



Kinetics of dissolution of thorium and uranium doped britholite ceramics

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ABSTRACT

In the field of immobilization of actinides in phosphate-based ceramics, several thorium and uranium doped britholite samples were submitted to leaching tests. The normalized dissolution rates determined for several pH values, temperatures and acidic media from the calcium release range from $4.7 \times 10^{-2} \text{ g m}^{-2} \text{ d}^{-1}$ to $21.6 \text{ g m}^{-2} \text{ d}^{-1}$. Their comparison with that determined for phosphorus, thorium and uranium revealed that the dissolution is clearly incongruent for all the conditions examined. Whatever the leaching solution considered, calcium and phosphorus elements were always released with higher R_l values than the other elements (Nd, Th, U). Simultaneously, thorium was found to quickly precipitate as alteration product, leading to diffusion phenomena for uranium. For all the media considered, the uranium release is higher than that of thorium, probably due to its oxidation from tetravalent oxidation state to uranyl. Moreover, the evaluation of the partial order related to proton concentration and the apparent energy of activation suggest that the reaction of dissolution is probably controlled by surface chemical reactions occurring at the solid/liquid interface. Finally, comparative leaching tests performed in sulphuric acid solutions revealed a significant influence of such media on the chemical durability of the leached pellets, leading to higher normalized dissolution rates for all the elements considered. On the basis of the results of chemical speciation, this difference was mainly explained in the light of higher complexation constants by sulfate ions compared to nitrate, chloride and phosphate.

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1. Introduction

Phosphate-based ceramics were already described as potential candidates for the specific immobilization of long-life radionuclides [1–7]. Since several phosphate-based minerals often present high weight loadings in actinides (up to 15 wt.% in ThO₂ or UO₂) associated to strong resistance to aqueous corrosion and to radiation damages [1–5,8,9], these matrices were especially dedicated to the specific immobilization of actinides. In this context, the French Research Groups NOMADE then MATINEX (CNRS/CEA/AREVA/EDF/French Universities) conducted various experiments to select then to study thoroughly four optimized matrices including three phosphate-based ceramics [10]: thorium phosphate-diphosphate (Th₄(PO₄)₄P₂O₇, β-TPD) [11–19] with associated β-TPD/monazite compounds [20], britholites (Ca₉Ln_{1-x}An_x^{IV}(PO₄)_{5-x}(SiO₄)_{1+x}F₂) [21–24] and monazites/brabantite solid solutions

Ln_{1-2x}Ca_xAn_x^{IV}PO₄ [8,25–37], this latter being recently renamed as monazite/cherilite solid solutions, according to the Commission on New Minerals and Mineral Names (CNMMN) nomenclature [38].

The incorporation of actinides in britholites Ca₉Ln_{1-x}An_x^{IV}(PO₄)_{5-x}(SiO₄)_{1+x}F₂, [23,24,34] was mainly driven by geological considerations based on natural apatites (particularly those coming from the Oklo fossil nuclear reactors – Gabon) [39–42]. Their structure can accept a large variety of cationic substitutions, leading to the simultaneous incorporation of lanthanides, thorium and uranium [22,41]. As instance, britholite samples (i.e. phosphate and silicate based apatites) of In Ouzal site (Algeria) were found to locally contain up to 50 wt.% of actinides (U, Th) [42]. Moreover, the apatite structure seems to be able to anneal the defects generated by self-irradiation even at low temperature [43,44]. However, the metamictization process (destruction of the crystal lattice due to radiation damage) strongly depends on the chemical composition of apatites [43,44] and led us to consider the mono-silicated britholite Ca₉Nd(PO₄)₅(SiO₄)F₂ as the starting material [40,42–45].

From literature, the incorporation of thorium in synthetic britholite samples was first examined to prepare fully-silicated apatite Ca₆Th₄(SiO₄)₆O₂ [46]. However, on the basis of the resistance of the material to radiation damage, thorium was more recently

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incorporated in $\text{Ca}_9\text{Nd}_{1-x}\text{Th}_x(\text{PO}_4)_{5-x}(\text{SiO}_4)_{1+x}\text{F}_2$ solid solutions ((Nd, Th)-britholites) through the coupled substitution (Nd^{3+} , PO_4^{3-}) \Leftrightarrow (Th^{4+} , SiO_4^{4-}) [24,34]. For the latter family of samples, the use of successive mechanical grinding steps (15 min, 30 Hz) allowed to increase the specific surface area, improve the reactivity of the mixture then led to a better homogeneity of the final samples [24]. Powdered and sintered samples of (Nd, Th)-britholites were thus prepared as pure and single phase compounds considering this way of preparation [34].

While the thorium incorporation in the britholite structure is easy and quantitative, that of tetravalent uranium is complicated by its redox properties in phosphate compounds [8,47–56]. In this field, several attempts to incorporate uranium in britholites were performed from both uranium oxidation states [53–56]. More recently, a systematic study was devoted to the preparation of $\text{Ca}_9\text{Nd}_{1-x}\text{U}_x(\text{PO}_4)_{5-x}(\text{SiO}_4)_{1+x}\text{F}_2$ ((Nd, U)-britholites) samples [23]. Using this method, all the final samples prepared at 1673 K were found to be composed by $\text{Ca}_9\text{Nd}_{1-x}\text{U}_x(\text{PO}_4)_{5-x}(\text{SiO}_4)_{1+x}\text{F}_2$ and calcium uranate $\text{CaU}_2\text{O}_{5+y}$ as a minor phase which results from the formation of CaUO_4 above 1073 K consequently to the direct reaction between UO_2 and CaO [23]. However, the stabilization of tetravalent uranium was significantly improved by using compaction of the initial mixture powder prior the heating treatment at 1663 K, re-heating steps at 1663 K or simultaneous incorporation of thorium and uranium in their tetravalent form as already described [23,34].

As it was stated previously, the synthesis then the sintering of homogeneous and single phase compounds of the three selected phosphate-based ceramics families was already reported in several papers [6,10,13–17,20–24,32–34,36,37]. Conversely, the literature dealing with the chemical durability of such materials, especially that describing the successive chemical steps occurring at the solid/liquid interface remains rather poor [57–68]. Only few results related to the chemical durability of synthetic monazite/brabantite solid solutions or thorium–phosphate diphosphate were recently reported in literature [57–65] while that driven on britholites mainly concerned natural samples [6,10,66]. Additionally, some data were recently published on Nd-britholite samples for several temperatures (298 K–373 K) and pH values [67]. The dissolution was clearly found to be incongruent on the basis of the preferential calcium or fluorine elementary releases in the leachate. For leaching tests with high renewal of the solution, the normalized dissolution rate determined from the calcium release was evaluated to $10^{-2} \text{ g m}^{-2} \text{ d}^{-1}$ at $\text{pH} = 5.7$ and $T = 363 \text{ K}$ [6]. On the basis of the release of the other elements, the normalized dissolution rates were also determined at room temperature from $\text{pH} = 4$ ($R_L \approx 2 \times 10^{-3} \text{ g m}^{-2} \text{ d}^{-1}$) to $\text{pH} = 7$ ($R_L \approx 5 \times 10^{-1} \text{ g m}^{-2} \text{ d}^{-1}$) [10,66]. Finally, when leaching the samples in the conditions of low renewal of the leachate, the precipitation of Nd-rhabdophane (i.e. $\text{NdPO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$) already reported for leached Nd-monazite samples was clearly evidenced [10,67].

Considering the scarce literature dealing with the resistance of An-ceramics to aqueous alteration, leaching experiments were developed in various leaching conditions. The behaviour of the ceramics loaded with actinides (Th, U) or with surrogate elements for americium or curium (Nd) was examined through a dual approach. It combined kinetics through the multiparametric expression of the normalized dissolution rates then thermodynamics of the dissolution by the way of the identification then complete characterization of alteration products and finally, the determination of the associated solubility constants. In this field, the release of these actinides during aqueous alteration was studied either by making leaching tests of sintered pellets in aggressive media and with high leachate renewals (called “under-saturation” experiments) or by studying the solubility-controlling alteration products through their precipitation in super-saturation conditions

(for low leachate renewals). The kinetic approach aiming at the determination of the real normalized dissolution rates of An-britholites is fully described in this paper while the thermodynamic approach including the complete characterization of alteration products will be discussed in more details in a forthcoming paper.

2. Experimental

2.1. Synthesis and characterization of the initial ceramics

As already described, An-britholite initial powders were obtained through dry chemistry methods after heating the initial reacting mixture ($\text{Ca}_2\text{P}_2\text{O}_7$, CaO , CaF_2 , Nd_2O_3 , SiO_2 and AnO_2 with $\text{An} = \text{U, Th}$) [23,24,34]. Indeed, consequently to the complexity of the chemical scheme and the various elements involved in the chemical formula of britholites, some wet chemistry methods of synthesis were developed without any success due to differential behaviour of the elements during the precipitation step. This aspect was confirmed by super-saturation experiments from dissolved elements in solution [68].

The green pellets were prepared from initial reacting mixtures preheated at 1173 K for 8 h after performing mechanical grinding cycles (30 Hz, 15 min, two steps) then pressing at 200–800 MPa at room temperature in tungsten carbide die. Sintered dense pellets of An-britholites were then prepared ($d = 90\text{--}95\%$ of d_{calc}) after heat treatment at 1573 K for 12 h. As described in the following section, the comparison of the leached materials requires the evaluation of the real surface of contact between the solid and the solution. The specific surface areas ($0.1\text{--}0.2 \text{ m}^2 \text{ g}^{-1}$) of all the samples were thus determined by the BET method using nitrogen or krypton adsorption. The obtained values differed significantly by one to two orders of magnitude from the geometrical surface, as already observed for β -TPD [14] or monazite/cheralite solid solutions [34].

Through an extensive characterization based on XRD, spectroscopic techniques (including infrared and μ -Raman), microscopic experiments (SEM, TEM) and Electron Probe MicroAnalyses, we checked that the final ceramics were single phase and homogeneous, excepted for pure U-britholites, leading to the preparation of solid solutions with the expected chemical composition [23,24,34]. The main results of characterization of the raw samples (XRD, μ -Raman, EPMA, SEM) are presented in Table 1 and in Figs. 1 and 2. Conversely, calcium uranate ($\text{CaU}_2\text{O}_{5+y}$) was observed in all the pure U-britholites samples. This secondary phase was evidenced unequivocally by using XRD, SEM including BSE mode and X-EDS analyses, EPMA and IR/ μ -Raman experiments as mentioned in our already published work [23,34]. It was mainly located at the surface of the pellets after heating and quantitatively eliminated through a polishing step [23,34]. This step allows to access to the true dissolution rate of the raw material without any perturbation of this less durable calcium uranate that could affect the determination of the normalized dissolution rates.

2.2. Leaching tests (under-saturation experiments)

The resistance of the prepared materials to aqueous alteration was evaluated through leaching tests. Such experiments were performed with low or high leachate renewal (called “static” or “dynamic” experiments, respectively) in High Density PolyEthylene (HDPE) or PolyTetraFluoroEthylene (PTFE) containers, as recommended in literature for sorption and leaching of trace-level metals [69]. We checked that, in the conditions of the leaching tests, less than 1% of the total dissolved elements were adsorbed onto the surface of the containers [60–63,65].

Prior to performing leaching experiments, all the samples were washed for 1–7 days at room temperature in order to avoid any

Table 1
Characterization of the raw An-britholite sintered samples.

Sample	$\text{Ca}_9\text{Nd}_{0.5}\text{Th}_{0.5}(\text{PO}_4)_{4.5}(\text{SiO}_4)_{1.5}\text{F}_2$		$\text{Ca}_9\text{Nd}_{0.5}\text{Th}_{0.25}\text{U}_{0.25}(\text{PO}_4)_{4.5}(\text{SiO}_4)_{1.5}\text{F}_2$	
Heating treatment	1663 K – 12 h – Ar atmosphere			
<i>Unit-cell parameters</i>				
<i>a</i> (Å)	9.407(5)	<i>9.408(2)^a</i>	9.397(8)	<i>9.398(2)^a</i>
<i>b</i> (Å)	6.911(4)	<i>6.910(1)^a</i>	6.911(6)	<i>6.9015(15)^a</i>
<i>V</i> (Å ³)	529.6(9)	<i>529.7(4)^a</i>	528.5(4)	<i>527.9(4)^a</i>
		<i>Calc.</i>		<i>Calc.</i>
<i>EPMA results (wt.%)</i>				
O	34.9 ± 0.2	33.4	34.6 ± 0.6	33.3
F ^b	1.8 ± 0.2	3.3	1.8 ± 0.8	3.3
Si	3.6 ± 0.1	3.7	4.1 ± 1.0	3.6
P	12.2 ± 0.2	12.1	11.5 ± 1.7	12.1
Ca	30.4 ± 0.3	31.3	30.0 ± 1.6	31.2
Nd	6.3 ± 0.4	6.3	6.4 ± 0.3	6.2
Th	10.5 ± 0.7	10.1	4.9 ± 0.4	5.0
U	0.1 ± 0.1	–	6.5 ± 1.0	5.2
<i>EPMA (mole ratios)</i>				
Si/P	0.32 ± 0.01	0.33	0.40 ± 0.16	0.33
Nd/Ca	0.06 ± 0.01	0.06	0.06 ± 0.03	0.06
(Th + U)/Ca	0.06 ± 0.01	0.06	0.07 ± 0.01	0.06
(Si + P)/Cat	0.62 ± 0.11	0.60	0.61 ± 0.11	0.60
<i>Raman (main bands)</i>				
δ_S (P–O)		428 cm ⁻¹		430 cm ⁻¹
δ_S (Si–O)		447 cm ⁻¹		448 cm ⁻¹
δ_{AS} (P–O) and (Si–O)		557–580–603 cm ⁻¹		563–585–606 cm ⁻¹
ν_S (Si–O)		856 cm ⁻¹		858 cm ⁻¹
ν_S (P–O)		958 cm ⁻¹		962 cm ⁻¹
ν_{AS} (P–O)		1026–1049 cm ⁻¹		1052 cm ⁻¹
Grain size		1–6 μm		3–20 μm
Pores		0.1–3 μm		1–3 μm
Relative density		90–95%		90–95%
Specific surface area		0.1–0.2 m ² g ⁻¹		0.05–0.15 m ² g ⁻¹

^a Target unit cell parameters of Th-britholite and (U,Th)-britholite single phase samples as reported in literature [23,24] are given in italic.

^b The samples were found to be fluorine-depleted due to its volatilization during the heating treatment, the balance charge compensation being ensured through the F/OH and F/O substitutions.

perturbation due to the presence of crystal defects, non-stoichiometric phases, minor phases or small particles at the surface of the unwashed minerals which could produce, as instance, large amounts of colloids during the first days of leaching tests. By this way, the initial pulse observed in the elementary releases at the beginning of the dissolution curves was usually removed.

Due to the usual strong resistance of phosphate-based ceramics to alteration processes and to the low solubilities associated to the alteration products in neutral or basic media [18–20,37,58–67], such leaching experiments were usually conducted in acid solutions (such as 10⁻⁴ M–10⁻¹ M HNO₃, HCl or H₂SO₄) in order to increase the elementary releases and the associated normalized dissolution rates and to avoid the establishment of any saturation process. By this way, it was possible to access then describe more readily the associated dissolution mechanisms. All the leaching solutions were prepared by dilution of concentrated acids (HNO₃, HCl, H₂SO₄) of analytical grade with deionized water (18.2 MΩ) prepared from Millipore™ apparatus. No particular attention was paid (i.e. outgas of the solutions, inert glove box) to avoid the presence of oxygen (thus the existence of redox reactions) in the leaching solutions.

The elementary concentrations were determined by Inductively Coupled Plasma–Mass Spectroscopy (ICP–MS), Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP–AES), α-scintillation technique or Time-Resolved Laser Fluorescence Spectroscopy (TRLFS) for several leaching times.

For “static” leaching experiments, the samples (100–200 mg) were put in contact with 5–10 mL of solution. At regular intervals, small amount of the leachate (100–200 μL) was removed then analyzed in order to determine the concentrations of several elements

released in the leachate. Only 1–2% of the leachate was renewed by fresh solution. This slow leaching flow (around 10⁻¹ mL day⁻¹) allowed to consider that the system was not significantly modified by this uptake. For several compounds, static experiments usually led to the rapid saturation of the leachate thus allowed to examine the behaviour of the pellets near solubility equilibrium, i.e. when saturation conditions are reached in the leachate.

Consequently, in order to avoid the establishment of thermodynamic control that could induce some discrepancies in the accurate determination of the normalized dissolution rates, dynamic leaching experiments (associated to continuous and rapid renewal of the leachate) were undertaken. Such experiments were performed in a home-made circulation reactor detailed in Fig. 3. Around 200 mg of sample was placed in a PTFE reactor and contacted with 20–25 mL of leaching solution. Sealing of the dispositive was ensured by a PTFE cap and clamping device made of aluminium cap, crown, screws and nuts. The circulation of the fluid inside the reactor was obtained through isoversinic® tubing and the circulation speed was adjusted from 0.5 to more than 50 mL h⁻¹ (i.e. two complete leachate renewals per an hour) thanks to a peristaltic pump. The leaching flow rate was optimized for each kind of samples to avoid the establishment of saturation processes (that occurred for too low leachate renewals) or hydrodynamic problems (associated to too high renewals). The determination of the accurate range of the leaching flow rate was thus examined by studying its influence on the normalized dissolution rate of the ceramics. Finally, the temperature of the experimental set-up was controlled by putting the reactor body in a dry-aluminium bath between room temperature and 363 K. Part of the leachate was periodically collected then the concentrations of selected

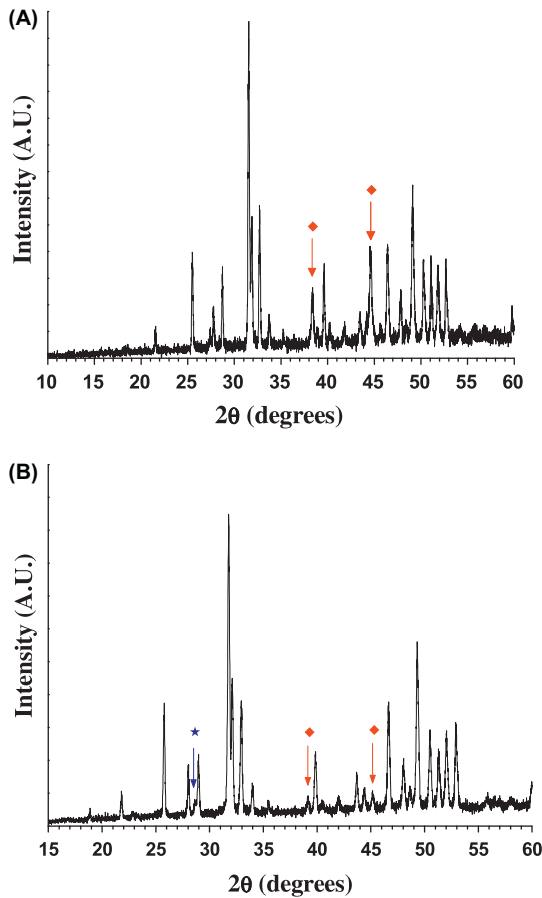


Fig. 1. XRD patterns of (Th)-britholite (A) and (Th, U)-britholite (B) prepared after heating at 1663 K for 12 h under inert atmosphere. XRD lines of the sample holder (♦) and of the main line of calcium uranate $\text{CaU}_2\text{O}_{5+y}$ (★) observed before the polishing step [23].

elements in solution were evaluated after centrifugation at 13,000 rpm for 15 min in order to avoid the presence of colloids.

2.3. Determination of the normalized leachings and normalized dissolution rates

In order to get an accurate comparison of the various materials studied, the leachability of the element i is usually described by its normalized leaching $N_L(i)$ (g m^{-2}). Depending on the conditions of leaching experiments (static or dynamic), the normalized leachings were determined for several elements of interest (usually Ca, P, Th and U in this study). For static experiments, the $N_L(i)$ values (expressed in g m^{-2}) were determined according to the following equation [60,63]:

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

where m_i is the total amount of i measured in solution (g), S the effective surface area (m^2) of the pellet in contact with the solution and f_i is the mass ratio of the element i in the solid.

For dynamic leaching experiments (using high leachate renewal), cumulative normalized leaching were also considered taking into account [70]:

$$N_L(i, t + \Delta t) = \frac{C_i(t) \times d \times \Delta t}{f_i \times S} + N_L(i, t) \quad (2)$$

where $N_L(i, t + \Delta t)$ and $N_L(i, t)$ correspond to the cumulative normalized leachings for i element for a leaching time equal to t and $t + \Delta t$,

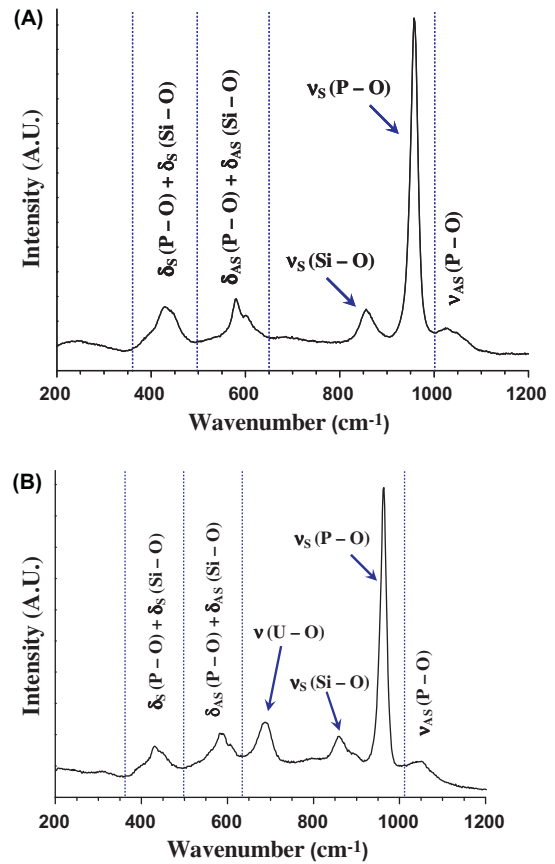


Fig. 2. μ -Raman spectra of (Th)-britholite (A) and (Th, U)-britholite (B) prepared after heating at 1663 K for 12 h under inert atmosphere.

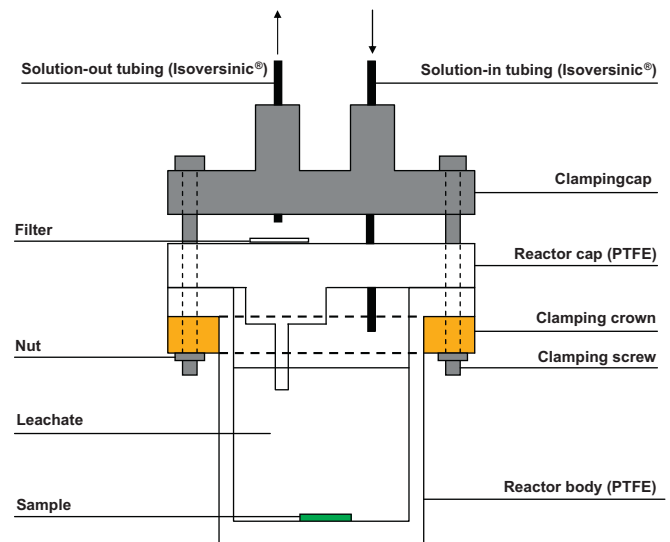


Fig. 3. Leaching device for high renewal dissolution experiments (dynamic leaching experiments).

respectively; t and $t + \Delta t$, the cumulative leaching times (hours or days), respectively, and Δt , the time interval between two uptakes; $C_i(t)$, the concentration of the element i determined by ICP-AES; d , the water flow rate (L h^{-1} or L day^{-1}).

The normalized dissolution rate R_L ($\text{g m}^{-2} \text{d}^{-1}$) which represents the mass loss of the dissolved solid per time and surface

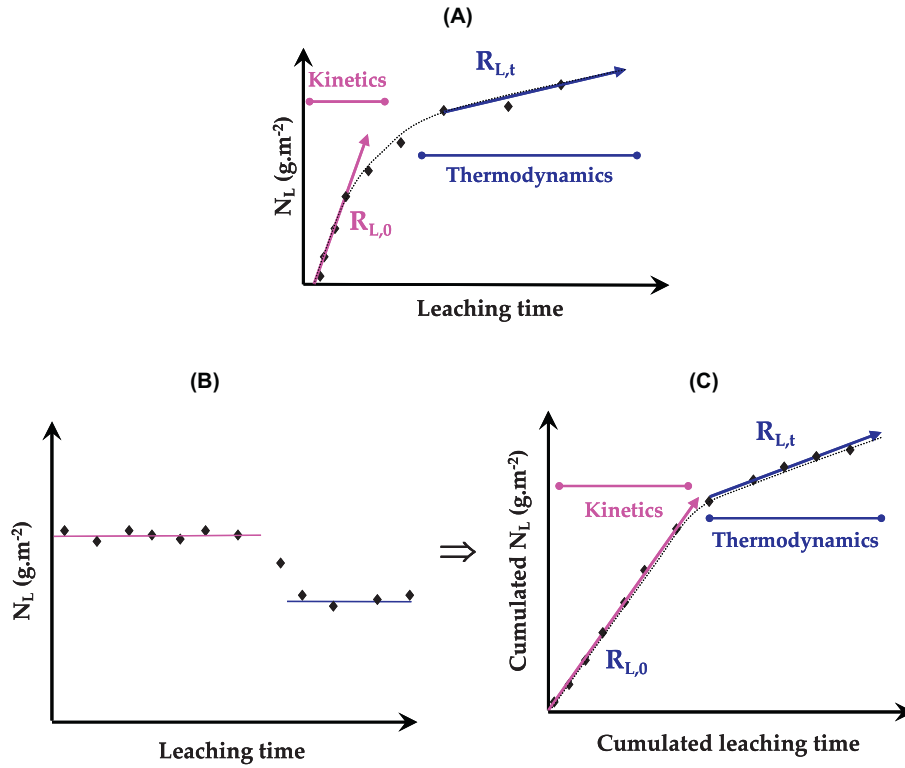


Fig. 4. Evolution of the normalized leaching obtained for leaching tests using static (A) and dynamic (B) conditions. Evolution of the cumulated normalized leaching by integration of the data according to Eq. (2) for dynamic leaching tests (C).

units, was determined from the evolution of the normalized leachings (or cumulative normalized leachings), N_L (g m^{-2}), according to [63]:

$$R_L(i) = \frac{dN_L(i)}{dt} \quad (3)$$

By this way, the chemical durability of the samples is normalized by the reactive surface of the solid in contact with the solution and by the elementary weight loading. When the dissolution occurs far from the equilibrium, the normalized dissolution rates are usually found to be constant as shown in Fig. 4 [63]. On the contrary, near the equilibrium, saturation processes associated to the precipitation of alteration products occur onto the surface of the solids then affect the accurate determination of such R_L values [63].

3. Results and discussion

3.1. Dissolution of britholite samples with low renewal of the leachate (static conditions)

The evolution of the normalized leachings determined during dissolution tests of (Th)-britholites and (Th, U)-britholites using low renewal of the leachate (static conditions) are illustrated in Fig. 5. One can note a similar tendency in the variations of thorium and neodymium releases during such leaching experiments on Th-britholites (Fig. 5A). Indeed, thorium and neodymium releases are observed during the first days of leaching while both elements quickly precipitate as alteration products for longer leaching times. This precipitation was also already mentioned for other phosphate-based ceramics [10,63,65,68]. It was clearly evidenced by

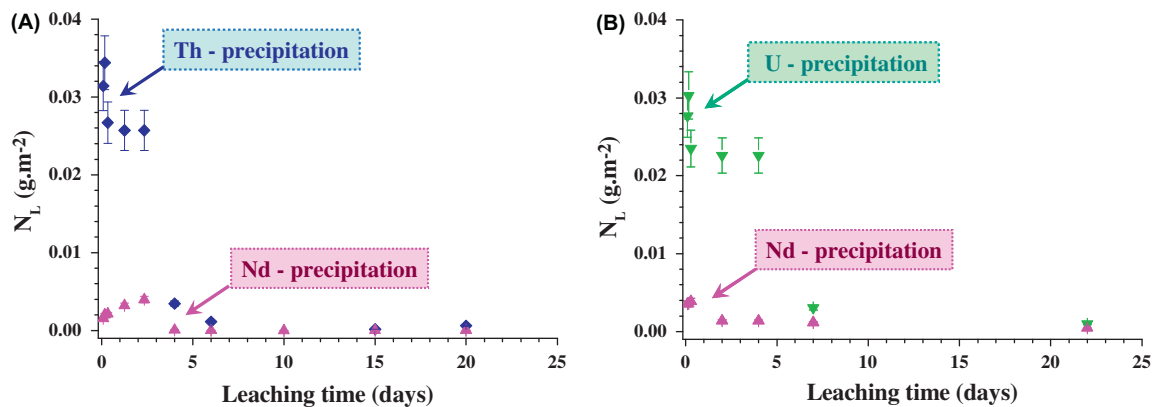


Fig. 5. Evolution of $N_L(\text{Th})$ (\blacklozenge) and $N_L(\text{Nd})$ (\blacktriangle) obtained during “static” leaching tests of (Th)-britholite samples (A) and of $N_L(\text{U})$ (\blacktriangledown) and $N_L(\text{Nd})$ (\blacktriangle) obtained during “static” leaching tests of (Th, U)-britholite samples (B) in 10^{-1} M HNO_3 and for $T = 363$ K.

reducing strongly the leaching flow rates or by extending the leaching time. Such saturation processes were extensively studied and will be described in a forthcoming paper. The rapid establishment of these saturation processes, that strongly depends on the leachate acidity and on temperature, induces some discrepancies in the normalized dissolution rates determined. Indeed, the $R_L(\text{Th})$ and $R_L(\text{Nd})$ values are usually found between $10^{-2} \text{ g m}^{-2} \text{ d}^{-1}$ and $10^{-3} \text{ g m}^{-2} \text{ d}^{-1}$ when leaching the samples at $\text{pH} = 1$ and for $T = 363 \text{ K}$. These values are significantly lower than that reported in literature for Nd-britholites leached in 10^{-4} M HNO_3 at 363 K ($R_L(\text{Ca}) = 10^{-1} \text{ g m}^{-2} \text{ d}^{-1}$) [34,67].

For (Th, U)-britholites, the uranium release slightly differs from that observed for neodymium and thorium, probably due to its oxidation at the solid/liquid interface as already described for the other analyzed phosphate-based ceramics [34,60–64]. Uranium is thus preferentially released in the leachate with a normalized dissolution rate $R_L(\text{U}) = 10^{-1} \text{ g m}^{-2} \text{ d}^{-1}$. This initial release is quickly followed by the uranium precipitation (Fig. 5B). This initial

uranium pulse could have been also attributed to the presence of remaining calcium uranate $\text{CaU}_2\text{O}_{5+y}$. However, the initial composition retained (simultaneous incorporation of thorium and uranium), the polishing procedure of the pellets (thus the elimination of calcium uranate that is mainly located at the surface of the pellets) [23,34] and the washing step performed in the aim to eliminate secondary less durable phases allowed to exclude this assumption.

From static leaching experiments, it is clear that the chemical durability of (Th)-britholites and (Th, U)-britholites are almost the same and that the incorporation of uranium in the material does not seem to affect strongly the chemical resistance of such materials to aqueous alteration near the establishment of thermodynamic equilibria. Moreover, the rapid precipitation of thorium and neodymium then uranium as alteration products at the surface of the leached pellets (as described in a forthcoming linked paper) led us to examine the behaviour of such sintered samples using dynamic leaching experiments.

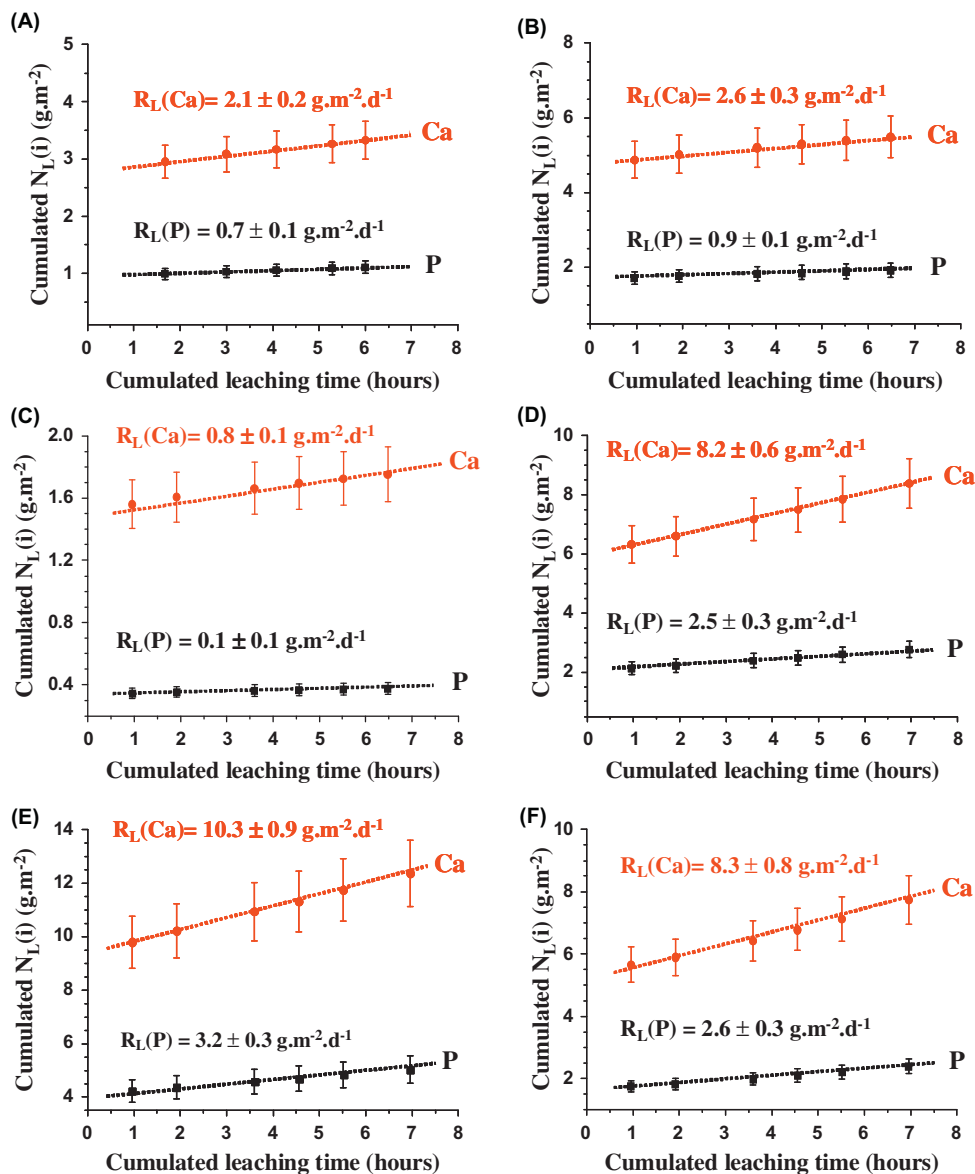


Fig. 6. Evolution of the cumulated normalized leachings $N_L(\text{Ca})$ (●) and $N_L(\text{P})$ (■), obtained during “dynamic” leaching tests on (Th)-britholite: 10^{-1} M HNO_3 and $T = 298 \text{ K}$ (A); 10^{-2} M HNO_3 and $T = 323 \text{ K}$ (B); 10^{-3} M HNO_3 and $T = 323 \text{ K}$ (C); 10^{-2} M HNO_3 and $T = 343 \text{ K}$ (D); 10^{-2} M HNO_3 and $T = 363 \text{ K}$ (E); 10^{-3} M HNO_3 and $T = 363 \text{ K}$ (F).

3.2. Dissolution of britholite samples in dynamic conditions (high renewal of the leachate)

The evolution of the normalized leachings determined during leaching tests of (Th)-britholites and (Th, U)-britholites using high renewal of the leachate (dynamic conditions) are reported in Figs. 6–8. On the basis of the strong dependence of the precipitation on experimental leaching conditions (pH, temperature, nature of the leachate), the leaching flow ranged from 1 to 40 mL h⁻¹ and was fixed depending on the leaching media considered and on the nature of the solid (through its expected chemical durability).

3.2.1. Dissolution of (Th)-britholites

As it was suggested by the leaching experiments performed in static conditions, the resistance of britholite samples appeared lower to that reported for other phosphate-based ceramics such as β-TPD, β-TPD/monazite and monazite/cherilite solid solutions [20,34,60,63,64]. In spite of dynamic leaching conditions, thorium was often precipitated sparingly onto the solid/liquid interface leading to inaccurate R_L(Th) values, conversely to that obtained when determining both R_L(Ca) and R_L(P) normalized dissolution rates (Fig. 6). For these reasons, calcium and phosphorus were favoured as tracer elements for the dissolution of (Th)-britholite samples.

In order to avoid the precipitation of both elements (e.g. as calcium phosphates) and based on the resistance of the examined samples during leaching tests, the leaching time did not exceed several days for leaching flows of 20–40 mL h⁻¹. Whatever the leachate acidity (10⁻¹ M, 10⁻² M and 10⁻³ M HNO₃) and the operating temperature (323 K, 343 K and 363 K), the behaviour of calcium and phosphorus remained almost identical. All the normalized dissolution rates determined (Table 2 and Fig. 6) remained rather high. Moreover, as it was noticed by Chaïrat et al. when leaching Nd-britholite samples, the R_L(Ca) values were sys-

tematically found to be higher than R_L(P) [67]. In order to evidence this point, the direct comparison of R_L(Ca) and R_L(P) values was achieved through the determination of the congruence ratio, $r = R_L(\text{Ca})/R_L(\text{P})$ which interval of variation (3.0 ≤ r ≤ 5.9) confirmed that the dissolution was clearly incongruent mainly due to the precipitation of rhabdophane-type needle crystals at the solid/liquid interface [68].

The direct comparison of the data obtained in acid solutions, confirmed the importance of the proton concentration on the resistance of the materials to aqueous alteration. As already described in several published works, the increase of both R_L(Ca) and R_L(P) values when decreasing the pH of the leachate led to the evaluation of the partial order related to the proton concentration, n_H. Its value was found between 0.1 (for T = 363 K) and 0.8 (for T = 298 K). This strong n_H variation appears to be rather surprising with respect of the data reported in literature for several minerals and materials [63,71–79]. It probably suggests the consequence of saturation processes located at the solid/liquid interface that could affect the release of the other elements by the way of diffusion phenomena. Since this precipitation (thus the formation of neoformed layer at the solid/liquid interface) is activated by the increase of temperature [70], the accurate n_H value probably corresponds to that obtained at room temperature (n_H = 0.8). It is worth to note that this latter value appears in rather good agreement with that obtained on natural britholite samples (coming from Durango) and on synthetic Nd-britholites (i.e. 1.07) [10].

Additionally, the variation of the normalized dissolution rates with temperature (Table 2) seems to indicate a low influence of this parameter on the dissolution of britholites compared to that reported for oxides or other phosphate-based ceramics [20,63,65], as already described for Nd-britholites (E_{App} = 30 kJ mol⁻¹) [10]. Even if such values suggest that the dissolution mechanism is probably controlled by chemical reactions occurring at the solid/liquid interface (E_{App} < 100 kJ mol⁻¹), an additional explanation could result

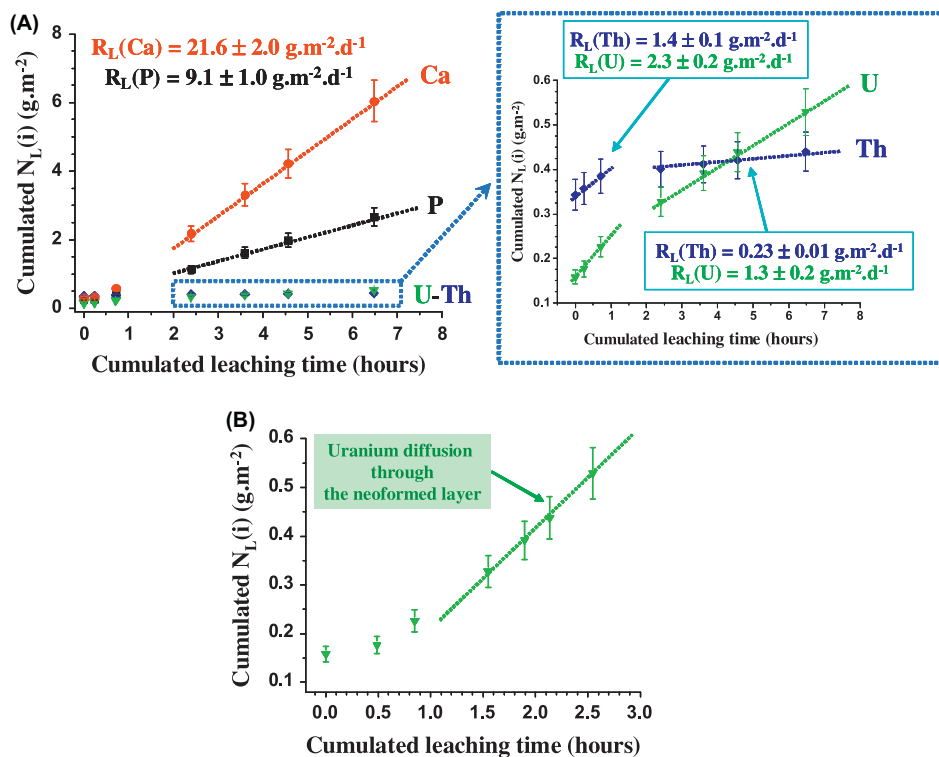


Fig. 7. Evolution of the cumulated normalized leachings $N_L(\text{Ca})$ (●), $N_L(\text{P})$ (■), $N_L(\text{Th})$ (◆) and $N_L(\text{U})$ (▼) (A) obtained during “dynamic” leaching tests on (Th, U)-britholite in 10⁻¹ M HNO₃ at 363 K and associated representation of $N_L(i)$ (▼) versus the square root of time (B).

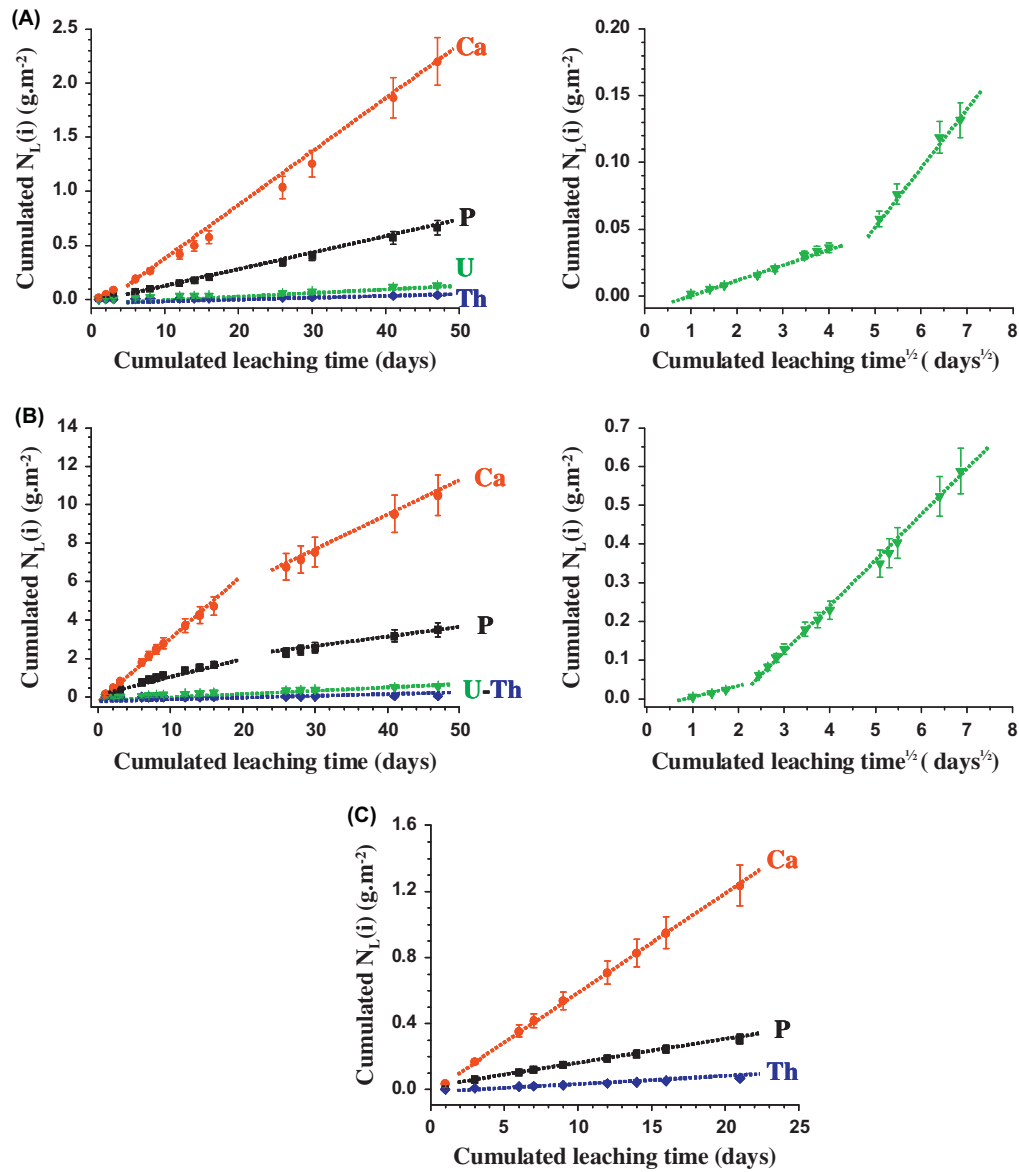


Fig. 8. Evolution of the cumulated normalized leachings $N_L(\text{Ca})$ (●), $N_L(\text{P})$ (■), $N_L(\text{Th})$ (◆) and $N_L(\text{U})$ (▼) obtained during “dynamic” leaching tests on (Th, U)-britholite at 343 K in 10⁻³ M HNO₃ (A), 10⁻³ M H₂SO₄ (B) and 10⁻³ M HCl (C) with associated representation of $N_L(\text{U})$ (▼) versus the square root of time.

Table 2
Normalized dissolution rates of (Th)-britholites obtained during leaching tests in nitric media using dynamic conditions.

Temperature (K)		R_L (g m ⁻² d ⁻¹) ^a		R_L (g m ⁻² d ⁻¹) ^a		R_L (g m ⁻² d ⁻¹) ^a	
		10 ⁻¹ M HNO ₃	r^b	10 ⁻² M HNO ₃	r^b	10 ⁻³ M HNO ₃	r^b
298	Ca	2.1 ± 0.2	3.1	–	–	–	–
	P	0.7 ± 0.1		–		–	
323	Ca	–	–	2.6 ± 0.3	3.0	0.8 ± 0.1	5.9
	P	–		0.9 ± 0.1		0.1 ± 0.1	
343	Ca	–	–	8.3 ± 0.8	3.3	–	–
	P	–		2.5 ± 0.3		–	
363	Ca	–	–	10.3 ± 0.9	3.3	8.3 ± 0.8	3.2
	P	–		3.2 ± 0.3		2.6 ± 0.3	

^a Several normalized dissolution rates were not reached from the ICP-AES experiments due to the rapid precipitation of the analyzed elements despite the high renewal of the leachate considered in this study.

^b Congruence ratio: $r = R_L(\text{Ca})/R_L(\text{P})$.

from the establishment of rapid saturation phenomena that would affect the experiments performed for the higher temperatures considered.

3.2.2. Dissolution of (Th, U)-britholites

On the basis of the results obtained on (Th)-britholites, several dynamic leaching tests were conducted on (Th, U)-britholites

Table 3

Normalized dissolution rates of (Th, U)-britholites obtained during leaching tests using dynamic conditions in 10^{-1} M HNO_3 and $T = 363$ K.

Leaching time (h)	$R_L(i)$ ($\text{g m}^{-2} \text{d}^{-1}$)			
	Ca	P	Th	U
$t < 2$ h	21.6 ± 2.0	9.1 ± 1.0	1.4 ± 0.1	2.3 ± 0.3
$t > 2$ h	21.6 ± 2.0	9.1 ± 1.0	$(2.3 \pm 0.1) 10^{-1}$	1.3 ± 0.2

Table 4

Congruence ratios obtained during leaching tests of (Th, U)-britholites performed in 10^{-1} M HNO_3 and $T = 363$ K and using dynamic conditions for $t < 2$ h and $t > 2$ h.

Leaching time (h)	Element	Ca	P	Th
$t < 2$ h	P	2.4	–	–
	Th	15.4	6.5	–
	U	9.4	4.0	0.6
$t > 2$ h	P	2.4	–	–
	Th	93.9	39.6	–
	U	16.7	7.0	0.2

samples (Figs. 7 and 8) with leaching flows of $1\text{--}40$ mL h^{-1} . The study was first focused on leaching tests performed in 10^{-1} M HNO_3 with high leachate renewals (Fig. 7 and Table 3).

These results clearly confirm the incongruence of the dissolution (with congruence ratios $R_L(\text{Ca})/R_L(\text{U})$ and $R_L(\text{Ca})/R_L(\text{Th})$ of 16.7 and 93.9, respectively: Table 4). Moreover, the direct comparison of thorium and uranium releases reveals different behaviour of both incorporated actinides. Indeed, the difference observed between the $R_L(\text{Th})$ and $R_L(\text{U})$ values evidence the efficient retention of thorium compared to uranium after only 2 h of leaching (Fig. 7A and Table 4: $R_L(\text{Th})/R_L(\text{U}) = 0.6$ for $t < 2$ h and 0.18 for $t > 2$ h). Moreover, the decrease of the $R_L(\text{U})$ value (by a factor of 1.8) is correlated to the quantitative thorium precipitation (which normalized dissolution rate is simultaneously reduced by a factor of 6). This observation probably results from the differences in the redox properties of thorium (that remains tetravalent) and uranium (that is surely oxidized in the uranyl form). It also suggests the establishment of diffusion phenomena of uranium through the neoformed thorium and/or neodymium enriched layer(s) formed at the solid/liquid interface. This assumption was confirmed by plotting the variation of the normalized leaching $N_L(\text{U})$ versus the square root of leaching time (Fig. 7B) that confirmed the linear variation of $N_L(\text{U})$ for $t > 1$ h and could underline the existence of diffusion phenomena [72,80–82].

On the basis of all the congruence ratios reported in Table 4, the leachability of the studied elements can be summarized in the following sequence: $\text{Ca} > \text{P} > \text{U} > \text{Th}$.

3.2.3. Influence of the leaching medium on the dissolution of (Th, U)-britholites

In order to check the influence of the complexing reagent on the chemical durability of the sintered samples, the dissolution tests initially developed in nitric media was extended in hydrochloric and sulphuric acid solutions. The evolution of the normalized leachings obtained during the dissolution of (Th, U)-britholites in 10^{-3} M HNO_3 , 10^{-3} M HCl and H_2SO_4 ($C_{\text{SO}_4} = 10^{-3}$ M, $\text{pH} = 3$) are presented in Fig. 8 while the associated normalized dissolution rates are gathered in Table 5. For the sulphuric acid solution, the final pH value was adjusted to 3 by partial neutralization of free hydronium concentration with concentrated sodium hydroxide solution. As it was already discussed for leaching tests performed at 363 K in 10^{-1} M HNO_3 , the dissolution of the (Th, U)-britholites appears thus clearly incongruent for all the media considered; the

Table 5

Normalized dissolution rates of (Th, U)-britholites obtained during the leaching tests at 343 K in 10^{-3} M HNO_3 , 10^{-3} M HCl and H_2SO_4 ($C_{\text{SO}_4} = 10^{-3}$ M, $\text{pH} = 3$) using dynamic conditions.

Element	$R_L(i)$ ($\text{g m}^{-2} \text{d}^{-1}$)			Leaching time (d)
	HNO_3	HCl	H_2SO_4	
Ca	$(4.7 \pm 0.5) \times 10^{-2}$	$(6.0 \pm 0.6) \times 10^{-2}$	$(3.3 \pm 0.3) \times 10^{-1}$	$t < 16$ d
P	$(1.4 \pm 0.1) \times 10^{-2}$	$(1.4 \pm 0.1) \times 10^{-2}$	$(1.9 \pm 0.2) \times 10^{-1}$	$t > 16$ d
			$(1.2 \pm 0.1) \times 10^{-1}$	$t < 16$ d
Th	$(8.6 \pm 0.9) \times 10^{-4}$	$(3.4 \pm 0.3) \times 10^{-3}$	$(6.0 \pm 1.0) \times 10^{-2}$	$t > 16$ d
			$(1.3 \pm 0.1) \times 10^{-3}$	$t < 16$ d
U	$(2.8 \pm 0.3) \times 10^{-3}$	–	$(1.3 \pm 0.1) \times 10^{-2}$	$t < 16$ d

behaviour of actinides differing significantly from that of calcium and phosphorus whatever the nature of the leaching solution (one to two orders of magnitude between $R_L(\text{Ca})$ and $R_L(\text{P})$, on one side, and $R_L(\text{Th})$ and $R_L(\text{U})$, on the other side). Additionally, the congruence ratios, $r = R_L(\text{Ca})/R_L(\text{P})$, appear consistent in the three media examined (3.4, 4.3 and 2.8 in nitric, hydrochloric and sulphuric acids, respectively) and of the same order of magnitude than that reported for (Th)-britholite samples. Moreover, the normalized dissolution rates $R_L(\text{Th})$ always appear to be very low compared to all the other elements. This confirms the efficient precipitation of thorium and explains the diffusion of uranium through neoformed layers at the solid/liquid interface (Fig. 8).

The direct comparison of the data obtained in the three media studied shows similar chemical durability of britholite ceramics in nitric and hydrochloric media. This can be correlated to the similar complexation constants of the studied elements with nitrate or chloride (e.g. $\log \beta_1(\text{Th}^{4+}, \text{NO}_3^-) = 0.94$ and $\log \beta_1(\text{Th}^{4+}, \text{Cl}^-) = 1.09$) [83].

On the contrary, a significant effect is observed for leaching tests performed in sulphuric acid. Indeed, the $R_L(\text{Ca})$ value reaches $(3.3 \pm 0.3) \times 10^{-1}$ $\text{g m}^{-2} \text{d}^{-1}$ in sulphuric acid (to be compared to $(4.7 \pm 0.5) \times 10^{-2}$ $\text{g m}^{-2} \text{d}^{-1}$ and $(6.0 \pm 0.6) \times 10^{-2}$ $\text{g m}^{-2} \text{d}^{-1}$ in nitric and hydrochloric media, respectively). This difference can be correlated to the stronger complexation constant of sulfate ions with respect to calcium ($\log \beta_1(\text{Ca}^{2+}, \text{NO}_3^-) = 0.28\text{--}0.31$ [84], $\log \beta_1(\text{Ca}^{2+}, \text{Cl}^-) = 0.42\text{--}0.43$ [85,86] and $\log \beta_1(\text{Ca}^{2+}, \text{SO}_4^{2-}) = 2.17\text{--}2.43$ [87–90]) and to the comparison of these three thermodynamic constants with that associated to phosphate complexation ($\log \beta_1(\text{Ca}^{2+}, \text{HPO}_4^-) = 1.64\text{--}2.54$ [91–94]). Indeed, while the complexation of calcium by phosphate should counterbalance efficiently that of calcium by nitrate or chloride at the surface of the leached pellets, the formed complexes are not strong enough with respect to those formed with sulfates. Consequently, the complexation of calcium by sulfate ions probably induces the reduction of the energy of cohesion of calcium atoms present at the surface of the leached pellets thus favours the dissolution of the ceramics. As a consequence, the release of phosphorus is significantly affected ($R_L(\text{P}) = (1.2 \pm 0.1) \times 10^{-1}$ $\text{g m}^{-2} \text{d}^{-1}$ in 10^{-3} M H_2SO_4 compared to $(1.4 \pm 0.1) \times 10^{-2}$ $\text{g m}^{-2} \text{d}^{-1}$ observed in 10^{-3} M HNO_3 or 10^{-3} M HCl). Although the $R_L(\text{U})$ value is found two orders of magnitude lower than $R_L(\text{Ca})$ and $R_L(\text{P})$, the same tendency is observed for uranium which release is increased in sulphuric acid by a factor of 5 compared to nitric acid. As already described for calcium, the higher constant of complexation of uranium by sulfate ions (compared to nitrate ions) can explain such an increase. Finally, as performed in nitric acid, a two-step diffusion phenomena of uranium through the neoformed layers is also evidenced. The second step (observed after more than 8–12 days) and correlated to the change in the evolution of normalized leachings $N_L(\text{Ca})$ and $N_L(\text{P})$ is affected by the

¹ Thermodynamic constant corresponding to the chemical reaction: $\text{M} + \text{L} \rightleftharpoons \text{ML}$, i.e. $\beta_1 = [\text{ML}]/[\text{M}][\text{L}]$.

precipitation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and rhabdophane-type phosphate phase [95].

4. Conclusions

All the static and dynamic leaching tests systematically revealed that the dissolution of britholite samples is incongruent. The normalized dissolution rates determined for several pH values, temperatures and acidic media were found to be higher than that reported for β -TPD, β -TPD/monazite association and monazite/cheralite solid solutions (e.g. the calcium release reaches $21.6 \text{ g m}^{-2} \text{ d}^{-1}$ when leaching (Th, U)-britholite ceramics in 10^{-1} M HNO_3 at 363 K). Whatever the leaching medium considered, calcium and phosphorus elements were always released with higher R_L values than the other elements (Nd, Th, U). Simultaneously, thorium was found to be quickly precipitated as alteration product leading to diffusion phenomena for uranium. For all the media considered, the uranium release is higher than that of thorium, probably due to its oxidation from the tetravalent oxidation state to uranyl.

Comparative leaching tests performed in sulphuric acid solutions revealed a strong influence of such media on the chemical durability of the leached pellets, leading to higher normalized dissolution rates for all the elements considered. The significant decrease of $R_L(\text{Ca})$ and $R_L(\text{P})$, not observed in nitric and hydrochloric media, suggests the precipitation of both elements as alteration products consequently to the more rapid reaching of saturation conditions. The difference observed in sulphuric acid (compared to the other studied media) can be explained in the light of higher complexation constants of the considered elements by sulfate ions.

The evaluation of the partial order related to the proton concentration as well as the apparent activation energy associated to the dissolution of britholite samples suggests that the reaction of dissolution is quickly controlled by chemical reactions occurring at the solid/liquid interface. In order to check this point and to get a better understanding of the dissolution mechanism, some experiments were conducted near the establishment of thermodynamic equilibria. They allowed the identification and the complete characterization of alteration products responsible for the incongruence of the dissolution then their thermodynamic stability. All these results will be published in a forthcoming paper mainly dedicated to the consequence of saturation processes on the chemical durability of britholite ceramics. Finally, the strong difference observed between britholites and monazite/cheralite solid solutions, in spite of some chemical similarities was recently analyzed in the light of periodic Density Functional Theory (DFT) calculations to explain the differences observed between An-bearing britholites and An-bearing monazite/brabantite solid solutions from structural and energetic points of view [96]. From these calculations, the weakness of the energy of cohesion of one calcium site appears to be responsible for such lower chemical durability of the material and can explain the higher leachability of calcium during the leaching tests.

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