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The kinetics of dissolution of $Th_{1-x}U_xO_2$ solid solutions in nitric media

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Abstract

The dissolution of thorium–uranium (IV) dioxide solid solutions has been investigated in nitric media as a function of several parameters (leaching time, acidity of the leachate, temperature and uranium substitution rate in the solid solution) by using batch experiments. The normalized dissolution rates were evaluated for $Th_{1-x}U_xO_2$ with $x < 0.5$, leading to the determination of the partial order related to the proton concentration, n, and to the corresponding normalized dissolution rate constant at $pH = 0$, $k'_{T,298\,K}$. The normalized dissolution rate of $Th_{1-x}U_xO_2$ increases with the acidity of the leachate, and with the amount of uranium in the solid for a given pH. As the thermodynamic equilibrium is not yet reached in acidic media after two years for the solid solutions with $x < 0.5$, only kinetics of the dissolution is described. The stoichiometry of the release of both actinides was verified until the precipitation of thorium occurred in the leachate for $pH > 2$, while uranium was released in the solution under uranyl form. The partial order related to the proton concentration was determined for ThO_2 and three compositions of solid solutions. The variation of the normalized dissolution rate with temperature allowed to determine the activation energy following the Arrhenius law (20, 33 and 16 $kJ\,mol^{-1}$ for ThO_2 $Th_{0.63}U_{0.37}O_2$ and $Th_{0.47}U_{0.53}O_2$ respectively) at pH 2. The dissolution mechanism of $Th_{1-x}U_xO_2$ solid solutions was explained by three steps: initial oxidation of the uranium at the surface, protonation at the U(VI), Th(IV), U(IV) sites, then finally detachment of the surface complexes.

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1. Introduction

Thorium based fuel containing uranium or plutonium appears to be promising in contrast with UO_2 fuel for several reasons. The use of high burn up fuel results in the decrease of the production of long-lived minor actinides production during the burn-up [1,2] and the incineration of plutonium which reduces the toxicity of the final radwaste compared to that obtained for the uranium dioxide. Moreover, ThO_2 is chemically stable while UO_2 can be oxidized further to U_4O_9, U_3O_7, U_2O_5, U_3O_8 or UO_3, more soluble than UO_2. Also $(Th,U)O_2$ or $(Th,Pu)O_2$ spent fuels appear to be a better waste form which could be stored directly in deep geological repository because of the low aqueous solubility of thoria [3,4]. As already reported [2,4–6], the solubility of the amorphous hydrated thorium dioxide remains very low (about 10^{-9} M in natural water conditions at room temperature). The dissolution of the crystallized thorium dioxide is lower [4] than that of amorphous thorium dioxide and limited by the solubility of the thorium hydroxide for $pH > 2$. In the case of Th-based mixed fuel, the ceramic is associated to solid solutions with other actinides U, Np or Pu.

An important question for evaluating the long term behaviour of a ceramic such as ThO_2 containing actinides, concerns the influence of tetravalent actinide such as uranium, neptunium or plutonium incorporated in the lattice on the chemical durability of the ceramic,

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especially in oxidizing medium. One of the main questions to answer concerns the verification (or not) of the congruence of the dissolution of solid solutions containing tetravalent uranium. The high capability of the tetravalent uranium to be oxidized in contact with aqueous solutions can influence the release of both actinides in the leachate by comparison to that of thorium in the pure matrix.

In order to evaluate the long term behaviour of the radionuclides which could be released from a thorium-based fuel, by using simulation codes [1], it is assumed that most of the radionuclides generated in the fuel which are bound to the matrix are released congruently with the dissolution of the matrix. If the solubility of the crystallized thorium dioxide is estimated to be about 10^{-10}–10^{-12} M [4,7] in neutral or basic media, the solubility of uranium dioxide can be highly dependent on the redox conditions of the leachate and varies between 10^{-10} and 10^{-5} M [8–11]. The oxidation of UO_2 into UO_{2+x} in mixed oxide $(Th,U)O_2$ can influence the dissolution behaviour of the ceramic. Up to now, very few dissolution experiments were carried out on solid solutions with tetravalent actinides [12–15].

The objective of this work is to determine experimentally the normalized dissolution rate of pure ThO_2 and several compositions of mixed oxides $Th_{1-x}M_xO_2$ in oxidizing conditions as a function of several chemical parameters (leaching time, proton concentration, temperature and concentration of uranium in the solid). Owing to the very low normalized dissolution rate of the ceramics in natural water, a systematic study was undertaken in acidic conditions. $Th_{1-x}M_xO_2$ solid solutions with various mole-ratios Th/(U + Th) ranging from 0 to 1 were synthesized, then characterized. Dissolution experiments were carried out on three compositions especially $Th_{0.76}U_{0.24}O_2$, $Th_{0.63}U_{0.37}O_2$, and $Th_{0.47}U_{0.53}O_2$ then compared to that of ThO_2 in nitric solution.

2. Experimental

2.1. Synthesis of thorium–uranium (IV) dioxide solid solutions

Thorium nitrate from FLUKA was used for synthesizing powdered thorium dioxide. Thorium oxalate was prepared by adding slowly oxalic acid (60 $g\,l^{-1}$) to the thorium nitrate solution (100 $g\,l^{-1}$) using a perilstatic pump. The oxalate was washed with deionised water, filtered and dried before first heating for 2 h at 500 °C in air, then for 10 h at 1300 °C under inert atmosphere.

Solid solutions of thorium–uranium (IV) dioxide were prepared by mixing concentrated thorium chloride (1.0 M) and uranium (IV) chloride (0.7 M) solutions, in order to keep uranium in its tetravalent state in the initial mixture. After precipitation of oxalate hydrates of the tetravalent cations by adding oxalic acid in excess, the precipitate was washed with deionized water, filtered then finally dried under vacuum. The dried powder was introduced in alumina boats heated in a PYROX furnace at 500 °C under argon for 2 h. Then it was heated at 1300 °C under reducing conditions (Ar–10% H_2 gas) for 10 h with a heating rate of 2–5 °C/min. Several compositions of thorium–uranium (IV) dioxide solid solutions were prepared using this procedure with mole-ratios Th/(U + Th) = 0.11, 0.24, 0.37, 0.53, 0.67, and 0.81.

2.2. Characterization of thorium–uranium (IV) dioxide solid solutions

All the samples were characterized by X-ray diffraction using a Philips PW 1050/70 diffractometer (Cu K_α rays, $\lambda = 1.5418$ Å). For all the samples, the diffraction patterns were identical and typical of a fluorite-related faced centred cubic structure. No additional peak corresponding to neither U_3O_8 nor U_4O_9 was observed. The variation of the unit cell parameters followed the Vegard's law, then clearly confirmed that solid solutions were synthesized [16,17]. The final composition of each solid solution was determined using particle induced X-ray emission (PIXE) analysis and electron probe micro analysis (EPMA). Both techniques gave results in good agreement with that expected (Table 1).

The specific surface area of all samples was determined with a Coulter SA 3100 apparatus, using nitrogen adsorption (BET method). While for pure powdered thorium dioxide a degassing was carried out at 120 °C during 300 min, it was performed at 70 °C during 600 min for solid solutions in order to avoid any oxidation of tetravalent uranium into uranyl species. The specific surface area measured for all samples (Table 2) was of the same order of magnitude (0.7–1.1 $m^2\,g^{-1}$) except for $x = 0.11$ and 0.24, which exhibited higher values (1.6 and 1.3 $m^2\,g^{-1}$, respectively).

The corresponding average grain size was typically of 0.5 μm. Moreover some square aggregates with grain

Table 1
EPMA and PIXE results obtained for $Th_{1-x}U_xO_2$

$X_{initial}$	0.10	0.25	0.35	0.50	0.65	0.80	0.90
x_{exp} (PIXE)	0.109 (2)	0.239 (4)	0.371 (7)	0.52 (1)	0.66 (2)	0.81 (4)	0.91 (5)
x_{exp} (EPMA)	–	0.24 (4)	–	0.53 (9)	–	0.81 (5)	–

Table 2
Specific surface area values of $Th_{1-x}U_xO_2$ solid solutions

Uranium mole ratio	0	0.11	0.24	0.37	0.53	0.67	0.81	0.91	1
Specific area ($m^2\,g^{-1}$)	0.7	1.6	1.3	0.9	1.1	0.8	0.7	0.7	0.8

With an accuracy of ±0.1.

sizes of about 1–2 μm were also observed as it is clearly shown from SEM micrographs (Fig. 1).

The X-ray photoelectron spectroscopy (XPS) was investigated to probe the chemical state of uranium at the surface of the solid solutions before leaching using an MgK_α source (1253.6 eV, FWHM: 0.9 eV). The spectrum, recorded for the solid solutions on an ESCA apparatus with a multidetection electron analyser VSW HA150 (in fixed analyser transmission (FAT) mode), is reported on Fig. 2(a). The U_{4f} spectra were fitted using the software XPSPeak 3.0, with a Gaussian–Lorentzian peak shape. The charge effects were corrected using the C_{1S} line from contamination at 284.6 eV to calibrate the energy scale. The $U_{4f(5/2)}$ and $U_{4f(7/2)}$ peaks fitting corresponds to the photoemission of U(IV) centred at 391 and 380.2 eV typical of the binding energies of UO_2. However, the presence of traces of U(VI) is observable on the surface of the solid with the presence of two peaks centred at 381.3 and 391.1 eV in good agreement with that reported for U(VI) in UO_3 [9].

2.3. Leaching test procedure

The leaching tests were performed using batch experiments in high density polyethylene containers (Nalgene™) at room temperature. Prior to leaching experiments, all the samples were washed in order to avoid any pertubation due to the presence of minor phases or small particles which could produce large amounts of colloids during the first days of the leaching tests. The solids were first washed for 15 days in acidic media

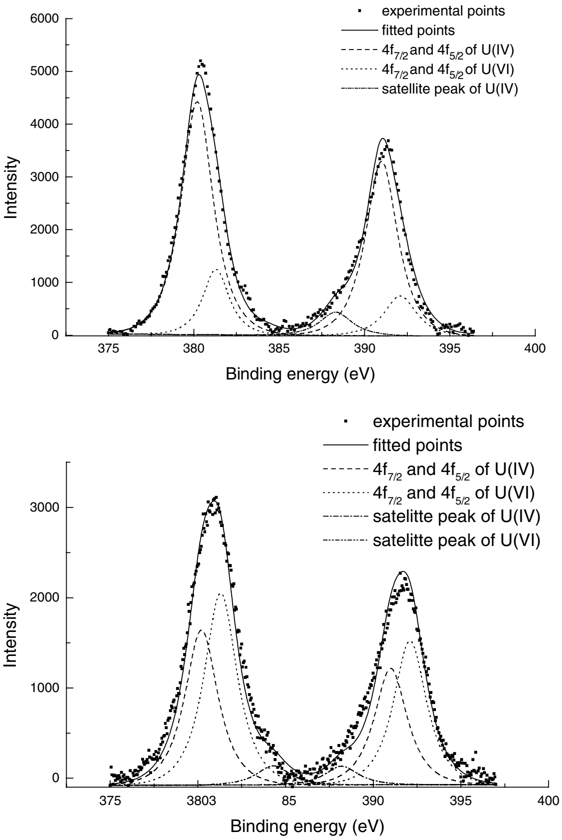

Fig. 2. Deconvolution of the $U_{4f(5/2)}$ and $U_{4f(7/2)}$ photoelectron peak into U(IV) and U(VI) from $Th_{0.47}U_{0.53}O_2$ before and after leaching during 2 years (HNO_3 10^1 M, $\theta = 25$ °C).

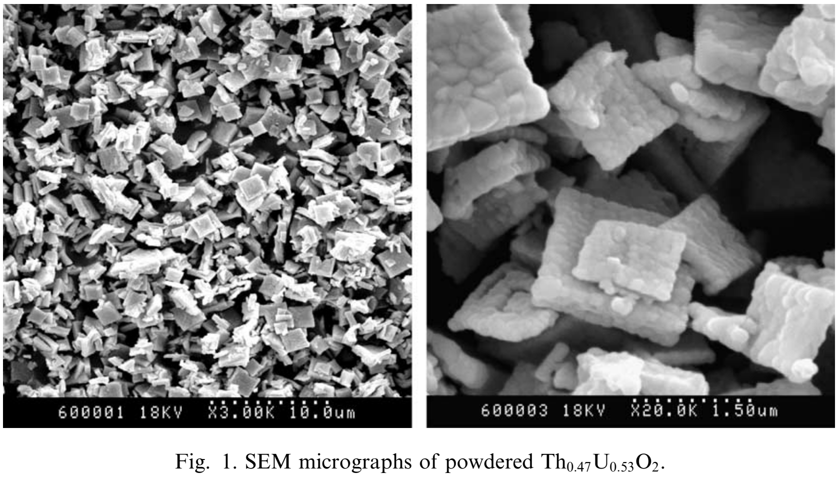

Fig. 1. SEM micrographs of powdered $Th_{0.47}U_{0.53}O_2$.

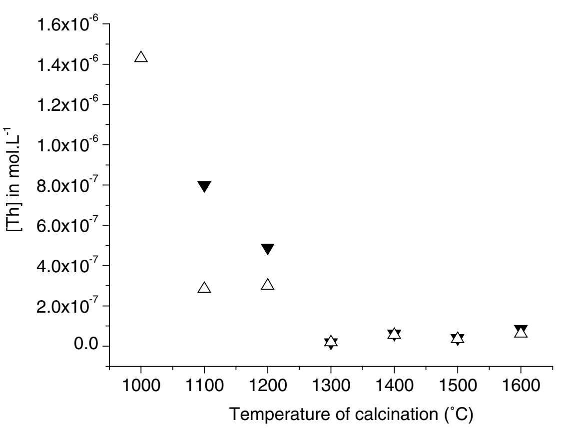

Fig. 3. Thorium concentration measured by ICP/MS in the leachate (leaching tests of ThO_2 in 10^{-1} M HNO_3 during 10 days) after centrifugation at 3000 rpm (▼) and ultracentrifugation at 13 000 rpm (△) as a function of calcination temperature.

(10^{-1} M HNO_3), washed in deionized water then finally in the electrolyte solution (10^{-1}–10^{-4} M HNO_3). The calcination temperature of the solids (1300 °C) was also chosen to produce as less colloids as possible during the leaching tests (Fig. 3). Since the dissolution of the thorium dioxide in neutral or basic media is very slow, the leaching tests of all solids were achieved in acidic media by mixing 300 mg of powder with 15 ml of solution. The leaching solutions were in contact with air in most of the case, except for basic solutions (pH 7 and 11) for which an argon atmosphere was kept for avoiding the presence of carbonate. The samples were kept under agitation during all the dissolution tests from few months to several years. We checked that, in the conditions of the leaching tests, less than 1% of the total dissolved elements were adsorbed onto the walls of the containers. The pH of the electrolyte was adjusted with 0.1 M HNO_3 (or 0.1 M KNO_3) in order to keep the ionic strength constant ($I = 0.1$ M) except for experiments in 1 M and 5 M HNO_3. The S/V ratio was chosen at nearly 200 cm^{-1}. After centrifugation at 3000 rpm, the pH was measured. 200 μl were removed, and then replaced by the same amount of fresh solution containing the electrolyte. Then liquid and solid in the aliquot phases were separated by centrifugation at 13 000 rpm to avoid colloids with size smaller than 11 nm. Finally, the concentration of thorium and uranium released in the leachate was determined either by inductively coupled plasma-mass spectrometry (ICP-MS, apparatus Fisons Plasma Quad) after dilution in HNO_3 1% and addition of two internal standards (1 ppb of Tb and Bi) or by α-liquid scintillation technique Photon Electron Rejecting Alpha Liquid Scintillation spectrometry.

The leaching tests were performed on powdered $Th_{1-x}U_xO_2$ solid solutions with $x = 0$, 0.24, 0.37 and 0.53 in HNO_3 solutions for $0 \leqslant pH \leqslant 7$, and in 5 M HNO_3. Except in 1 and 5 M HNO_3, the ionic strength was kept at 0.1 M.

3. Results

We investigated the dissolution of several $Th_{1-x}U_xO_2$ solid solutions containing different amount of uranium (IV) in nitric media where U(IV) in contact with the solution was oxidized in U(VI) more soluble than U(IV) and compared to that of thorium dioxide. In these conditions, we expect an oxidative/dissolution mechanism as described by Pablo et al. [18] in three steps: initial oxidation of uranium at the solid surface of the solid solution, protonation at the U(VI), Th(IV), U(IV) sites then detachment of the surface complexes.

3.1. Kinetics of the ThO_2 and $Th_{0.76}U_{0.24}O_2$ dissolution

The experiments were performed at 25 °C on pure thorium dioxide and $Th_{0.76}U_{0.24}O_2$ in 10^{-1}–10^{-4} M, 1 and 5 M HNO_3. For leaching tests carried out in HNO_3 concentration less than 10^{-3} M, the thorium concentration in the leachate was always very low ($C_{Th} < 10^{-8}$ M) compared to the uranium concentration. Then, in most of the experimental dissolution curves, only the normalized mass loss of uranium will be reported. For ThO_2, the dissolution kinetics was investigated until pH 11, but the dissolution curves are reported only for pH < 3. However the Th and U concentration in the leachate are given for ThO_2 and $Th_{0.76}U_{0.24}O_2$ in Tables 3 and 4 for some leaching times and most of the studied pH.

The normalized leaching of thorium and uranium from the thorium–uranium (IV) dioxide solid solutions was calculated from the elementary concentration measured in the leachate following the equation [1]:

$$N_L(i) = \frac{m_i}{f_i S}, \tag{1}$$

where m_i corresponds to the total amount of the element i measured in the solution (g), S, the corresponding solid area (m^2) and f_i, the mass ratio of the element i in the solid.

For a congruent dissolution, all the elements are dissolved with the same normalized dissolution rate and do not form secondary phases in the back-end of the initial process of the dissolution. In these conditions, the mass of dissolved matrix can be calculated directly from the concentration of each element measured in the leachate.

The normalized leaching was determined for the first 300 days of leaching time for ThO_2 and 800 days for $Th_{0.76}U_{0.24}O_2$ in several nitric solutions from pH = 1–7, in 1 M and 5 M HNO_3. The evolution of the normalized

Table 3
Th concentration (M) released in nitric solutions for ThO_2

Leaching time (days)	5 M	1 M	10^{-1} M	10^{-2} M	10^{-4} M	10^{-7} M
1	2×10^{-7}	6.1×10^{-8}	10^{-8}	2.2×10^{-8}	7.5×10^{-9}	2.3×10^{-9}
3	4.5×10^{-7}	1.4×10^{-7}	3.3×10^{-8}	3.3×10^{-8}	1.6×10^{-8}	8.8×10^{-9}
10	8.4×10^{-7}	2.8×10^{-7}	8.8×10^{-8}	6.5×10^{-8}	2.2×10^{-8}	1.4×10^{-8}
30	1.5×10^{-6}	–		–	5.1×10^{-9}	5×10^{-9}
45	1.9×10^{-6}	5.4×10^{-7}	2.1×10^{-7}	–	–	1×10^{-9}
90	3.1×10^{-6}	–		2.6×10^{-7}	9.9×10^{-9}	–
150	3.6×10^{-6}	–		2.7×10^{-7}	1.2×10^{-8}	–
300	5.4×10^{-6}	1.3×10^{-6}	7×10^{-7}	–	–	–
500	6.5×10^{-6}	1.7×10^{-6}	10^{-6}	8.7×10^{-7}	–	–

With an accuracy of 8%.

Table 4
Th and U concentrations (M) released in HNO_3 solutions for $Th_{0.76}U_{0.24}O_2$

Leaching time (days)	5 M	1 M	10^{-1} M	10^{-2} M	10^{-3} M	10^{-4} M	10^{-7} M
1	1.9×10^{-5}	8.9×10^{-6}	1.5×10^{-6}	7.2×10^{-7}	4.9×10^{-8}	5×10^{-10}	–
	8.3×10^{-6}	*4.1×10^{-6}*	*1.1×10^{-6}*	*6.4×10^{-7}*	*5.5×10^{-7}*	*3.7×10^{-7}*	*1.9×10^{-9}*
3	4.1×10^{-5}	1.5×10^{-5}	3.4×10^{-6}	1.3×10^{-6}	5.4×10^{-8}	9.7×10^{-10}	3.2×10^{-10}
	1.6×10^{-5}	*8.7×10^{-6}*	*2.7×10^{-6}*	*1.2×10^{-6}*	*8.6×10^{-7}*	*6.1×10^{-7}*	*4.5×10^{-9}*
10	1.2×10^{-4}	4.8×10^{-5}	1.1×10^{-5}	3×10^{-6}	7.8×10^{-8}	–	–
	4.6×10^{-5}	*2.4×10^{-5}*	*8.4×10^{-6}*	*3×10^{-6}*	*2.2×10^{-6}*	*10^{-6}*	*10^{-8}*
30	2.5×10^{-4}	8.8×10^{-5}	2×10^{-5}	5.5×10^{-6}	1.4×10^{-7}	2.2×10^{-8}	
	9.8×10^{-5}	*4.4×10^{-5}*	*1.6×10^{-5}*	*7.5×10^{-6}*	*3.4×10^{-6}*	*1.7×10^{-6}*	*1.9×10^{-8}*
50	3.4×10^{-4}	1.2×10^{-4}	2.6×10^{-5}	7.7×10^{-6}	6.3×10^{-8}		
	1.3×10^{-4}	*6×10^{-5}*	*2×10^{-5}*	*1.1×10^{-5}*	*4.1×10^{-6}*		
130	7.2×10^{-4}	2.3×10^{-4}	4.6×10^{-5}	1.7×10^{-5}			
	2.4×10^{-4}	*9.2×10^{-5}*	*3.2×10^{-5}*	*2×10^{-5}*	*6.9×10^{-6}*	*2.7×10^{-6}*	*6×10^{-8}*
275	1.1×10^{-3}	3.3×10^{-4}	6.9×10^{-5}	2.2×10^{-5}	1.6×10^{-6}		
	4.1×10^{-4}	*1.3×10^{-4}*	*4.1×10^{-5}*	*2.3×10^{-5}*	*9.4×10^{-6}*		
450	1.6×10^{-3}	4.2×10^{-4}	7.5×10^{-5}	2.8×10^{-5}			
	5.6×10^{-4}	*1.7×10^{-4}*	*4.4×10^{-5}*	*2.6×10^{-5}*	*1.1×10^{-5}*		
735	2.7×10^{-3}	7.2×10^{-4}	7.1×10^{-5}	3.5×10^{-5}			
	8.8×10^{-4}	*2.5×10^{-4}*	*6×10^{-5}*	*3.2×10^{-5}*	*1.3×10^{-5}*	*1.2×10^{-5}*	*3.3×10^{-6}*

Italic numbers correspond to U concentration with an accuracy of 8%.

mass losses of thorium from ThO_2 and $Th_{0.76}U_{0.24}O_2$ in acidic media is given in Fig. 4. For both solids, the behaviour during leaching tests is almost the same whatever the pH, however the thorium concentration in the leachate was about two orders of magnitude higher for $Th_{0.76}U_{0.24}O_2$ than for ThO_2 in acidic solution. As expected, an increase of the concentration of the dissolved matrix with the presence of uranium in the solid was generally observed in acidic nitric solution for each pH.

The evolution of the normalized mass losses N_L (U) and N_L (Th) for the solid solution $Th_{0.76}U_{0.24}O_2$ is presented for several pH in Fig. 5. As expected, an increase of the concentrations of Th and U when increasing the leaching time was observed for each pH (see Table 4). For leaching times beside 20 days, uranium was released preferentially from the solid compared to the thorium while for longer leaching times and for $pH < 3$, both actinides were released congruently with a slower normalized dissolution rate. The different behaviour observed in the first part of the leaching curve was explained by the preferential release of minor phases containing probably small amount of U(VI) more mobile than U(IV) or Th(IV). In the second part of the leaching curves (after 50 days), because of the very slow dissolution, as for ThO_2, the normalized mass loss of U and Th from $Th_{0.76}U_{0.24}O_2$ varies linearly until about 800 days, and the kinetics of the dissolution was estimated from the linear part of the curves.

While the normalized mass loss N_L (U) for $Th_{0.76}U_{0.24}O_2$ decreased when increasing the pH from $pH = 1$ to 7, as expected in the literature [19,20], the normalized mass loss N_L (Th) decreased from log $[H_3O^+] = -0.6$ up to 2. For $pH > 3$, the thorium concentration measured in the leachate was always close to

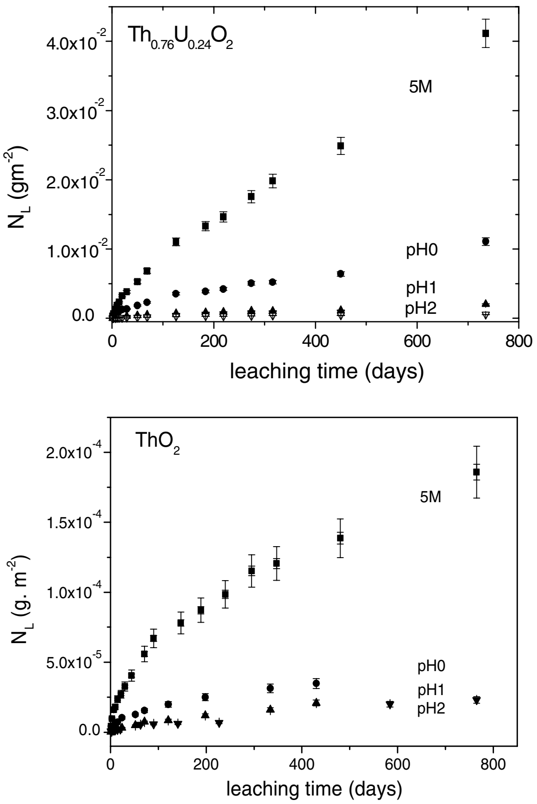

Fig. 4. Evolution of the normalized dissolution for $Th_{0.76}U_{0.24}O_2$ (U release) and for ThO_2 (Th release).

the detection limit of the ICP-MS (10^{-10}–10^{-11} M), underlining the formation of precipitate or colloids larger than 11 nm, in the leachate (probably $Th(OH)_4$). This behaviour is almost the same for both solids. For $Th_{0.76}U_{0.24}O_2$, the reversible equilibrium was not yet reached after 800 days and the dissolution was mainly controlled by kinetic processes, however after 200 days, a slowing down of the dissolution rate is observed.

Considering that the first part of the curves was probably due to the dissolution of crystal defects or impurities such as minor phases, we did not use this part of the curves to estimate the initial dissolution rate as it is currently performed for glasses. We only considered the second part of the curves after 100 days to estimate the normalized dissolution rate.

The expression of the normalized dissolution rate was deduced from the evolution of the normalized mass loss. Using the approach described by Lasaga [21], the normalized dissolution rate of the solid, R_L ($g\,m^{-2}\,d^{-1}$) can be written as follows:

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

When the dissolution is congruent, dm_i/dt being the mass change of the element i measured in the solution.

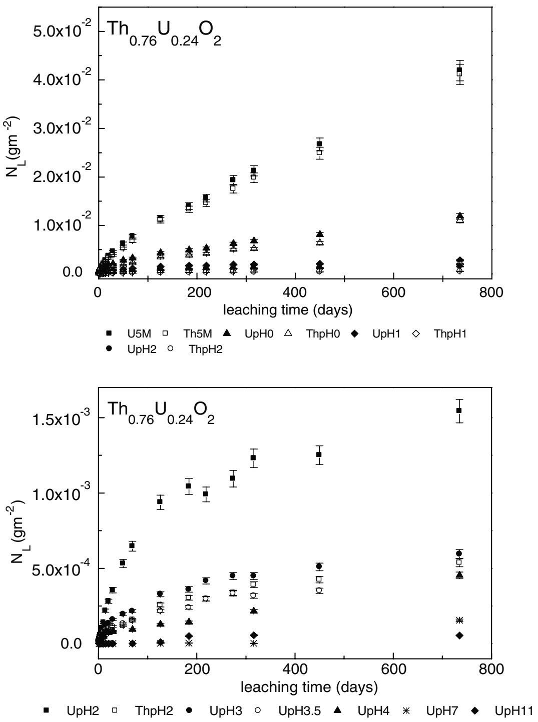

Fig. 5. Evolution of the normalized leaching for $Th_{0.76}U_{0.24}O_2$ in several acidic media.

In acidic medium, the dissolution rate is usually noted R_H.

From the linear part of the leaching curves (between 100 and 800 days), the normalized dissolution rate R_H was estimated for each pH value and for each actinide released from the solid by linear regression of the experimental data.

The R_H values determined for $Th_{0.76}U_{0.24}O_2$ and ThO_2 are given in Table 5. For both actinides, the normalized dissolution rates calculated from the dissolution curve were of the same order of magnitude. However, it appeared that the dissolution rate of the solid solution was one to two orders of magnitude higher than that of ThO_2, whatever the pH considered. This result was interpreted by the oxidation of U(IV) in contact with the solution into U(VI) which increased the normalized dissolution rate of the matrix, both thorium and uranium being released congruently. For $pH > 3$, the Th(IV) concentration in the leachate was very low ($\sim 10^{-9}$ M) and probably controlled by the precipitation of the thorium hydroxide [4], while the uranium released in the leachate was due to the detachment of uranyl species.

The XPS analysis on the surface of the solid solution $Th_{0.47}U_{0.53}O_2$, after leaching at $pH = 1$ during two years (Fig. 2(b)) confirmed the increase of the quantity of U(VI) at the surface of the sample. The $U_{4f(5/2)}$ and

Table 5
Normalized dissolution rates obtained for $Th_{1-x}U_xO_2$ ($g\,m^{-2}\,d^{-1}$) versus leachate acidity

$[HNO_3]$ M	ThO_2	$Th_{0.76}U_{0.24}O_2$		$Th_{0.63}U_{0.37}O_2$		$Th_{0.47}U_{0.53}O_2$
	R_H (Th)	R_H (Th)	R_H (U)	R_H (Th)	R_H (U)	R_H (U)
5	$(1.7\pm0.1)\times10^{-7}$	$(5.0\pm0.1)\times10^{-5}$	$(5.0\pm0.1)\times10^{-5}$	$(5.1\pm0.1)\times10^{-4}$	$(5.1\pm0.1)\times10^{-4}$	–
1	$(8.3\pm0.2)\times10^{-8}$	$(1.3\pm0.1)\times10^{-5}$	$(1.3\pm0.1)\times10^{-5}$	$(8.1\pm0.1)\times10^{-5}$	$(8.1\pm0.1)\times10^{-5}$	–
10^{-1}	$(4.8\pm0.1)\times10^{-8}$	$(2.0\pm0.2)\times10^{-6}$	$(2.2\pm0.1)\times10^{-6}$	$(6.4\pm0.1)\times10^{-6}$	$(6.9\pm0.1)\times10^{-6}$	$(2.5\pm0.2)\times10^{-3}$
10^{-2}	$(7.0\pm0.1)\times10^{-9}$	$(4.5\pm0.1)\times10^{-7}$	$(9.7\pm0.1)\times10^{-7}$	$(3.3\pm0.1)\times10^{-6}$	$(3.3\pm0.1)\times10^{-6}$	$(1.3\pm0.2)\times10^{-4}$
10^{-3}	–	–	$(4.5\pm0.1)\times10^{-7}$	–	–	$(1.3\pm0.1)\times10^{-5}$
$10^{-3.5}$	–	–	$(6.0\pm0.2)\times10^{-7}$	–	–	
10^{-4}	–	–	$(5.4\pm0.1)\times10^{-7}$	–	–	
10^{-7}	–	–	$(1.7\pm0.2)\times10^{-8}$	–	–	

$U_{4f(7/2)}$ peaks fitting of the final solid surface showed that the contribution of U(VI) (at 381.3 and 392.1 eV respectively) was more important in comparison of the unleached solid.

This observation indicated that the oxidation of uranium at the surface occurred before the detachment of the uranyl complex.

3.2. Influence of the composition of the solid solution on the normalized dissolution rate

The leaching experiments were performed on three compositions of $Th_{1-x}U_xO_2$ solid solutions with U/U + Th mole ratios of 0.24, 0.37 and 0.53 in several nitric solutions (5M, 1M, 10^{-1} M and 10^{-2} M HNO_3) during about 800 days. The values of Th and U concentrations in the leachate for all samples and different pH are gathered in Tables 6 and 7. An example of the evolution of the dissolved mass of thorium for ThO_2, $Th_{0.76}U_{0.24}O_2$ and $Th_{0.67}U_{0.37}O_2$ is given in Fig. 6 at pH = 2. For a given pH, the normalized dissolution rate of both actinides increased all the more since the substitution rate of thorium by uranium increased. Between 50 and 700 days, the variations of the normalized leaching were linear in most of the case. This behaviour typical of surface controlled mechanism was similar for both actinides, whatever the pH considered. The corresponding normalized dissolution rates R_H are given in Table 5. Both actinides U and Th released congruently, whatever the composition of the solid solutions, until pH = 2. Beyond this value, the precipitation of thorium hydroxide occurred, while the uranium, which was oxidized in the U(VI) state at the surface of the solid, remained in the leachate. Fig. 7 shows an example of the evolution of the dissolved mass of thorium and uranium for $Th_{0.47}U_{0.53}O_2$. In this case, we observed a fast dissolution step in the first 100 days, followed by a second step of decrease of the dissolution rate whatever the pH.

3.3. Influence of the proton concentration on the normalized dissolution rate

Many authors [18,19] already demonstrated that the normalized dissolution rates of most of the minerals

Table 6
Th and U concentrations (M) released in HNO_3 solutions for $Th_{0.63}U_{0.37}O_2$

Leaching time (days)	5 M	1 M	10^{-1} M	10^{-2} M
1	1.3×10^{-5}	3.4×10^{-6}	1.1×10^{-6}	5.9×10^{-7}
	10^{-5}	*2.6×10^{-6}*	*1.1×10^{-6}*	*7.1×10^{-7}*
3	3.3×10^{-5}	8.1×10^{-6}	3.5×10^{-6}	2×10^{-6}
	1.1×10^{-5}	*5.7×10^{-6}*	*3×10^{-6}*	*1.9×10^{-6}*
10	8.8×10^{-5}	2.4×10^{-5}	8.6×10^{-6}	5.1×10^{-6}
	6.8×10^{-5}	*1.7×10^{-5}*	*6.6×10^{-6}*	*4.1×10^{-6}*
30	2.3×10^{-4}	5.4×10^{-5}	1.6×10^{-5}	9.7×10^{-6}
	1.6×10^{-4}	*4.1×10^{-5}*	*1.2×10^{-5}*	*6.9×10^{-6}*
90	9.9×10^{-4}	2×10^{-4}	4.2×10^{-5}	1.9×10^{-5}
	7.9×10^{-4}	*1.6×10^{-4}*	*3.1×10^{-5}*	*1.4×10^{-5}*
230	4.1×10^{-3}	7×10^{-4}	8.7×10^{-5}	3.5×10^{-5}
	2.8×10^{-3}	*4.9×10^{-4}*	*6.3×10^{-5}*	*2.4×10^{-5}*
585	8.1×10^{-3}	1.7×10^{-3}	1.8×10^{-4}	8.8×10^{-5}
	5.3×10^{-3}	*1.2×10^{-3}*	*1.2×10^{-4}*	*5.3×10^{-5}*

Italic numbers correspond to U concentration with an accuracy of 8%.

Table 7
Th and U concentrations (M) released in HNO_3 solutions for $Th_{0.47}U_{0.53}O_2$

Leaching time (days)	10^{-1} M	10^{-2} M	10^{-3} M
1	3×10^{-5}	1.6×10^{-5}	4.6×10^{-7}
	3.6×10^{-5}	*1.9×10^{-5}*	*8.1×10^{-6}*
3	1.6×10^{-4}	2.7×10^{-5}	8.6×10^{-7}
	2.1×10^{-4}	*3.5×10^{-5}*	*1.6×10^{-5}*
10	10^{-3}	5.5×10^{-5}	9.2×10^{-7}
	1.2×10^{-3}	*7.5×10^{-5}*	*1.9×10^{-5}*
25	2.2×10^{-3}	1.4×10^{-4}	2.4×10^{-6}
	2.7×10^{-3}	*1.8×10^{-4}*	*2.4×10^{-5}*
130	7.4×10^{-3}	3.6×10^{-4}	2.6×10^{-6}
	8.3×10^{-3}	*5.4×10^{-4}*	*4.9×10^{-5}*
210	8.4×10^{-3}	4.4×10^{-4}	4×10^{-6}
	9.7×10^{-3}	*6.4×10^{-4}*	*5.1×10^{-5}*
585		6.7×10^{-4}	5.9×10^{-6}
		8.8×10^{-4}	*6.6×10^{-5}*

Italic numbers correspond to U concentration with an accuracy of 8%.

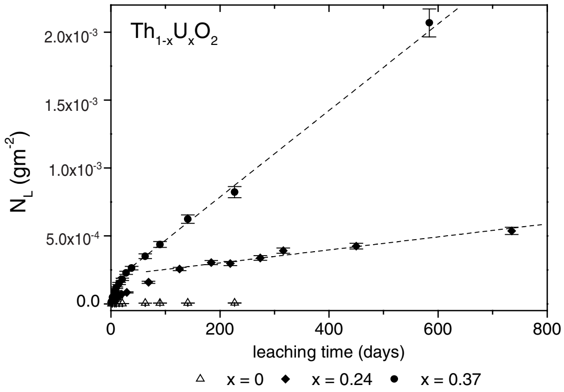

Fig. 6. Comparison of the normalized leaching for several compositions of solid solutions in 10^{-2} M HNO_3.

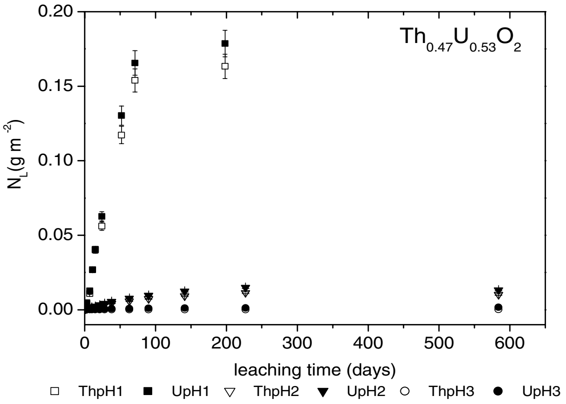

Fig. 7. Evolution of the normalized leaching for $Th_{0.47}U_{0.53}O_2$ in several acidic media.

increased with the proton concentration for pH < 7. In acidic media, the experimental normalized dissolution rate values were found to be proportional to a fractional power of the proton activity as follows:

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

where R_H refers to the proton-promoted normalized dissolution rate and $k'_{T,298\,K}$ (expressed in g m^{-2} d^{-1}) represents the apparent normalized dissolution rate constant at pH = 0. It is independent of the acidity of the leachate but temperature dependent. n is the partial order related to the proton concentration and $\gamma_{H_3O^+}$ corresponds to the proton activity coefficient. Fractional reaction orders are usually observed for different types of minerals including oxides. Several investigators [21–23] showed that it could be described in terms of surface complexation as controlling step for the mineral dissolution, the ion detachment depending on the number of adjacent bound sites. In the case of slow dissolution reactions like the oxide minerals one, this step occurred after an initial step for which defects or minor phases, still present on the surface, were dissolved after washing process.

The R_H values calculated for several pH and for several compositions of solid solutions, allowed the determination of the partial order, n, related to the proton concentration and the apparent normalized rate constant $k'_{298\,K}$. Fig. 8 represents the variation of log R_H as a function of the leachate acidity for ThO_2, $Th_{0.76}U_{0.24}O_2$ and $Th_{0.63}U_{0.37}O_2$.

As expected, the logarithm of the normalized dissolution rate R_H, decreased linearly with the pH, until pH = 7 for U. The positive dependence on $[H_3O^+]$ between pH = 0 and 7 for $Th_{0.76}U_{0.24}O_2$ and between pH = 0 and 2 for ThO_2, and $Th_{0.63}U_{0.37}O_2$ shows that the dissolution rate is favoured by the presence of protons in

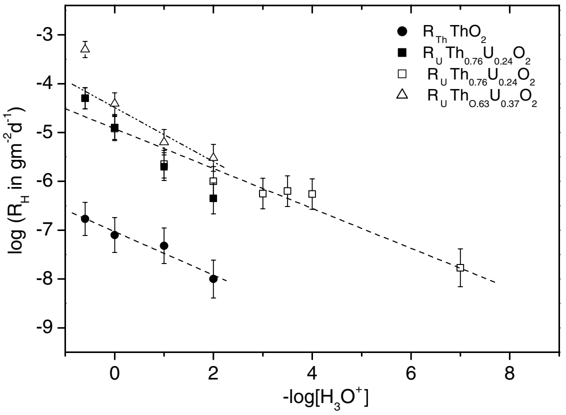

Fig. 8. Variation of log R_H versus $-\log[H_3O^+]$ for ThO_2 and $Th_{1-x}U_xO_2$ solid solutions.

the solution. The partial order related to the proton concentration was found to be 0.41 ± 0.05 for ThO_2, and 0.44 ± 0.07 (calculated from uranium) for $Th_{0.76}U_{0.24}O_2$, indicating that both solids had the same behaviour during the dissolution. The *n* values were of the same order of magnitude to that mentioned in the literature for several minerals and especially oxides.

In the case of the $Th_{0.76}U_{0.24}O_2$ solid solution for which the dissolution experiments were carried out until pH = 7, the linear increase occurs until pH = 7 for uranium. It was proton promoted to pH = 7, as long as precipitation did not occur. That was also in agreement with the value of the pH_{PZC} measured on ThO_2 ($pH_{PZC} \sim 9$) [3]. However, $Th_{0.76}U_{0.24}O_2$ released two orders of magnitude higher than ThO_2 because of the oxidation of uranium at the surface of the solid. The corresponding apparent normalized dissolution rate constant was found to be equal to $(1.00 \pm 0.05) \times 10^{-7}$ and $(1.3 \pm 0.1) \times 10^{-5}$ $g\,m^{-2}\,d^{-1}$ for ThO_2 and $Th_{0.76}U_{0.24}O_2$, respectively.

The values obtained for the $Th_{0.63}U_{0.37}O_2$ solid solution between pH = 0 and 2 are reported in Fig. 8, indicating that this composition followed a similar behaviour than $Th_{0.76}U_{0.24}O_2$ and ThO_2. We can note however that the values obtained in very corrosive media (5 M HNO_3) are most of the time higher compared to the other values. It may be due to the high electrolyte ionic strength effect. Other experiments dealing with other compositions of solid solutions enriched in uranium (0.67 and 0.81) are now under study in order to correlate the dissolution rate of both thorium and uranium with the uranium amounts in the $Th_{1-x}U_xO_2$ solid solutions.

3.4. Influence of the temperature on the normalized dissolution rate

The temperature is also considered as an important parameter affecting the normalized leaching rate according to the Arrhenius law, by the following equation:

$$R_L = k\,e^{-E_{app}/RT},$$

where *k* is the normalized dissolution rate constant independent of the temperature ($g\,m^{-2}\,d^{-1}$) and E_{app} (in $J\,mol^{-1}$) is the apparent activation energy of the dissolution of the solid.

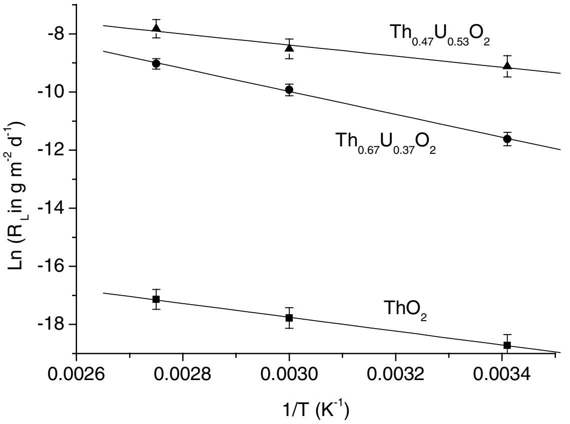

Fig. 9. Dissolution rate (at pH 2) as a function of $1/T$ for ThO_2, $Th_{0.63}U_{0.37}O_2$ and $Th_{0.47}U_{0.53}O_2$.

Leaching tests were performed on ThO_2, $Th_{0.63}U_{0.37}O_2$, $Th_{0.47}U_{0.53}O_2$ in 10^{-2} M HNO_3 $I = 0.1$ M (by adding KNO_3), at several temperatures (25, 60 and 90 °C). The procedure was identical to the one described above. The variation of ($\ln R_L$) versus the reciprocal temperature is plotted for ThO_2 and $Th_{1-x}U_xO_2$ solid solutions in Fig. 9. The slope obtained from the linear regression led to apparent activation energy equal to (20 ± 3) $kJ\,mol^{-1}$ for ThO_2, (33 ± 4) $kJ\,mol^{-1}$ for $Th_{0.63}U_{0.37}O_2$, and (16 ± 4) $kJ\,mol^{-1}$ for $Th_{0.47}U_{0.53}O_2$. The apparent activation energy measured for these solids revealed a weak dependence of R_L with the temperature. They were in good agreement with that reported in the literature [18,24,25] for other kinds of materials.

4. Discussion

All parameters (fractional order *n*, normalized dissolution rate constants, apparent activation energy) describing the dissolution behaviour of the solid solutions are summarized in Table 8. The fractional partial order for the various actinide dioxides ThO_2, $Th_{0.76}U_{0.24}O_2$,

Table 8
Summarize of several parameters affecting the dissolution for $Th_{1-x}U_xO_2$

	ThO_2	$Th_{0.76}U_{0.24}O_2$	$Th_{0.63}U_{0.37}O_2$	$Th_{0.47}U_{0.53}O_2$
n	0.41 ± 0.05	0.44 ± 0.07	0.55 ± 0.1	
k'_{298} ($g\,m^{-2}\,d^{-1}$)	$(1.00 \pm 0.05) \times 10^{-7}$	$(1.3 \pm 0.2) \times 10^{-5}$	$(3 \pm 1) \times 10^{-5}$	
E_{app}($kJ\,mol^{-1}$)	20 ± 3		33 ± 4	16 ± 4

and $Th_{0.63}U_{0.37}O_2$ is roughly the same (0.45 ± 0.05), while the apparent normalized dissolution rate constant increases with the substitution of thorium by uranium (IV) in the structure. Moreover the apparent activation energy of the reaction of dissolution (16–33 $kJ\,mol^{-1}$) was almost the same for ThO_2, $Th_{0.63}U_{0.37}O_2$ and $Th_{0.47}U_{0.53}O_2$.

The dissolution of crystallized metal oxide has been extensively studied. Stumm et al. have proposed a generalization of a surface controlled mechanism [23,26]. For metal oxides, the dissolution reaction is the result of a series of sequential steps: mass transport of solutes (H^+, OH^-, ligand) to the mineral surface: Me > OH, adsorption of the solutes to the hydrated mineral surface: $Me > OH_2^+$, then detachment of the reactants from the surface. Most of the time, the transport of solutes and reactants is generally faster than the detachment of the reactants from the surface. In this case, the reaction of dissolution is surface controlled and the dissolution rate is proportional to the activity of the adsorbed species.

For the dissolution of ThO_2, the mechanism can be described into two steps as below:

Fast protonation of the surface layer:

$$> \text{Th–OH} + H^+ \rightarrow > \text{Th–OH}_2^+$$

Detachment of the metal ion:

$$> \text{Th–OH}_2^+ + (n-1)\ H_2O \rightarrow \text{Th}\ (OH)_n^{(4-n)+} + nH^+$$

The nitrate ions seem to have no influence on the dissolution mechanisms because the logarithm of the leaching rate increases linearly with the acidity of the leachate, even for very acidic solution where the nitrate concentration is about 1 and 5 M compared to 0.1 M for the other solutions.

On the other hand, for the solid solutions, this increase is exponential from a concentration of nitrate of 1 and 5 M. The increase of dissolution of the solid solution with high concentration of nitrate ions could be explained by an enhancement of the oxidation of U(IV) in U(VI) on the surface of the solid by nitrate ions or by the HNO_2 species which are more important in very concentrated nitric acid. Furthermore, HNO_2 species ions have a kinetic of oxidation faster than nitrate ions ones due to their greater mobility.

In the case of $Th_{0.47}U_{0.53}O_2$, XPS measurement on the surface of the leached solid, underlined the oxidation of the surface layer of the solid solution in contact with the solution, as $Th_{1-x}U_xO_{2+n}$. The average O/M ratio of the leached $(Th,U)O_2$ solid solutions increased when increasing urania content in the mixed oxide.

Also we can propose a mechanism in three steps for the mixed oxides:

(i) Oxidation of uranium site at the surface by oxygen (a), nitrate ions (b) or HNO_2 ions (c) according to these equations,

$$> UO_2 + \tfrac{1}{2}\,O_2 \leftrightarrows > UO_3 \quad (a)$$

$$> UO_2 + 2NO_3^- + 2H^+ \leftrightarrows > UO_3 + 2NO_2\uparrow + H_2O \quad (b)$$

$$> UO_2 + 2HNO_2 \leftrightarrows > UO_3 + 2NO\uparrow + H_2O \quad (c)$$

(ii) fast protonation of the different sites (Th and U) from the surface layer,

(iii) detachment of the complexes formed with Th and U sites.

From the reduction potential values of the species involved in the mechanism of the oxidation reactions ((a)–(c)), the oxidation of uranium sites by oxygen ($E^0_{O_2/H_2O} = 1.229$ V) is more likely to occur than oxidation by nitrate ions ($E^0_{NO_3^-/NO_2} = 0.809$ V) or HNO_2 species ions ($E^0_{HNO_2/NO} = 0.983$ V). However in very acidic media (1 M and 5 M) where the ionic strength is high, HNO_2 species ions are more important in the leachate and have a great mobility, which accelerate the oxidation of uranium sites at the surface. In the case of mixed oxide with equal concentration of Th and U, a faster dissolution rate is observed in the first period (<100 days), while a decrease of this rate occurs for longer leaching time whatever the pH. These phenomena can not be due to uranium saturation in the leachate since U(VI) does not precipitate in nitric media at this concentration scale. It can be explained by the formation of a protective layer (probably based on thorium hydroxide) at the interface which reduces the dissolution of the solid.

5. Conclusion

The dissolution of the thorium oxide and associated solid solutions formed with uranium $Th_{1-x}U_xO_2$ ($x = 0.24$, 0.37 and 0.53) was studied as a function of the leaching time, the acidity of the leachate in nitric solution and the temperature. In acidic media ($1 < pH < 2$), the normalized dissolution rate of ThO_2 is around 10^{-8} $g\,m^{-2}\,d^{-1}$, compared to about 10^{-6}, 5×10^{-6}, and 10^{-4}–10^{-3} $g\,m^{-2}\,d^{-1}$ for $Th_{0.76}U_{0.24}O_2$, $Th_{0.63}U_{0.37}O_2$ and $Th_{0.47}U_{0.53}O_2$, respectively. While uranium is preferentially released during the first 40 days of leaching because of traces of U(VI) at the surface of the solid, U is released congruently with Th for longer leaching time, whatever the composition of the solid solution for $pH < 3$. However the normalized dissolution rate of both actinides is dependent on the concentration of uranium in the solid solution, and increases all the more the concentration of uranium becomes similar to that of thorium. For higher pH values, the behaviour of both actinides differs because of the presence of U(VI) in the leachate which hydrolyses at higher pH than the tetravalent state, while thorium released in the leachate precipitates as $Th(OH)_4$ probably. The partial order related to the proton concentration is about 0.45 for ThO_2, $Th_{0.76}U_{0.24}O_2$, and $Th_{0.63}U_{0.37}O_2$. The apparent activation energy of the reaction of dissolution at pH 2, has similar values for ThO_2, $Th_{0.63}U_{0.37}O_2$ and $Th_{0.47}U_{0.53}O_2$ (20, 16 and 33 $\mathrm{kJ\,mol^{-1}}$) and is rather low, which is in favour of the formation of an activated complex on the Th and U(IV and VI) sites before detachment. The dissolution experiments were performed in a larger pH range for $Th_{0.76}U_{0.24}O_2$. The linear dependence of the logarithm of the normalized dissolution rate with the pH, until $\mathrm{pH} = 7$ allows the estimation of the normalized dissolution rate of all the solid solutions and ThO_2 at pH 7 by linear extrapolation. The values obtained for $Th_{0.76}U_{0.24}O_2$, $Th_{0.47}U_{0.53}O_2$ are $3.5\times10^{-8}\ \mathrm{g\,m^{-2}\,d^{-1}}$ and around $10^{-6}\ \mathrm{g\,m^{-2}\,d^{-1}}$ respectively compared to about $10^{-10}\ \mathrm{g\,m^{-2}\,d^{-1}}$ for ThO_2, values which remain very low. The dissolution of other compositions of solid solutions ($x = 0.61$ and 0.81) are under study. Moreover because of the different behaviour of U and Th depending on the red ox conditions of the electrolyte, dissolution experiments are also under investigation in several electrolytes such as chloride, sulphate (salts in large concentration in the actual French site) and groundwater.

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References

[1] H. Gruppelaar, J.P. Schapira (Eds.), Project Report EUR 19412, Thorium as a waste management option, Nuclear Science and Technology Series, 2000.

[2] B. Fourest, T. Vincent, G. Lagarde, S. Hubert, P. Baudoin, J. Nucl. Mater. 282 (2000) 180.

[3] S. Hubert, K. Barthelet, B. Fourest, G. Lagarde, N. Dacheux, J. Ritt, J. Nucl. Mater. 297 (2001) 206.

[4] V. Neck, J.I. Kim, Radiochim. Acta 89 (2001) 1.

[5] D. Rai, D.A. Moore, C.S. Oakes, M. Yui, Radiochim. Acta 88 (2000) 297.

[6] A.R. Felmy, D. Rai, S.M. Sterner, M.J. Mason, N.J. Hess, S.D. Conradson, J. Solut. Chem. 26 (1997) 399.

[7] D. Rai, A.R. Felmy, S.M. Sterner, D.A. Moore, M.J. Mason, C.F. Novak, Radiochim. Acta 79 (1997) 239.

[8] M.C.A. Sandino, B. Grambow, Radiochim. Acta 66&67 (1994) 37.

[9] T. Yamamura, A. Kitamura, A. Fukui, A. Nishikawa, T. Yamamoto, T. Moriyama, H. Moriyama, Radiochim. Acta 83 (1998) 139.

[10] J. Bruno, I. Casas, I. Puigdomènech, Geochim. Cosmochim. Acta 55 (1991) 647.

[11] J. Bruno, I. Grenthe, B. Lagerman, Mater. Symp. Proc. 50 (1985) 299.

[12] S. Sunder, N.H. Miller, J. Nucl. Mater. 279 (2000) 118.

[13] A.C. Thomas, N. Dacheux, J. Aupiais, J. Nucl. Mater. 306 (2002) 134.

[14] A.C. Thomas, N. Dacheux, P. Le Costumer, V. Brandel, M. Genet, J. Nucl. Mater. 281 (91) (2000) 15.

[15] A.C. Thomas, N. Dacheux, P. Le Costumer, V. Brandel, M. Genet, J. Nucl. Mater. 295 (2001) 249.

[16] G. Heisbourg, N. Dacheux, G. Lagarde, J. Ritt, S. Hubert, in: Proceedings of the International conference ICEM'01, Brugges, 2001.

[17] J. Cohen, R.M. Berman, J. Nucl. Mater. 18 (1996) 77.

[18] J. Pablo, I. Casas, J. Gimenez, M. Molera, M. Rovira, L. Duro, J. Bruno, Geochim. Cosmochim. Acta 63 (1999) 3097.

[19] L. Chou, R. Wollast, Am. J. Sci. 258 (1985) 963.

[20] A.E. Blum, A.C. Lasaga, Nature 331 (1988) 431.

[21] A.C. Lasaga, J. Geophys. Res. 89 (1984) 4009.

[22] A.C. Lasaga, Rev. Mineral. (Mineral. Soc. Am.) 8 (1981) 45.

[23] W. Stumm, G. Furrer, in: W. Stumm (Ed.), Aquatic Surface Chemistry, J. Wiley, 1987.

[24] K.B. Helean, W. Lutze, R.C. Ewing, in: J.C. Marra, G.T. Chandler (Eds.), Environmental Issues and Wastes Management Technology in the Ceramic and Nuclear Industries, vol. 93, 1999, p. 297.

[25] A.E. Ringwood, S.E. Kesson, K.D. Reeves, D.M. Levins, E.J. Ramm, in: W. Lutze, R.C. Ewing, North Holland, Amsterdam, 1988.

[26] E. Wieland, B. Wehrli, W. Stumm, Geochim. Cosmochim. Acta 52 (1988) 1969.