions, the formation of thorium phosphate-based secondary phases is suggested at the surface of the pellets inducing the decrease of the uranium release in the leachate by the way of diffusion processes through the alteration layer. Consequently, the dissolution clearly becomes incongruent and controlled by thermodynamic equilibria which are described in the second part of this paper [60].

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