



Influence of the precursor and the calcination temperature on the dissolution of thorium dioxide

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Abstract

The effect of the precursor and temperature of calcination on the dissolution of thorium dioxide was carried out. The dissolution of crystallized ThO₂ has been studied as a function of pH to evaluate the solubility product of a high temperature calcinated thorium oxide. However no equilibrium was reached after 4 months (at least in acidic media). Nevertheless, high temperature crystallized ThO₂ is less soluble by two orders of magnitude than the amorphous hydrated ThO₂. We have pointed out a correlation between the surface of the solid and its apparent leachability in acidic perchlorate solutions, resulting mainly in the thorium site concentration differences between the solids. The normalized dissolution rate of crystallized ThO₂ which was found to be $1\text{--}3 \times 10^{-6} \text{ g m}^{-2} \text{ d}^{-1}$ in 0.1 M acid solutions is independent of the way of synthesis of the solid. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Thorium dioxide is an important material due to its interesting properties: high temperature refractory material, good resistance to irradiation, and a cubic structure isomorphic with that of tetravalent actinides dioxides (UO₂, PuO₂, NpO₂). ²³²Th is a fertile radionuclide, which can replace ²³⁸U, especially in breeder reactor concepts. Recently, there has been a considerable interest in studying the feasibility of thorium-based fuel reactors, in order to decrease the radionuclides production and specially that of minor actinides and plutonium [1]. Well-crystallized thorium dioxide is known to be very insoluble in aqueous media [2]. For this reason, most of the solubility studies were performed on hydrous thorium oxide up to now [3–5]. However, the solid phase of the pseudo-amorphous form was never well defined and consists certainly in a mixture of Th(OH)₄ and ThO₂ · H₂O. Thorium dioxide is also an interesting material for long-lived actinides and fission products transmutation or for immobilizing

tetravalent actinides. As a matter of fact, this material is a high temperature refractory material with a high fusion temperature ($\theta = 3360^\circ\text{C}$), and exhibits a good resistance to radiation damages. Moreover, the solubility of the amorphous solid is known to be very low in basic media [3–6].

In order to assess the long-term radiological impact of thorium-based fuel in the case of a direct storage in deep geological repository, the leaching tests of well-crystallized thorium dioxide (heated at 1600°C) were studied in synthetic granite waters [1,7]. As already observed for hydrous thorium oxide, in neutral and basic media ($I = 0.1 \text{ M}$), a detection limit of $10^{-9}\text{--}10^{-10} \text{ M}$ is measured after a contact time of 123 days. Nevertheless, a stationary state is not yet reached after 123 days for this ceramic.

For the preparation of thorium-based fuels, thorium dioxide powdered samples are usually produced by converting a thorium nitrate solution into a sinterable powder, using a sol–gel process [8]. Nevertheless, well-crystallized thorium dioxide can be also obtained by heating various precursors such as thorium nitrate, thorium oxalate or thorium hydroxide at several temperatures ranging from 700°C up to 1600°C [9,10]. For the fabrication of the fuel, the sol–gel process is usually

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used, in the case of mixed fuel (uranium or thorium-based MOX), an other fabrication route using the oxalate is favored. Thus, different way of synthesis and thermal treatments yields to physical properties of the solid such as surface conditions, composition, and porosity which can influence the leachant factors.

In order to assess the long term behaviour of a direct storage of spent fuel (thorium- or uranium-based fuel) in a repository, several leaching tests were carried out on numerous oxides synthesized using various conditions (calcination temperature, nature of the precursor, morphology of the powder, single crystals, . . .). The present study deals with the understanding and the quantification of the processes controlling the long term dissolution/alteration of crystallized ThO₂ with various precursors and thermal treatments, in order to correlate the physical properties of the solid with the normalized dissolution rate measured.

2. Experimental details

2.1. Chemicals

P.a. grade Th(NO₃)₄ · 5H₂O from FLUKA was used for preparing thorium oxide, thorium oxalate and thorium oxide hydrate/thorium hydroxide. Concentrated NH₄OH solution (25% in volume) was used for the hydroxide precipitation. The thorium oxalate was prepared by adding slowly a solution of oxalic acid to the thorium nitrate solution using a peristaltic pump. The precipitates were filtered on a Büchner, washed with water then dried under vacuum. The electrolyte was prepared by adding NaOH or HClO₄ to a 0.1 M sodium perchlorate solution. All the solutions were prepared using a MilliQ water pack (supplied by Millipore).

2.2. Preparation of thorium dioxide

The ThO₂ powdered samples were prepared by applying a thermal treatment in two steps: 2 h at 400°C (oxalate, hydroxide) or 500°C (nitrate) then 10 h at 900°C. Thorium dioxide heated at 1600°C was produced from thorium oxalate, heated at 900°C for 10 h, and then at 1600°C for 10 h. The purity of each powder was controlled by using the particle-induced X-ray emission (PIXE) method. A purity of 99.98% was obtained for all the solids.

2.3. Powder characterization

Each powder was characterized before and after the leaching tests, using several techniques such as X-ray powder diffraction (XRD), granulometry and scanning electron microscopy (SEM) for studying the morphology and the grain size, the determination of the specific

surface area by using the Brunauer et al. [11] method. The surface of the grains was characterized by X-photoelectron spectroscopy (XPS).

2.3.1. X-ray diffraction

The X-ray diffraction patterns were recorded using a Philips PW 1050/70 diffractometer using CuK_α ray ($\lambda = 1.5418 \text{ \AA}$). They were recorded on powders prepared from the three precursors (Th(NO₃)₄, Th(C₂O₄)₂, and Th(OH)₄) at three temperatures (600°C, 900°C, 1300°C). The XRD analysis showed the typical pattern of the cubic face centred lattice with linewidth depending on the conditions of synthesis (precursor, calcination temperatures). By comparing the linewidth of the diffraction lines obtained with different precursors and different temperatures (600°C, 900°C, 1300°C and 1600°C), we observed that the thorium oxalate yields to narrower XRD peaks and consequently a better crystallization of the thorium dioxide compared to the other precursors used (thorium nitrate and thorium hydroxide) and considering the same conditions of heating treatment.

2.3.2. Granulometry

The particle size distribution of powders calcinated at 900°C was determined without grinding using an apparatus Coulter LS230 based on laser light diffraction. Samples were analyzed as suspensions of thoria dispersed in an aqueous solution of sodium phosphate (1 g l⁻¹). Whatever the precursor used, the major part of the grains had an average grain size in the submicrometer range. However the relative volume distribution pointed out two particles populations: submicrometric particles which are the most important population and larger particles (10–40 μm) which correspond to aggregates of primary grains. However in the case of the oxalate route, the size of the aggregate is more homogeneous and was found to be around 20 μm.

2.3.3. SEM

The surface state of the raw solid being leached influences its behaviour during leaching tests. Microscopic surface roughness may differ following the various routes of synthesis under consideration. As the leachabilities are usually calculated from geometric or superficial surface areas, greater surface roughness for example would have greater apparent leachability. SEM was used in order to determine the morphology of the particles. As shown from the micrographs collected in Fig. 1, the morphology of the powder heated at 900°C depends on the precursor used. For the thorium dioxide prepared from hydroxide, agglomerates of micrometric grains (from 10 to 30 μm) with irregular shape are observed. On the other hand, aggregates or twins of nice cubic crystals with smooth surface and rectangular plate with size of 5 μm along the square edge, are observed for

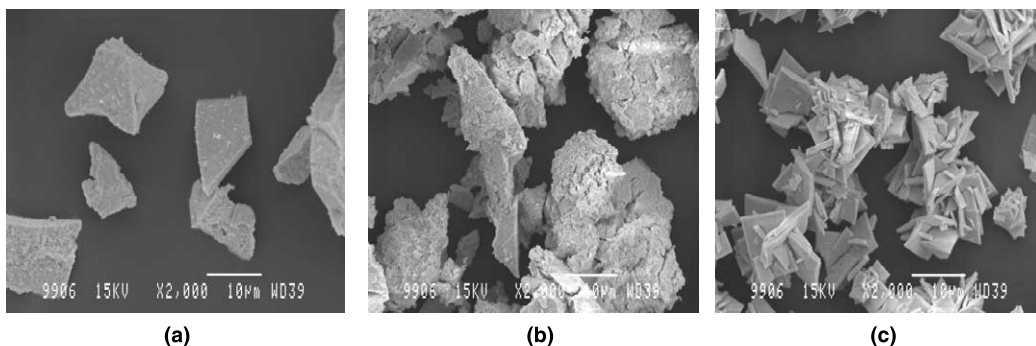


Fig. 1. Morphology of thorium dioxide prepared with different precursors. (a) ThO₂ from nitrate precursor; (b) ThO₂ from hydroxide precursor; (c) ThO₂ from oxalate precursor.

thorium dioxide prepared from the oxalate route. The agglomerates of these cubic plane range from 5 to 20 µm. The use of thorium nitrate as precursor in the same conditions leads to isolated aggregate particles with size from 5 to 15 µm.

2.3.4. Specific surface area measurements

The specific surface area was measured with a Coulter SA3100 apparatus using nitrogen gas (BET method). Prior to the measurements, the samples were dried at 250°C for 10 h. The powders prepared from the hydroxide, the oxalate and the nitrate heated at 900°C had specific surface area values of 0.3, 1.1, and 5.9 m² g⁻¹, respectively. The increase of the calcination temperature (from 900°C to 1600°C) of the solid produced by the oxalate route led to a decrease of the specific area from 1.1 to 0.2 m² g⁻¹. The small specific surface area obtained for the thorium dioxide produced from the hydroxide route compared to the other powdered sample can be explained by the observation of numerous agglomeration of primary particles observed on the SEM photographs, which decreases the surface area of the samples.

2.3.5. XPS measurements

XPS was investigated in order to determine the stoichiometry of the solid at the surface through the orbital energies by using the Al K α ray as an excitation source. The ratio between the intensities of thorium and oxygen photoemissions calculated from the surface of the Th_{4f} and O_{1s} peaks, led to the stoichiometry of the solid. The ratio which should be equal to 0.5 was found to be 0.48, 0.46 and 0.47 for the samples prepared from the thorium nitrate, the thorium oxalate and the thorium hydroxide, respectively. All the samples appear to be thorium deficient, indicating that the surface of thorium dioxide tends to form over-stoichiometry with excess of oxygen. The solid in contact with air may develop an oxidized surface layer.

2.3.6. Electrophoretic mobility measurements

The isoelectric point was measured on colloidal suspension of thorium dioxide powder prepared from various precursors, using a Doppler electrophoretic light scattering analyzer Coulter DELSA 440. Colloidal suspensions were prepared from 50 mg of powder in 10 ml of 0.1 M NaClO₄ at constant ionic strength ($I = 0.1$ M). The pH of the solution was adjusted with 0.1 M HClO₄ or 0.1 M NaOH. The tubes were shaken for 24 h, then centrifugated in order to get the separation of submicrometric size particles. The typical variation of the electrophoretic mobility (zeta-potential) of thoria colloids with the pH is given in Fig. 2 for a sample prepared from thorium nitrate route. Below pH = 4, the surface charge of the particles is positive, then becomes negative above this pH value, showing the amphoteric behaviour of the thorium dioxide. The p*H*_{IEP} values obtained for the various precursors, and for the hydrated thorium dioxide/thorium tetrahydroxide prepared by precipitation are given in Table 1.

The pH of isoelectric point of most of the samples heated at 900°C is about 4. However, the p*H*_{IEP} value is higher for the thorium dioxide calcinated at higher

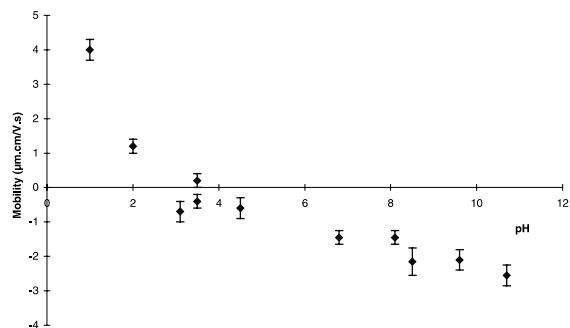


Fig. 2. Variation of the electrophoretic mobility of thoria colloids of ThO₂ as a function of pH in 0.1 mol/l NaClO₄.

Table 1
Values of pH_{PIE} of ThO_2 synthesized with various precursors

Sample	Precursor	T_{calc} ($^{\circ}\text{C}$)	pH_{PIE}	pH_{ZPC}
ThO_2	Thorium nitrate	900	4 + 0.2	
ThO_2	Thorium oxalate	900	4 + 0.2	
ThO_2	Thorium oxalate	1600	5.5 + 0.2	
ThO_2	Thorium hydroxide	900	4.5 + 0.2	
$\text{ThO}_2 \cdot 2.5\text{H}_2\text{O}/\text{Th}(\text{OH})_4$	Thorium nitrate	25	6.0 + 0.2	9.8 [13]

temperature or prepared through the thorium hydroxide route. In any case these values are very low compared to the expected value of the pH at the zero point of charge (pH_{ZPC}), which tends to show that sodium ions are not indifferent ions. Moreover, their role seems to be dependent on the surface state of the solid [12].

2.4. Leaching tests procedure

Leaching test were performed using static experiments in batch. They were carried out in high density polyethylene (HDPE) containers sealed with screw caps at room temperature. The pH of the electrolyte was adjusted with 0.1 M HClO_4 or NaOH in order to fix the ionic strength at 0.1 M. Argon atmosphere was maintained during the preparation of the tubes until sealing. pH from 1 to 9 was measured, using a Tacussel combination glass electrode which was calibrated against 4 pH buffers before and after each experiment. Before leaching, the powder was first washed in 0.1 M HClO_4 for several days, then washed with deionized water and then finally with the electrolyte solution.

200 mg of solid phase was mixed with 10 ml of the solution (0.1 M NaClO_4). The tubes were shaken for several leaching times. 3 ml of the leachate were taken off after separation of the two phases by centrifugation

then the pH was measured. This fraction was ultra-centrifugated to avoid colloids with size larger than 1.7 nm, and then diluted in 1% nitric acid by a factor of at least 50 before analysis. For several pH, centrifugation and ultra-centrifugation were used to check the presence of possible colloids. It was observed for $\text{pH} > 3$.

The thorium concentration, C_{Th} was determined in the leachate using inductively coupled plasma – mass spectrometry (ICP–MS) technique, apparatus Fisons Plasma Quad). Owing to the very low thorium concentration values, a special attention was paid to the experimental procedure (quality of the reagents, preconditioning of the glass vessel) as already described [13]. Two internal standards (1 ppb Tb and Bi) were added to each sample.

The influence of the surface to volume ratio, S/V , on the normalized leaching was studied by varying the amount of solid in contact with the solution from 1 mg to 1 g. The powdered thorium dioxide used was synthesized using thorium nitrate or thorium oxalate calcinated at 900°C . As expected, the variation of C_{Th} with the surface is linear with a slope of 1 (Fig. 3) which indicates the absence of saturation of the leachate. A ratio of 200 mg of powder for 10 ml of solution was chosen for all further leaching experiments.

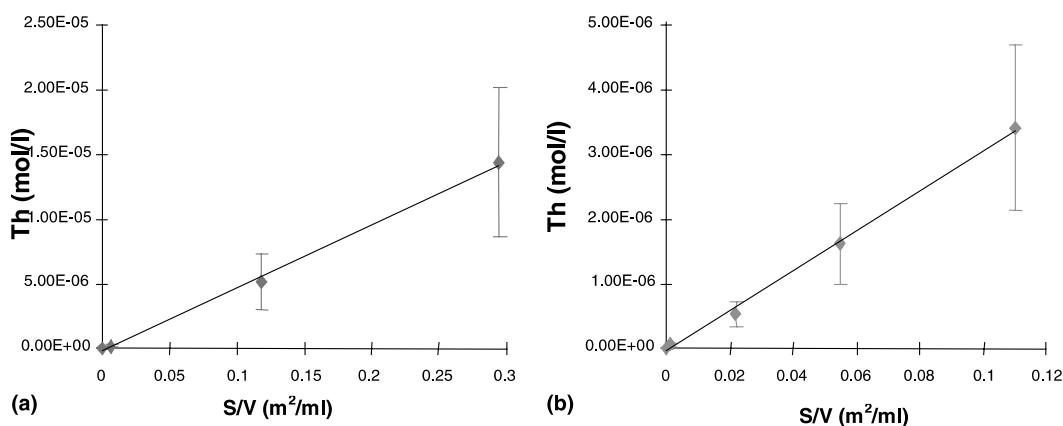


Fig. 3. Influence of the S/V ratio, on the dissolution rate of thoria after 10 days of leaching, at pH 1. (a) Nitrate precursor, (b) oxalate precursor.

3. Results and discussion

3.1. Effect of pH on the ThO₂ normalized dissolution rate

Fig. 4 represents the variation of the thorium concentration in the leachate as a function of the acidity of the leachate for several samples synthesized with three precursors (thorium nitrate, thorium hydroxide and thorium oxalate) at two heating temperatures. As shown in Fig. 4, whatever the route of synthesis, the variation of the thorium concentration measured in the solution as a function of pH has the same behaviour.

In acidic media, a plateau is systematically obtained from pH 1 to 3. This plateau was already observed by other authors [4] but not yet really explained. The C_{Th} value corresponding to this plateau depends on the way of synthesis of the solid. The concentration of thorium in the leachate is the smallest for the thorium dioxide prepared from the nitrate route at 1600°C compared to the other routes at 900°C. Moreover, among the three precursors calcinated at 900°C, the oxalate route yields to the smallest thorium concentration in the leachate while the hydroxide has a greater apparent leachability.

For pH > 3, the ThO₂ solubility decreases sharply until reaching the limit of detection for pH > 5 ($C_{Th} < 2.2 \cdot 10^{-10}$ M). A similar behaviour has been

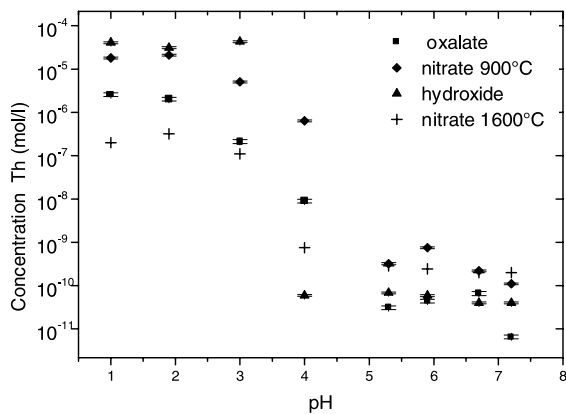


Fig. 4. Variation of the total thorium concentration with pH for different precursors after 10 days of leaching.

already observed by Ryan and Rai [3] on hydrous thorium oxide. However compared to the results obtained with a pseudo-amorphous hydrous thorium dioxide in basic media (few 10^{-6} – 10^{-8} M), the solubility appears two orders of magnitude lower for high temperature crystallized. In this range, Th(OH)₄ is the predominant equilibrium aqueous species and may be formed at the surface of the solid.

Some experimental K_{sp} determinations concerning hydrous ThO₂ are based on solubility measurements [3] (Table 2). The difficulty, which can explain discrepancies in the results, is that the pH-range considered also corresponds to the formation of the first hydrolyzed thorium species. These species, which are always assumed to be mononuclear, are known to be sorbable and there is likely a competition between the >Th–OH groups of the solid and the free aqueous OH[−] species. Moreover, the hydrolysis constants of thorium are always under discussion (very different sets of data can be found in the literature [14–20]). For these reasons, it appeared difficult to reach experimentally a correct absolute solubility product of ThO₂, specially in the case of a crystalline powder calcinated at high temperature. As already discussed by Bruno [21] and Osthols and Malmström [4], larger crystals with smaller specific area and less surface layer –OH groups are expected to be less soluble and the time required to reach the solubility equilibrium can be very long in this case (this point will be detailed in Section 3.2). However, from the C_{Th} values of Fig. 4 measured at pH 3 after 10 days of leaching, K_s values can be estimated for crystallized thorium dioxide prepared through three precursors between 5.5 and 7.8, which are in agreement with the values reported in the literature [2] (see Table 2).

3.2. Kinetics of dissolution of ThO₂ in acidic media

Dissolution kinetics were investigated on the thorium dioxide produced by calcinating the three precursors at 900°C, then leached in 0.1 M HClO₄–NaClO₄ solutions with leaching-time varying between 10 and 50 days. The variation of the thorium concentration versus leaching time is plotted in Fig. 5 for several precursors and calcination temperature.

Table 2
Bibliographic review of the solubility products of ThO₂

	Experimental data	Calculated data
ThO ₂ · xH ₂ O	log K_s = 10.1 ± 0.5 (in 0.1 M NaClO ₄) [3] log K_{sp} = 9.37 ± 0.13 (in 0.5 M NaClO ₄) [5]	log $K_{s,0}$ = 7.3 [6] log $K_{s,0}$ = 7.3 ± 0.3 [5]
Crystallized ThO ₂	log K_s = 5.24 ± 0.08 (in 0.1 M NaClO ₄) [14]	log K_s = 6.3 (1 M NaClO ₄) [2] log $K_{s,0}$ = 2 [16] log $K_{s,0}$ = 1.86 [3]

Equilibrium under consideration: ThO₂ + 4H⁺ ⇌ Th⁴⁺ + 2H₂O.

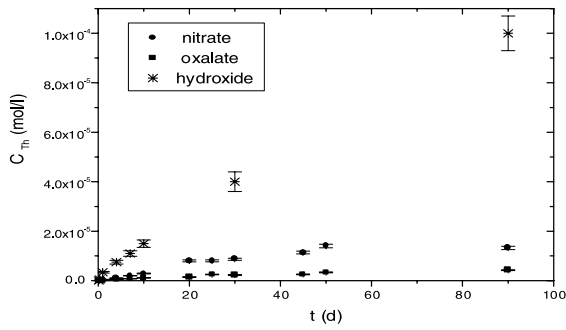


Fig. 5. Thorium concentration versus leaching time at pH 1 for ThO₂ prepared with different precursors.

Several parameters have influence on the leachability of an element. Among them, we can note the leaching time, temperature, solid surface area, or porosity. As observed in Fig. 5, the apparent leachability is the lowest for the oxalate route which corresponds to the smallest specific surface area. On the other hand, the comparison of the apparent leachability between thorium dioxide calcinated at 900°C and 1600°C, shows that it is higher for the lowest calcination temperature (e.g. for the higher surface). These observations are coherent and tend to show that the apparent leachability is directly related with the surface area of the solid in contact with the solution.

The dissolution rate of a material can be described by its normalized leaching which takes into account the solid surface area following the expression

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

where S refers to the solid area (m²) in contact with the solution, f_i is the mass ratio of the element i in the solid, and m_i the mass of i released in the solution.

As shown in Fig. 6, the variation of the normalized leaching of the thorium dioxide as a function of contact time is found to be independent of the precursor or the calcination temperature.

Whatever the precursor or the calcination temperature, the normalized leaching increases linearly with the same slope until about 40 days, indicating that the dissolution mechanism occurs without any formation of secondary phase (precipitation) at pH = 1. The same behaviour is also observed for several pH values (pH < 3) as shown in Fig. 7.

Since the expression of the normalized dissolution rate R_L can be deduced from the slope of the corresponding straight line by using the expression:

$$R_L = \frac{1}{f_i S} \frac{dm_i}{dt}, \quad (2)$$

where dm_i/dt is the mass change of the element i measured in the solution. The R_L values calculated for the three

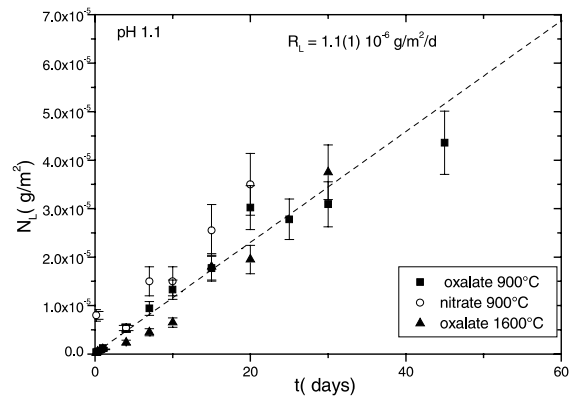


Fig. 6. Evolution of the normalized leaching rate for ThO₂ prepared at several heating temperature using different precursors.

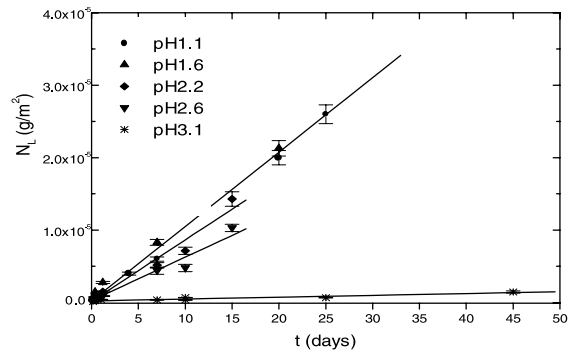


Fig. 7. Normalized dissolution rate of ThO₂ prepared from thorium nitrate at different pH.

precursors at pH = 1 are gathered in Table 3. The normalized leaching rates R_L are usually noted as R_H in acidic media and R_{OH} in basic media. As all the leaching tests were achieved in acidic media we will use the R_H notation instead of R_L in the following section. The normalized leaching rates are of the same order of magnitude for thorium dioxide synthesized from nitrate and oxalate, whatever the calcination temperature. The average value can be estimated to be about $1.7 \times 10^{-6} \text{ g m}^{-2} \text{ d}^{-1}$. In these calculations, the specific surface area of the solid was assumed to be constant and this is not always the case, specially in acidic media. However, Osthols and

Table 3
Normalized dissolution rate of thorium oxide at pH = 1 for several precursor

Precursor	Temperature	R_L (g m ⁻² d ⁻¹)
Th(NO ₃) ₄	900	(1.1 ± 0.2)10 ⁻⁶
Th(C ₂ O ₄) ₂	900	(8.8 ± 0.2)10 ⁻⁷
Th(C ₂ O ₄) ₂	1600	(3.2 ± 0.2)10 ⁻⁶

Malmström [4] pointed out that this assumption can be used since a loss of mass of the solid, and an increase of the porosity, gives opposite effects on the surface area. The initial surface area can be used in the leaching rate calculations. The micro-porosity was not measured in the solids, and this porosity could be higher for the hydroxide precursor than for the others, which could explain the higher leaching rate observed.

The normalized dissolution rate was calculated for several pH values from the evolution of the normalized leaching (Fig. 7). As shown in Table 4, it decreases as the pH increases.

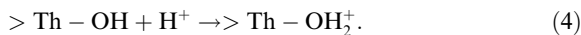
The dependence of the normalized dissolution rate on the proton concentration in the leachate can be expressed according to the expression [22]

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

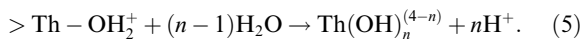
Many authors investigated the influence of the pH on the normalized dissolution rate. They showed that the normalized leaching rate of most of the minerals increases with the proton activity in acidic media. In the present study, kinetics of dissolution have been also performed between pH = 1 and pH = 3. As expected from Eq. (3), the logarithm of the normalized dissolution rate varies linearly with the pH (Fig. 8), with a slope corresponding to the partial order related to the proton, 0.30 ± 0.07 , and the corresponding apparent normalized dissolution rate constant equal to $\log k'_{T,I} = -5.6 \pm 0.1$. The dependence on $[H_3O^+]$ between 1 and 3 shows that the dissolution of ThO_2 is favored by the presence of H^+ ions in solution. The fractional partial order shows that dissolution is controlled by surface reactions involving probably the formation of an activated complex at the interface.

We can propose the following mechanism for the dissolution of ThO_2 :

A fast protonation of the surface layer,



Then the detachment of the metal ion



The protonation step is in agreement with the relatively high value of pH_{PIE} measured for thoria (around

Table 4
Normalized dissolution rate of thorium oxide in terms of the leachate acidity

pH	R_L ($g\ m^{-2}\ d^{-1}$)
1.1	$(1.1 \pm 0.2)10^{-6}$
1.6	$(1.0 \pm 0.2)10^{-6}$
2.2	$(8.5 \pm 0.2)10^{-7}$
2.6	$(6.0 \pm 0.2)10^{-7}$
3.1	$(2.5 \pm 0.2)10^{-8}$

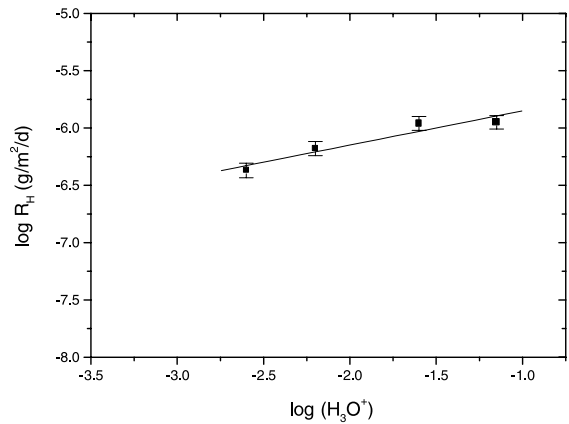
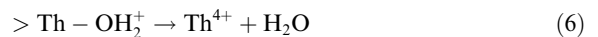


Fig. 8. Variation of the normalized dissolution rate as a function of pH.

9). This protonation is also responsible of a pH shift observed in the neutral aqueous solutions in contact with a powdered thorium dioxide, when this one has not been previously washed.

Moreover, the mechanism described above can simply explain the plateau of the C_{Th} versus pH curves. If we can neglect the hydrolysis of thorium at pH values below 3 ($n = 0$), we can write



which leads to

$$\log C_{Th} = \log [Th^{4+}] = \log K_{Eq.(5)} + A. \quad (7)$$

The constant value A is dependent on the concentration of the protonated sites which depends upon the characteristics of both the solution (pH) and the solid surface. Since the site concentration does not vary very much with the pH of the solution at $pH < 3$, $\log C_{Th}$ appears as a constant in this pH range and this constant is different for the different solids under consideration.

4. Conclusions

The physical characteristics of powdered thoria samples are dependent on the precursor and the calcination temperature, and especially the surface properties (specific surface area, surface state, size of aggregates) which are important parameters influencing the apparent leachability of a solid. Oxalate precursor leads to a better crystallized powder with smooth surface, and small specific area, which yields to the lowest apparent leachability, while the hydroxide precursor produces rough surface aggregates and larger apparent leachability. We have shown that such a result was due to differences in the thorium site concentrations of the different solids

under comparison. In the other hand, normalized leaching rate N_L seems to be independent of the route of synthesis, except in the case of the oxide produced from the hydroxide for which an abnormal small value of specific surface area have been measured. Leaching is a very complex phenomenon, which depends on numerous factors. However it seems that normalizing the apparent leachability by the surface area of the solid in contact with the solution leads to the same leaching rate whatever the precursor and the calcination temperature. As a matter of fact, the normalized dissolution rate of crystallized ThO_2 which is particularly low (about $1 \cdot 10^{-6} \text{ g m}^{-2} \text{ d}^{-1}$ at $\text{pH} = 1.1$), is independent of the synthesis conditions used for the preparation of the solid.

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References

- [1] Thorium as a waste management option. Final Report of European Contract No. FI4I/CT95-011, 1999.
- [2] C.F. Baes, R.E. Mesmer, *The Hydrolysis of Cations*, Wiley-Interscience, New York, 1976, p. 129.

- [3] J.L. Ryan, D. Rai, *Inorg. Chem.* 26 (1987) 4140.
- [4] E. Osthols, M. Malmström, *Radiochim. Acta* 68 (1995) 113.
- [5] D. Rai, A.R. Felmy, S.M. Sterner, D.A. Moore, M.J. Mason, C.F. Novak, *Radiochim. Acta* 79 (1997) 239.
- [6] E. Osthols, J. Bruno, I. Grenthe, *Geochim. Cosmochim. Acta* 58 (1994) 613.
- [7] B. Fourest, V. Tanguy, G. Lagarde, S. Hubert, P. Baudoin, *J. Nucl. Mater.* 282 (2000) 180.
- [8] P.A. Haas, Oak Ridge National Laboratory Report ORNL-TN-3978, 1972.
- [9] B.J.F. Palmer, J.A. Scoberg, A.Y.H. Hin, *Ceram. Bull.* 62 (1982) 627.
- [10] B.J.F. Palmer, L. E Bahen, A.Y.H. Gin, J.E. Winegar, A. Celli, *J. Phys.* 47 (1986) C1.
- [11] S. Brunauer, P. Emmet, E. Teller, *J. Am. Chem. Soc.* 60 (1938) 309.
- [12] Y. Harada, Y. Baskin, J.H. Handwerk, *J. Am. Ceram. Soc.* 45 (1962) 253.
- [13] B. Fourest, G. Lagarde, J. Perrone, V. Brandel, N. Dacheux, M. Genet, *New J. Chem.* 23 (1999) 645.
- [14] H. Moon, *Bull. Kor. Chem. Soc.* 10 (1989) 270.
- [15] I. Grenthe, B. Lagerman, *Acta Chem. Scand.* 45 (1991) 231.
- [16] B. Allard, *Actinides in Perspectives*, in: N. Edelstein (Ed.), Pergamon, 1982, p. 553.
- [17] A.R. Felmy, D. Rai, M.J. Mason, *Radiochim. Acta* 55 (1991) 177.
- [18] J. Fuger, *Radiochim. Acta* 58&59 (1992) 81.
- [19] L. Cromieres, V. Moulin, B. Fourest, R. Guillaumont, E. Giffaut, *Radiochim. Acta* 82 (1998) 249.
- [20] C. Ekberg, Y. Albinsson, M. Josick Comarmond, P.I. Brown, *J. Solids Chem.* 29 (2000) 63.
- [21] J. Bruno, *Acta Chem. Scand.* 43 (1989) 99.
- [22] P.V. Brady, W.A. House, in: P.V. Brady (Ed.), *Surface-controlled Dissolution and Growth of Minerals, Physics and Chemistry of Minerals Surface*, vol. 225, CRC, Albuquerque, NM, 1996.