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Effect of Inorganic Ligands and Hydrogen Peroxide on ThO_2 Dissolution. Behaviour of $Th_{0.87}Pu_{0.13}O_2$ during Leaching Test

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The dissolution of ThO_2 powdered samples was examined in various conditions of pH and concentration of anions in the leachate. The first part of this paper describes the influence of pH on the dissolution of ThO_2 in both nitric and hydrochloric media. The partial order relative to the proton concentration and the apparent normalized dissolution rate constants were determined. The second part of the paper describes the influence of other ligands such as perchlorate, chloride, sulfate, and hydrogen peroxide on the dissolution kinetics (at pH 1). An increase of R_L was observed correlatively with the increase of complexing affinity of the ligand with Th. While nitric and hydrochloric media, which are weakly complexing, lead to R_L values with the same order of magnitude as those for perchlorate media, the presence of sulfate or peroxide in the leachate significantly enhances the dissolution of ThO_2. Consequently, the dissolution mechanism can be explained by the weakening of Th–O bonds through the formation of surface complexes at the solid/liquid interface, which enhance the detachment and thus accelerate the global dissolution. In addition, the dissolution of $Th_{0.87}Pu_{0.13}O_2$ solid solution was also examined. The increase of the dissolution kinetics of $Th_{0.87}Pu_{0.13}O_2$, in comparison with that of ThO_2, is considered to be caused by the presence of hydrogen peroxide formed by radiolysis of the leachate. Moreover, the redox properties of plutonium in acidic media, like disproportionation of Pu(IV) and Pu(V) and reduction of Pu(VI) and Pu(IV) in Pu(III) by H_2O_2, probably increase the dissolution of plutonium.

Introduction

In the context of the nuclear waste geological repository, an important objective consists in the prediction of the release of radionuclides from the fuel. In this frame, the dissolution of tetravalent actinide dioxides (UO_2, ThO_2, $Th_{1-x}U_xO_2$ solid solutions) was extensively studied in several leaching conditions. Among them, the most extensive dissolution studies was achieved for UO_2 in numerous conditions (acidic, neutral, basic, and salted media, oxidizing or reducing conditions).[1–5] Some of theses studies, based on the determination of the dissolution rate of UO_2 in different environments, demonstrate that the presence of complexing agents such as carbonates or hydrogen peroxide strongly influence the dissolution behavior of uranium dioxide during dissolution. However, the instability of U(IV) with oxidizing ligands makes the interpretation of the results more difficult because of its oxidation into more mobile uranyl species. More recently, dissolution experiments were also performed on ThO_2 and $Th_{1-x}U_xO_2$ solid solutions, in the frame of other type of spent fuels for advanced reactors.[6–10] A complete

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kinetic and thermodynamic study of the dissolution of $Th_{1-x}U_xO_2$ solid solutions has been carried out in nitric acid solutions for several pH values.[8,9] The normalized dissolution rate constants were obtained for ThO_2 and several compositions of $Th_{1-x}U_xO_2$ solid solution ($0 \leq x \leq 1$). The parameters describing the kinetic law were determined in acidic nitric media, for ThO_2 and $Th_{1-x}U_xO_2$ mixed dioxides, while the thermodynamic equilibrium was reached around pH 4 for solid solutions with $x > 0.5$. For the latter samples, a significant increase of the dissolution rate caused by the oxidation of U(IV) in oxidative conditions, leads to the precipitation of hydrated thorium oxide/hydroxide forming a protective layer onto the surface of the leached pellets and the solubility constant of hydrated thorium dioxide could be determined. In contrast, in synthetic clay groundwater (i.e., reducing conditions), the U/(U + Th) mole ratio has no influence on the normalized dissolution rates, R_L(Th) and R_L(U) because of the stabilization of uranium in its tetravalent state.[10]

In the French underground repository (Bure), the groundwater is highly charged with anions such as Cl^- (10^{-1} M) and SO_4^{2-}/HSO_4^- (10^{-1} M).[11] These anions are, more or less, complexing agents related to the tetravalent actinides. Therefore, their presence can influence the dissolution behavior of the actinide dioxide. For instance, the role of the carbonate ions on the UO_2 dissolution in groundwater was extensively studied. [2] However, no systematic leaching experiments has been done on the influence of a given set of ligands on the dissolution behavior of actinide dioxide.

In addition to the presence of some ligands in groundwater, the effect of α-, β-, or γ-irradiation from the spent fuel leads to water radiolysis. One of the key parameter identified during the spent fuel dissolution is associated to the formation of hydrogen peroxide (H_2O_2) as a radiolysis product.[12–14] The effect of hydrogen peroxide on the dissolution of UO_2 was also studied in acidic and basic media.[2] However, because of the oxidation of U(IV) in presence of H_2O_2 and the possible precipitation of the uranyl peroxide, the mechanism of UO_2 dissolution is complicated. In contrast to that if U(IV), no redox reaction occurs with Th(IV) in presence of H_2O_2. Therefore, ThO_2 is a good reference material to understand the role of hydrogen peroxide on the dissolution behavior. Indeed, hydrogen peroxide exhibits strong complexing affinity with Th^{4+} that can affect the dissolution process. Nevertheless, at high H_2O_2 concentration, precipitation of thorium peroxide can occur.[15]

If the dissolution experiments of ThO_2 were carried out in various conditions, no systematic study was investigated to describe the effect of complexing ligands on the dissolution of thorium dioxide samples. Several authors studied the effect of organic or inorganic ligands on the dissolution rate coefficient of other mineral oxides.[16–20] Furrer and Stumm[18] established a framework for studying the dissolution of oxide minerals by showing that the dissolution rates are proportional to the concentration of adsorbed protons and surface metal–ligand complexes. They showed that in the case of organic ligands, bidentate rings are more effective than monodentate ligands in promoting dissolution. Ludwig et al. [19] showed that the dissolution rate coefficient can be predicted from the equilibrium constant associated to the metal complexation in solution, indicating that activated surface complexes resemble the corresponding dissolved complexes. More recently, Pokrovsky et al. [20] correlated the effect of inorganic and organic ligands on the brucite ($Mg(OH)_2$) dissolution with the stability constant of surface complexes.

In order to predict the long-term chemical durability of such materials, it appears important to study the effect of inorganic ligands on the dissolution kinetics of ThO_2. In the present work, the influence of the proton activity on the dissolution of ThO_2 was first studied in nitric acid solutions at constant ionic strength ($I = 0.1$ M). Then, several ligands, such as ClO_4^-, Cl^-, NO_3^-, SO_4^{2-}, and H_2O_2, were introduced in the leachate, using batch dissolution experiments, then the influence of complexing ligands on the dissolution kinetics of ThO_2, was examined at pH = 1. Finally, the dissolution behavior of $Th_{0.87}{}^{239}Pu_{0.13}O_2$ solid solutions was compared to that of ThO_2 in nitric solution.

Experimental Section

Sample Preparation. Thorium nitrate from Fluka was used for synthesizing thorium oxalate, which was obtained by slowly adding the oxalic acid solution into the thorium nitrate solution using a perilstatic pump. The precipitate was first filtered, dried, and then heated in a PYROX furnace at 500 °C and finally at 1300 °C for 10 h with a heating rate of 2–5 °C min^{-1}.

In the case of $Th_{0.87}Pu_{0.13}O_2$ solid solution, tetravalent actinides were coprecipitated by addition of an excess of ammonium oxalate in nitric acid media (0.2 M $H_2C_2O_4$/3.5 M HNO_3). The precipitate was washed several times with deionized water, filtered, dried, and then finally heated in air in a glovebox, using a tubular furnace at 900 °C for 12 h after a preheating stage at 100 °C for one hour. The stoichiometry of the sample was verified by determination of the concentration of both actinides using ICP-MS after their

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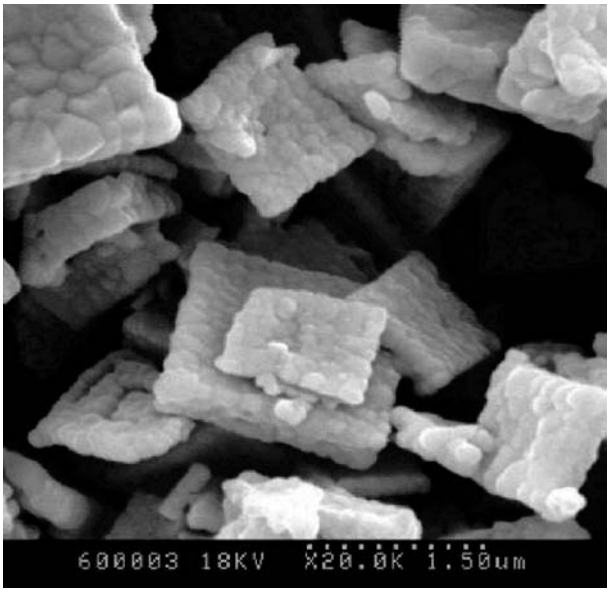

Figure 1. SEM micrographs of powdered ThO_2.

complete dissolution in 14 M HNO_3/5 × 10^{-2} M HF. The specific activity of plutonium used in the synthesis was 3.62 × 10^9 Bq/g Pu.

Characterization of the Samples. All the samples were characterized through XRD and EXAFS, as already described in a previous paper.[21] The powdered samples were observed using scanning electron microscopy (SEM). SEM images (Figure 1) show that the grain size and the morphology of the powder are homogeneous. It consists mostly of square-shaped agglomerates of about 1−2 μm composed of spherical particles.

The specific surface area of each sample was measured by the Brunauer−Emmett−Teller (BET) method, using 10-point N_2-adsorption isotherms on a COULTER SA 3100 apparatus. The sample degassing lasted 10 h at 100 °C prior to performance of the measurements. The values obtained for ThO_2 and $Th_{0.87}Pu_{0.13}O_2$ were found to be 1.0 ± 0.1 $m^2\ g^{-1}$ and 4.9 ± 0.1 $m^2\ g^{-1}$, respectively. The difference between the initial and the final surface area was verified for some experiments. A variation of less than 8% was observed between the initial and final BET surface areas because of the high chemical durability of the material (only few 10^{-3}% of dissolved materials in most of the experiments). Therefore, it appears as a good approximation to keep the specific area constant during the calculations. In these conditions, the dissolution rates were normalized with regard to the initial surface area. Similar observations have already been reported for other materials.[22]

Batch Dissolution Experiments. As already mentioned, the long-term dissolution experiments were carried out in batch reactors.[7] Pretreated powdered samples (100−300 mg) were placed into acid-cleaned Nalgene bottles (high-density polyethylene) with 5−15 mL of solution. The S/V ratios of the experiments were 200 and 500 cm^{-1} for ThO_2 and $Th_{0.87}Pu_{0.13}O_2$, respectively. The reaction vessels were continuously shaken for several months to keep the solid phase in suspension. The rotation speed of the agitation was maintained at 40 rpm during all the leaching experiments. At regular intervals, both phases were separated by centrifugation at 13 000 rpm to avoid the presence of colloids in the remaining solution. An aliquot of 100−200 μL was taken off from the top of the solution and then renewed by the equivalent volume of fresh solution. Since only 1–2% of the leaching solution was added at each sampling, it was possible to consider that the system was not affected during this renewal. The elementary concentrations of Th and Pu were determined by inductively coupled plasma-mass spectroscopy (ICP-MS Fisons plasma quad) and α-liquid scintillation technique (PERALS), respectively.

Table 1. Specific Interaction Coefficients $\epsilon_{i,j}$ (kg mol^{-1}) between Ions[30]

anions/cations	Cl^-	NO_3^-
H^+	0.12	0.07
Th^{4+}	0.25	0.11

Since ThO_2 exhibits a strong resistance to aqueous alteration,[9] batch experiments were performed in acidic media. To determine the influence of the complexing ligands on the normalized dissolution rates, various anions were introduced in the leachate at ionic strength ($I = 10^{-1}$ M), which was maintained by addition of KNO_3 or KCl, except for concentration larger than 10^{-1} M. Dissolution batch experiments were performed on ThO_2 in nitric acid (0 < pH < 4), hydrochloric acid (1 < pH < 4), sulfuric, and perchloric acids (pH 1).

Chemical Treatment of Pu Aliquot Solution for Quantitative Analysis by PERALS. PERALS spectrometry was used for the analytical measurement of low concentrations of plutonium. The analysis of α-nuclides combines chemical separation by liquid–liquid extraction after redox adjustment with measurement of α-activity by liquid scintillation in the same procedure. The principle of the analysis results in an extraction of plutonium from aqueous solution, by using an organic phase containing a complexing extractant (ALPHAEX).[23] Prior to the extraction procedure, a redox treatment of Pu aliquot is realized. First, the plutonium is totally reduced to the trivalent state by using an ascorbic acid solution with a concentration near 1g L^{-1} and after the solution was shaken for 10 min. Second, Pu(III) was totally oxidized by addition of sodium nitrite ($NaNO_2$, 1 g L^{-1}) and immediately extracted by ALPHAEX in nitric acid (pH 1). Using this redox cycle, the recovery yield of plutonium reached 100%. On the other hand, one notices that an extraction of Pu by ALPHAEX without redox treatment leads to a recovery of only 70%, indicating that about 30% of Pu is already present in the trivalent state of plutonium.

Theory

Expression of the Normalized Leaching Rate. The leachability of one element *i* from the solid to the solution can be described by its normalized leaching, $N_L(i)$ (g m^{-2}), which is defined by the following equation

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

where m_i is the total amount of *i* released in the solution, *S* is the corresponding effective surface area of the solid (m^2) in contact with the leachate, and f_i is the mass ratio of the element *i* in the solid. For ThO_2, N_L(Th) (g m^{-2}) is equal to the mass loss of the solid (N_L). In previous papers,[8,9] we always observed a congruent release of the actinides for all the $Th_{1-x}U_xO_2$ solid solutions, at pH < 3, regardless of the composition considered. Therefore, in such solid solutions, all the $N_L(i)$ (g m^{-2}) values correspond to the mass

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Table 2. Thermodynamic Constants of Formation of Thorium (IV) and Pu Complexes with Sulfate, Nitrate, Chloride Ligands and Hydroxide[a]

complexation reactions	log $\beta°$	ref	R_L (g m^{-2} day^{-1})
$Th^{4+} + SO_4^{2-} \Leftrightarrow ThSO_4^{2+}$	5.45	32, 34	$(20.0 \pm 2) \times 10^{-8}$
$Th^{4+} + 2SO_4^{2-} \Leftrightarrow Th(SO_4)_2$	9.73		
$Th^{4+} + 3SO_4^{2-} \Leftrightarrow Th(SO_4^2)_3^{2-}$	10.50		
$Th^{4+} + 4SO_4^{2-} \Leftrightarrow Th(SO_4^2)_4^{4-}$	8.48		
$Th^{4+} + NO_3^- \Leftrightarrow ThNO_3^3$	1.47–0.94	31	$(3.9 \pm 0.1) \times 10^{-8}$
$Th^{4+} + 2NO_3^- \Leftrightarrow Th(NO_3)_2^{2+}$	1.97		
$Th^{4+} + Cl^- \Leftrightarrow ThCl^{3+}$	1.09	32	$(1.8 \pm 0.2) \times 10^{-8}$
$Th^{4+} + 2Cl^- \Leftrightarrow Th(Cl)_2^{2+}$	0.8		
$Th^{4+} + 3Cl^- \Leftrightarrow Th(Cl)_3^+$	1.65		
$Th^{4+} + 4Cl^- \Leftrightarrow Th(Cl)_4$	1.26		
$Th^{4+} + H_2O \Leftrightarrow ThOH^{3+} + H^+$	−2.2	32	
$Th^{4+} + 2H_2O \Leftrightarrow Th(OH)_2^{2+} + 2H^+$	−6		
$Th^{4+} + 3H_2O \Leftrightarrow Th(OH)_3^+ + 3H^+$	−11		
$Th^{4+} + 4H_2O \Leftrightarrow Th(OH)_4 + 4H$	−17		
$Pu^{4+} + NO_3^- \Leftrightarrow PuNO_3^{3+}$	1.95	32, 34	$(19 \pm 2) \times 10^{-8}$
$Pu^{4+} + H_2O \Leftrightarrow PuOH^{3+} + H^+$	−0.6	32, 34	
$Pu^{4+} + 2H_2O \Leftrightarrow Pu(OH)_2^{2+} + 2H^+$	−0.63		
$Pu^{4+} + 3H_2O \Leftrightarrow Pu(OH)_3^+ + 3H^+$	−2.25		
$Pu^{4+} + 4H_2O \Leftrightarrow Pu(OH)_4 + 4H$	−8.54		
$Pu^{3+} + NO_3^- \Leftrightarrow PuNO_3^2$	1.33[b]		
$Pu^{3+} + H_2O \Leftrightarrow PuOH^{2+} + H^+$	−6.9		
$Pu^{3+} + 2H_2O \Leftrightarrow Pu(OH)_2^+ + 2H^+$	−15		
$Pu^{3+} + 3H_2O \Leftrightarrow Pu(OH)_3 + 3H^+$			

[a] $R_L = 0.1 \times 10^{-8}$ (g m^{-2} day^{-1}) in $HClO_4$ (0.1M). [b] Equilibrium constant for Am which can be used as guideline for Pu^{3+} (recommended from OECD).

loss of the solid (N_L) as well. The same behavior is expected for $Th_{1-x}Pu_xO_2$ solid solutions.

The expression of the normalized dissolution rate of the solid, R_L (also noted as R_H in acidic medium) expressed in g m^{-2} day^{-1}can be deduced from the evolution of the normalized leaching, N_L(i), as follows

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

Far from equilibrium, the normalized dissolution rate is usually found to be constant for most of the minerals.[24–27] In the opposite, parabolic evolution of the normalized leaching observed near the equilibrium, usually suggests the formation of precipitate, when the saturation conditions are reached in the leachate, leading to the diffusion of the elements through a protective layer formed onto the surface of the samples.

General Rate Law for Surface-Controlled Dissolution. The dissolution rate of a solid is related to the surface charge imparted to the surface by H^+, OH^-, or both. The dissolution rate increases both, with increasing positive charge when decreasing the pH values of the solution, and with increasing negative charge when increasing the pH values. The minimum dissolution rate is usually observed at the pH of zero point of charge (pH_{PZC} for which the surface charge density is zero). We measured the appropriate pH which minimizes the adsorption of ionic substances by potentiometric titration for ThO_2 around pH = 9.2, which value is consistent with that published in previous work (pH_{ZPC} = 9.8). [28]

Several authors already described the dissolution reaction from a kinetic point of view.[18,26–30] In the absence of complexing ligand, species interacting with the surface of the oxide are mainly protons and hydroxide ions under acidic, and basic conditions, respectively. The rate dependence on pH can then be described by

$$R = k_H'(a_{H_3O^+})^n + k_{OH}'(a_{OH^-})^m \qquad (3)$$

where $a_{H_3O^+}$ is the proton activity, a_{OH^-} is the hydroxide ion activity, k_H', and k_{OH}' are the apparent normalized dissolution rate constant at pH 0 and 14, respectively, and n and m are the corresponding partial orders related to proton and hydroxide concentrations, respectively.

Consequently, in acidic solution and in absence of complexing ligands, the dissolution kinetics is controlled by the surface-bound protons following the law

$$R_H = k_H'(a_{H_3O^+})^n \qquad (4)$$

where R_H refers to the proton-promoted normalized dissolution rate.

When ligands are present, the normalized dissolution rate of the dioxide is thus the sum of proton- and ligand-controlled dissolution

$$R_H = k_H'[a_{H_3O^+}]^n + k_L'[a_L]^l \qquad (5)$$

where a_L is the ligand activity, and l and k_L' are the partial order and the dissolution rate constant related to the ligand, respectively.

When the ligand concentration remains constant, the dissolution kinetics in acidic media is then described by the following equation

$$R_H = k_H'[a_{H_3O^+}]^n + k_L'' \qquad (6)$$

The SIT model was used to calculate the proton activity with the specific interaction coefficients gathered in Table 1.[31]

Speciation of Actinides in Solution. Prior to the Results and Discussion, it is important to consider the speciation of thorium and plutonium in presence of the ligands used in this study, that is, NO_3^-, Cl^-, and SO_4^{2-}. The thermodynamic constants are given in Table 2 with the corresponding complexation reactions. From the stability constant of Th(IV) with the common inorganic ligands

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Table 3. Normalized Dissolution Rates R_L(Th) and R_L(Pu) of ThO_2 and $Th_{0.87}Pu_{0.13}O_2$, Respectively, in Several Media (Expressed in g m^{-2} day^{-1})

$[H^+]$		1 M	10^{-1} M	10^{-2} M	10^{-3} M
ThO_2/HCl	R_H	$(74 \pm 7) \times 10^{-8}$	$(1.8 \pm 0.2) \times 10^{-8}$	$(0.56 \pm 0.06) \times 10^{-8}$	
ThO_2/HNO_3	R_H	$(6.0 \pm 0.6) \times 10^{-8}$	$(3.9 \pm 0.1) \times 10^{-8}$	$(2.7 \pm 0.3) \times 10^{-8}$	
$Th_{0.87}Pu_{0.13}O_2/HNO_3$	R_H	$(67 \pm 7) \times 10^{-8}$	$(19 \pm 2) \times 10^{-8}$	$(4.5 \pm 0.5) \times 10^{-8}$	$(1.6 \pm 0.2) \times 10^{-8}$

Cl^-, NO_3^-, and SO_4^{2-}, it is clear that weak complexes are formed with chloride and nitrate ligands while strong complexes are formed with SO_4^{2-}. Since tetravalent actinides also exhibit a strong affinity with hydrolysis, in addition to the complexation constants, hydrolysis constants are also given for Th(IV) and Pu(IV). As examples, Figure 2a and b represents the distribution of the species versus pH for 10^{-6} M Th(IV) in hydrochloric media ($I = 0.1$ M) and 10^{-6} M Pu(IV) in nitric media ($I = 0.1$ M). As observed in Figure 2a, although NO_3^- or Cl^- are weak complexing ligands, in acidic conditions (pH < 2), Th^{4+} is the major species in aqueous solution (about 90%), while about 15% of thorium is complexed as $ThCl^{3+}$. The first hydrolyzed species $ThOH^{3+}$ appears above pH 1.5 and becomes preponderant between pH 3 and 4. A similar speciation diagram is obtained with nitrate ligands with a slightly larger amount of $ThNO_3^{3+}$ species. However, the databases of the stability constants of thorium nitrate complexes are not well estimated. However, a stronger complexation constant for sulfate ligands makes the sulfato complex $ThSO_4^{2+}$ the main species until pH 4. Indeed, for Pu(IV), the hydrolysis appears at lower pH values compared to that for Th(IV), as can be seen in Figure 2b. Several hydrolyzed species ($PuOH^{3+}$, $Pu(OH)_2^{2+}$, and $Pu(OH)_3^+$), coexist with Pu^{4+} and $PuNO_3^{3+}$ for pH < 2, while only the first hydrolyzed complex appears weakly with $ThCl^{3+}$ or $ThNO_3^{3+}$. At pH 3, $Pu(OH)_3^+$ is the major species in solution.

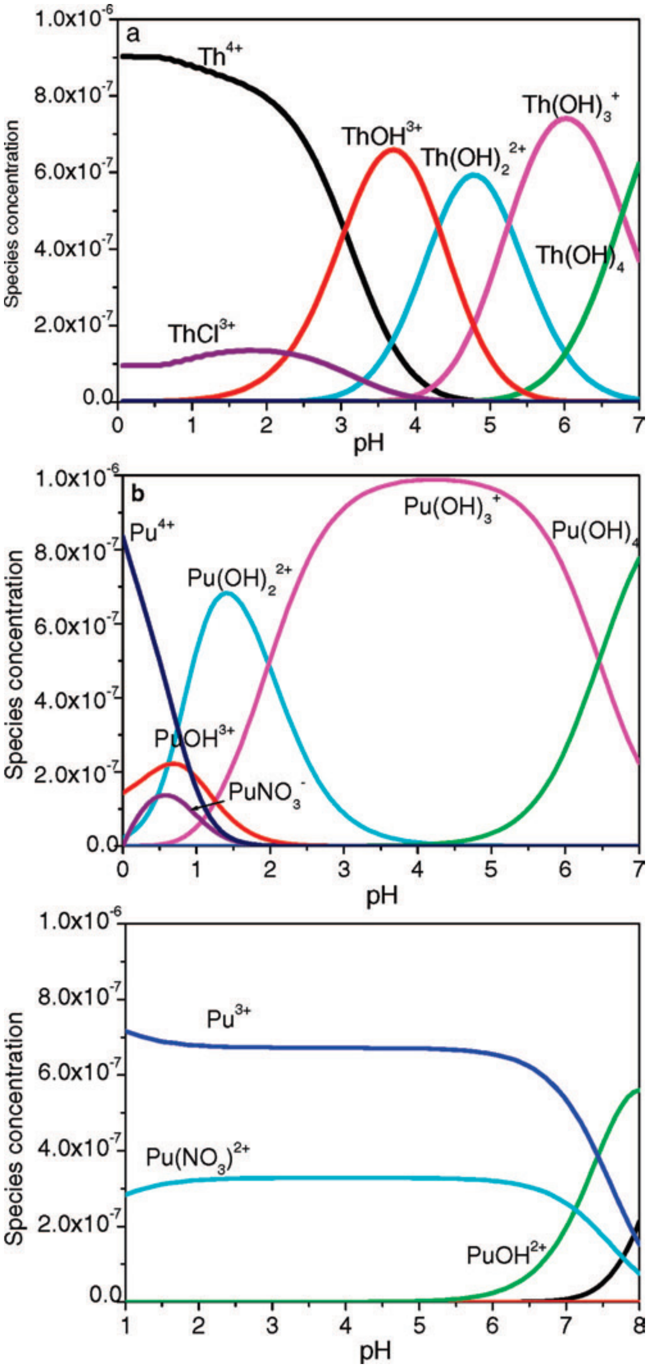

Figure 2. Speciation diagram of Th^{4+}(1×10^{-6} M) in chloride media and $Pu^{4+}$and Pu^{3+} (1×10^{-6}M) in nitrate media ($I = 0.1$M, T =298 K)

Because of the possible reduction of Pu(IV) into Pu(III) in presence of hydrogen peroxide, it is also interesting to report the hydrolysis constants of Pu(III), in addition to those of Pu(IV) in Table 2. The tendency to undergo hydrolysis decreases with the ionic potential (often similar to the effective charge of the ion ρ_{ionic} = charge/r_{ionic}). The speciation diagram of 10^{-6} M Pu^{3+} in nitrate media ($I = 0.1$ M) is shown in Figure 2c. From this figure, it is clear that only Pu^{3+} and $Pu(NO_3)^{2+}$ are present in the solution up to pH 5.

Results and Discussion

Influence of the pH on the Normalized Dissolution Rate of ThO_2. The dissolution of pure ThO_2 was studied in nitric and hydrochloric acid at different pH values ranging from 0 to 2, keeping constant the ionic strength at $I = 10^{-1}$ M, except for 1 M acid solutions, by using KNO_3 or KCl as support electrolyte. The thorium concentration was followed versus the leaching time for at least one year. The evolution of the normalized leaching N_L(Th) in nitric and hydrochloric media is reported in Figure 3 for several acid concentrations. Whatever the pH and the leaching media, the dissolution curves exhibit the same feature. The fast initial leaching process is thus followed by the decrease in the thorium release after about one month of leaching with a quasi linear trend. As usually observed, the initial parabolic part of the curve is caused by defects and inhomogeneity of surface sites. This behavior is typical of surface-controlled mechanism. In these experiments, the concentration of the anions is maintained constant ($I = 0.1$ M), while the protons concentration varies. Therefore the partial order related to the proton, as well as the normalized dissolution rate constant, can be determined from the best fit of the linear part of the kinetics curve. As usually observed for minerals, the normalized dissolution rate of ThO_2 increases with that

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(33) Lemire, R. J. *Chemical Thermodynamics of Neptunium and Plutonium*; OECD, Nuclear Energy Agency, Elsevier: New York, 2001.

(34) Guillaumont, R.; Fanghanel, T.; Fuger, J.; Grenthe, I.; Neck, V.; Palmer, D. A.; Rand, M. H. *Update on the Chemical Thermodynamics of U, Np, Pu, Am, and Tc*; Elsevier: Amsterdam, 2003.

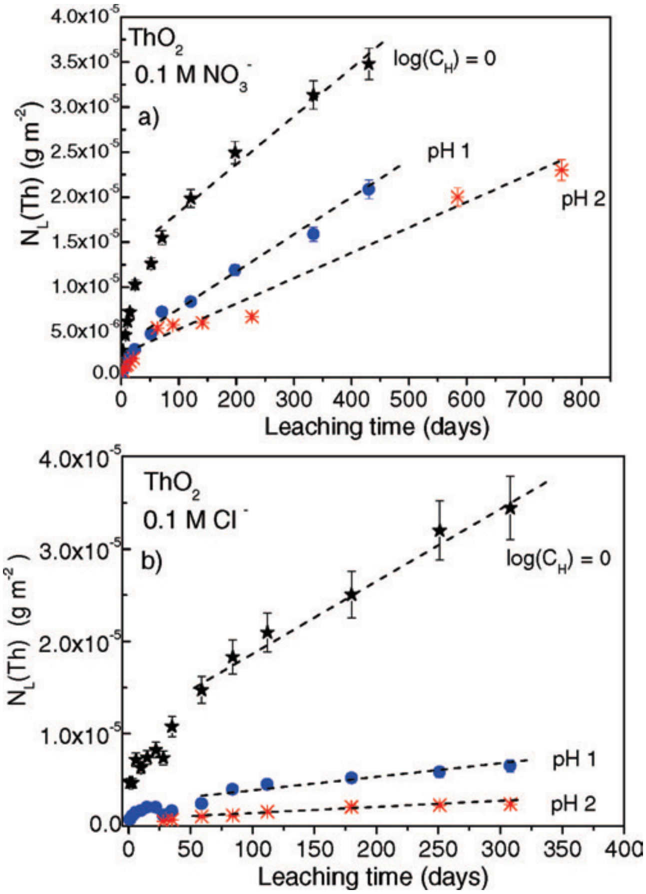

Figure 3. Evolution of N_L (Th) during the Dissolution of ThO_2 (S/V = 160 cm^{-1}) in 1 M (star), 10^{-1} M (circle), and 10^{-2} M (asterisk) HNO_3 (a) and HCl (b).

of the proton activity in the leachate, whatever the electrolyte considered. The thorium concentration in the leachate was too low to be measured with a good accuracy for pH > 2.5 because of the precipitation of hydrated thorium dioxide/thorium hydroxide.[35]

The normalized dissolution rates determined from the linear regression are given in Table 3, for several pH conditions in hydrochloric and nitric media ($I = 0.1$ M). It decreases with the increase of the proton activity. However, one can notice that these values are slightly lower in hydrochloric acid than in nitric acid, except for higher concentration (1 M).

The partial order related to the proton concentration was obtained by plotting log(R_H) versus log ($a_{H_3O^+}$) in HCl and HNO_3 (Figure 4). The linear variation of the normalized dissolution rate versus the proton activity was found to be in agreement with eq 6, regardless of the acid considered. It is interesting to note that the value obtained for the normalized dissolution rate is close to the linear variation, for a concentration of ligand larger than 10^{-1} M, indicating that NO_3^- and Cl^- ions are weak complexing species. From eq 6 with consideratio of the specific interaction theory (SIT) for the determination of the proton activity, the linear regression of the experimental data obtained for ThO_2 led to partial orders relative to the proton concentration of $n = 0.50 \pm 0.05$ and 0.30 ± 0.05 in hydrochloric and nitric media, respectively. The associated values obtained for the apparent normalized dissolution rate constants, k_H', and the partial order related to the proton concentration, n, are gathered in Table 4. These parameters are similar, regardless of the media. Nevertheless, the partial order related to the proton concentration is slightly larger in hydrochloric media than in nitric media.

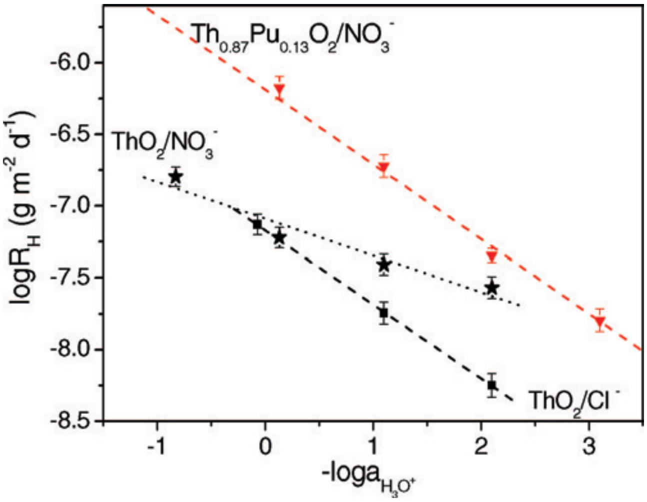

Figure 4. Variation of log (R_H) versus pH for ThO_2 (in nitric and chloride media) and $Th_{0.87}Pu_{0.13}O_2$(in nitric media)

Table 4. Kinetic Parameters Associated with the Dissolution of ThO_2 and $Th_{0.87}Pu_{0.13}O_2$

solid	ligand	k_{298K} (g m^{-2} day^{-1})	n
ThO_2	NO_3^-	$(8.0 \pm 0.5) \times 10^{-8}$	0.30 ± 0.05
ThO_2	Cl^-	$(6.8 \pm 0.2) \times 10^{-8}$	0.50 ± 0.05
$Th_{0.87}Pu_{0.13}O_2$	NO_3^-	$(65 \pm 0.6) \times 10^{-8}$	0.50 ± 0.06

Influence of the Ligands NO_3^-, Cl $^-$, HSO_4^-/SO_4^{2-}, and H_2O_2 on the Normalized Dissolution Rate of ThO_2 at pH 1. Leaching experiments performed on ThO_2 in solutions containing various ligands provide insight onto the effects of competiting anions on the proton activity and the mechanism of the dissolution in presence of complexing anions at constant pH values. The aim of this work was focused on the influence of ligands such as nitrate, chloride, sulfate, and hydrogen peroxide on the normalized dissolution rate of ThO_2, which was evidenced through the comparison with non-complexing perchlorate ions. In this aim, the evolution of the normalized leaching, N_L(Th), was examined at 298 K for several months in several inorganic acids ($HClO_4$, HNO_3, HCl, H_2SO_4, and H_2O_2) at constant proton concentration ($C_H = 10^{-1}$M). The evolution of the normalized mass loss of ThO_2 in 0.1 M $HClO_4$, HNO_3, HCl, and H_2SO_4 is reported in Figure 5. The direct comparison of all these data indicates that the normalized dissolution rate of thorium dioxide depends significantly on the composition of the leaching solution.

Indeed, in the case of non-complexing media, the thorium release is very low ($R_L \approx 0.1 \times 10^{-8}$ g m^{-2} day^{-1}). It increases linearly during the first two months of leaching time. Except in the case of perchloric acid, regardless of the acid considered (pH 1), the same behavior occurs as already

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(35) Heisbourg, G.; Dacheux, N.; Lagarde, G.; Hubert, S. *Radioactive Waste Management and Environmental Remediation*; American Society of Mechanical Engineers: New York, 2001.

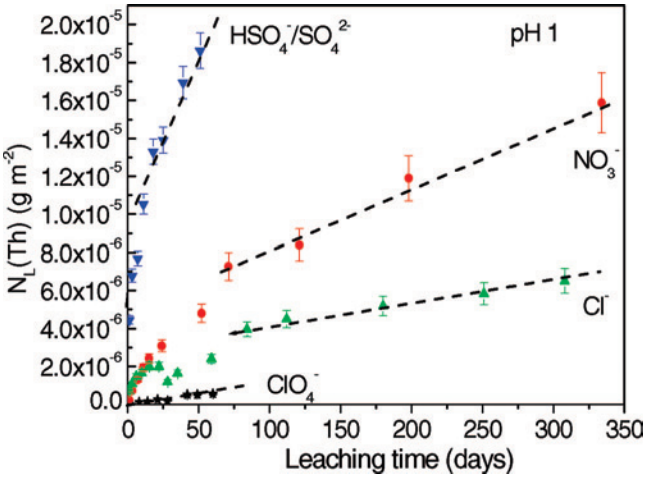

Figure 5. (a) Evolution of N_L(Th) obtained when leaching ThO_2 in 10^{-1} M $HClO_4$ (star), 10^{-1} M HCl (triangle), 10^{-1} M HNO_3 (circle), and 10^{-1} M H_2SO_4 (inverted triangle) at pH 1 and $T = 298$ K.

observed above. After about one month of leaching time, a quasi linear variation is observed. However, some acids enhanced the dissolution rate more than others. The effect of sulfuric acid on the thorium release (and associated normalized dissolution rate) is much greater than that reported in nitric or hydrochloric acid. Moreover, the thorium release appears slightly larger in nitric and hydrochloric media compared to perchloric acid. Thus, the relative normalized dissolution rate of thorium follows the sequence $SO_4^{2-} > NO_3^- > Cl^- > ClO_4^-$.

Because the proton concentration is the same for all the leaching media considered and no redox reaction is expected for Th(IV), only complexing reactions at the interface can play an important role in the dissolution processes. In these conditions, complexing anions such as SO_4^{2-}, NO_3^-, or Cl^- participate to the formation of activated complex at the solid/liquid interface.

The stability constants of thorium complexes formed with Cl^-, NO_3^-, and SO_4^{2-} ligands are reported with the corresponding normalized dissolution rate in Table 2. The stability constant of thorium complexes increases with the charge and the basicity of inorganic anions. Therefore, thorium sulfate complexes have the greatest stability constant compared to nitrate or chloride. Indeed, sulfate is the strongest acid in promoting thorium dioxide dissolution. The normalized dissolution rates, R_L, obtained by linear regression of the normalized leaching is spread from 0.1×10^{-8} g m^{-2} day^{-1} in perchloric medium up to $(20.0 \pm 0.3) \times 10^{-8}$ g m^{-2} day^{-1} in sulfate solution with intermediate values for weak complexing media such as nitrate and chloride, that is, $(3.9 \pm 0.1) \times 10^{-8}$ g m^{-2} day^{-1} and $(1.8 \pm 0.2) \times 10^{-8}$ g m^{-2} day^{-1}, respectively. It is clear that the associated normalized dissolution rate increases substantially with the stability constant of the thorium complexes formed with the ligands considered. From Figure 2a, the major species are Th^{4+} and $ThCl^{3+}$(∼15%), and no hydrolyzed species are present at pH 1. Thus, the percentage of complexes in solution increases with the increase of the stability constant, leading to the increase of the concentration of the surface complexes that labilize the Th−O bonds. The tendency to form more soluble surface complexes increases with the tendency to form solute complexes.

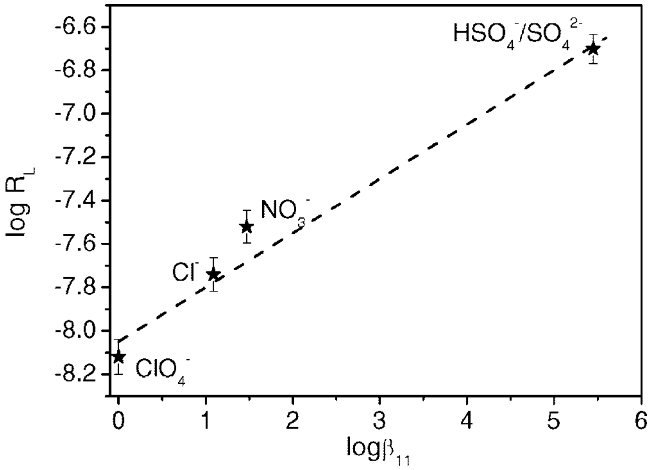

Figure 6. Variation of log R_L versus log β_{11}.

Since the acidity is the same for all the leaching media considered, the increase of the normalized dissolution rate with the increase of the stability constant of the aqueous complexes indicates that the dissolution rate is ligand promoted. As a matter of fact, we can observe that log(R_L(Th)) increases quite linearly with the logarithm of the equilibrium constant of thorium complexes, log β_{11}, as shown in Figure 6, which appears to be consistent with eq 5.

This linear variation with the logarithm of the stability constant was already observed for other oxide minerals.[18,19] Furrer and Stumm[18] determined experimentally the concentrations of ligands at the surface for Al_2O_3 and determined the associated surface coordination equilibrium constants. They concluded that the rate law can be expressed in terms of the concentration of solutes and that the concentrations of ligands present at the surface are proportional to their concentration in solution in a fractional power function. Ludwig et al.[19] correlated the dissolution rate coefficient of bunsenite (NiO) with equilibrium constants of organic ligands and demonstrated that the rate coefficient for ligand-promoted dissolution can be predicted in a manner similar to that for the proton-promoted rates.[18] They demonstrated that the strengths of organic acids to promote dissolution are related to the strength of the metal–ligand complex formed in solution or on the mineral surface. The simplest explanation is that the ligand displaces surface hydroxyl groups or water molecules from around a metal surface site to form a surface complex. Then the formation of surface complexes weakens the M−O bonds, thereby enhancing the detachment of the metal and accelerating the dissolution. Consequently, the formation of such surface complexes could lower the activation energy of the rate-limiting step of dissolution, thereby increasing the apparent solubility of the oxide in aqueous solution, as well as increasing the associated normalized dissolution rate. The same argument can be applied for inorganic acids. Pokrovsky et al. also demonstrated the catalyzing effect of organic and inorganic ligands on brucite ($Mg(OH)_2$).[20]

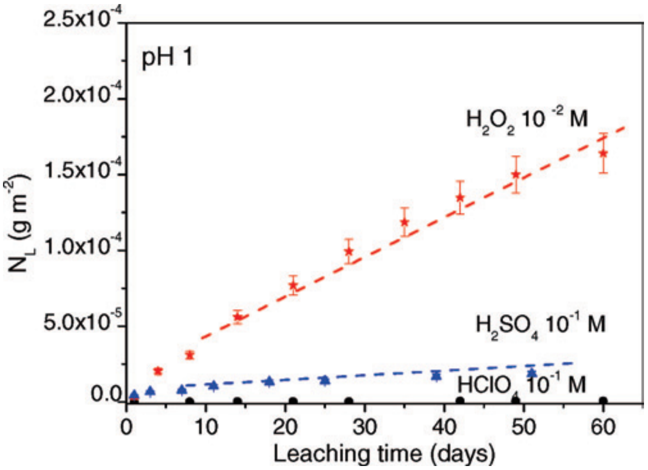

Figure 7. Evolution of N_L(Th) in 10^{-1} M $HClO_4$ with and without 10^{-2} M H_2O_2 at pH 1. Comparison with that of N_L(Th) in 10^{-1}M H_2SO_4

It is clear that strong complexing ligands such as sulfate ions increase the dissolution rate of ThO_2 by a factor of 5 compared to that observed in nitric media, which is consistent with the ratio obtained for the complex stability constants of thorium in both media. From this variation, the normalized dissolution rate of thorium dioxide in other complexing inorganic media could be predicted, and these effects could be extrapolated to other inorganic ligands for a given pH.

In addition to the presence of complexing ions in groundwater, the hydrogen peroxide produced through water radiolysis can be considered as an important reagent to be studied in the framework of the performance assessment of the final nuclear fuel disposal. Its impact on the dissolution of UO_2 has been already studied.[13] However, the dissolution mechanism is more difficult because of the oxidation of the UO_2 surface. Production from 10^{-2} to 10^{-5} M of hydrogen peroxide concentration is expected in the groundwater.[36] Although data concerning the stability constant of thorium complexes formed with hydrogen peroxide are scarce, one expects strong affinity of this ligand with Th(IV) because it was found with tetravalent plutonium and neptunium.[37,38] High stability constants were measured for two complexes involving two plutonium ions. More recently, Dgocic et al.[39] measured the high stability constant values of two peroxo complexes formed with U(VI). Then, to study the influence of irradiation effect on the normalized dissolution rate R_L(Th), through the formation of such species the dissolution of sintered pellets of ThO_2 was also examined in 10^{-1} M $HClO_4$ in presence of 10^{-2} M H_2O_2 (Figure 7).

As expected, the thorium release is significantly increased in presence of 10^{-2} M H_2O_2 compared to that obtained in pure 10^{-1} M $HClO_4$ solution. The associated normalized dissolution rate, R_L(Th), determined by linear regression from the evolution of N_L(Th), is evaluated to be 3.2×10^{-6} g m^{-2} day^{-1}, which appears to be about 2 orders of magnitude larger than that determined in 10^{-1}M $HClO_4$. This effect is even stronger than that observed with sulfate ions. The global release of thorium in presence of 10^{-2} M H_2O_2 is enhanced by 1 order of magnitude in comparison with that obtained in presence of 10^{-1} M SO_4^{2-}/HSO_4^- ions. Because the sequence of acceleration found here is in agreement with the strengths of the metal–ligand complexes, from this variation, one should expect stronger complex stability constant of thorium with hydrogen peroxide than that of thorium sulfato complex.

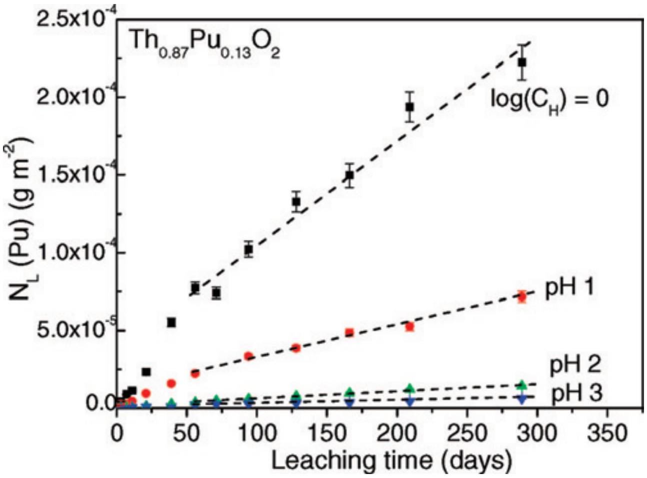

Figure 8. Evolution of N_L(Pu) during the dissolution of $Th_{0.87}Pu_{0.13}O_2$ in 10^{-1} M HNO_3 (circle), 10^{-2} M HNO_3 (triangle), and 10^{-3} M HNO_3 (inverted triangle) ($S/V = 500$ cm^{-1}).

Dissolution Behavior of $Th_{0.87}Pu_{0.13}O_2$. Influence of the pH on the Normalized Dissolution Rate of $Th_{0.87}Pu_{0.13}O_2$. It was also interesting to study the dissolution behavior of a highly radioactive mixed oxide containing plutonium instead of uranium. $Th_{0.87}Pu_{0.13}O_2$ powdered solid solutions were leached for one year in nitric acid solutions at constant ionic strength ($I = 0.1$ M) with pH ranging from 1 to 3. Some additional leaching tests were also carried out in 1 M HNO_3. Because of the higher specific activity of plutonium compared to that of thorium, only the plutonium concentration could be measured during the leaching test of $Th_{0.87}Pu_{0.13}O_2$. Nevertheless, we assume that thorium dissolves congruently with plutonium, as is the case for thorium and uranium in $Th_{1-x}U_xO_2$ solid solutions,[8,9,35] until the precipitation of hydrated thorium oxide/thorium hydroxide occurs (pH > 2.5). The evolution of N_L(Pu) obtained when leaching $Th_{0.87}Pu_{0.13}O_2$ in HNO_3 with pH ranging from 1 to 3 is reported in Figure 8. The dissolution curves exhibit the same tendency as those for ThO_2 (see Figure 3). The dissolution rates normalized to the initial surface area, determined after 50 days from the linear regression are gathered in Table 3. Compared to that of ThO_2 in the same media, the normalized dissolution rates obtained for $Th_{0.87}Pu_{0.13}O_2$ in nitric acid are roughly 1 order of magnitude larger. Indeed, only the release of the dissolved plutonium ion could be measured in the case of $Th_{0.87}Pu_{0.13}O_2$ solid solution. However, in previous dissolution studies performed with $Th_{1-x}U_xO_2$, a congruent dissolution of the mixed oxide was observed under acidic conditions (pH < 3).[35] Therefore,

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[36] Sattonay, G.; Ardois, C.; Corbel, C.; Lucchini, J. F.; Barthe, M. F.; Garrido, F.; Gosset, D. *J. Nucl. Mater.* **2001**, *288*, 11–19.

[37] Connick, R. R.; Mc Vey, W. H. *J. Am. Chem. Soc.* **1949**, *71*, 1534–1542.

[38] Moskvin, A. I. *Radiokhimiya* **1968**, *10*, 13–21.

[39] DgocicP.; Cuculic, V.; Branica, M. *Croat. Chem. Acta* **2005**, *78*, 575–580.

one can expect the same behavior for $Th_{0.87}Pu_{0.13}O_2$ solid solution.

The partial order related to the proton concentration was obtained by plotting log(R_H) versus log ($a_{H_3O^+}$) in nitric media (see Figure 4). As already obtained for ThO_2, a linear variation of the normalized dissolution rate with respect to the proton activity was found. [35] The partial order is slightly larger for $Th_{0.87}Pu_{0.13}O_2$ solid solution than for ThO_2 in the same media ($n = 0.50 \pm 0.06$). However, this value is close from the fractional reaction order found by Alliot et al. [10] for $Th_{1-x}U_xO_2$ in reducing conditions ($n = 0.51 \pm 0.04$). The difference in the normalized dissolution rate between ThO_2 and $Th_{0.87}Pu_{0.13}O_2$ decreases slightly with the decrease of proton concentration. The presence of hydrolyzed Pu(IV) colloids could play a significant role. However, after centrifugation of the solids at 13 500 rpm, sampling from the top of the solution, and redox cycle for liquid–liquid plutonium extraction prior the analytical analysis by PERALS, we made the assumption that colloids do not exist in the analyzed solution. Thus, the slight difference in the partial order can be explained by the presence of hydrolyzed species which become preponderant at pH > 1 for Pu(IV), while in the case of ThO_2, only Th^{4+} and $ThNO_3^{3+}$species are present.

On the other hand, the normalized dissolution rate constant for $Th_{0.87}Pu_{0.13}O_2$ is increased by a factor of 2−10, compared to that of ThO_2, depending on the pH. Compared to ThO_2, the larger dissolution rate values obtained for the solid solution regardless of the pH, could be explained by the formation of small amount of hydrogen peroxide resulting from the radiolysis effect in the leachate. It is worth noticing that, unlike thorium dioxide (R_L(Th), the variation of log(R_L(Pu)) versus pH is linear in the whole concentration range studied (until pH 3). In these conditions, plutonium certainly does not precipitate, unlike thorium which is usually precipitated above pH 2.5. This point appears in contradiction with the solubility data deduced from the solubility of plutonium tetrahydroxide $Pu(OH)_4$ ($\log K^0_{SP} = -58 \pm 1$),[33] considering the plutonium concentrations determined in the leachate (10^{-3} M HNO_3) after 300 days of leaching time ($C_{Pu} \approx 6 \times 10^{-6}$ M). This result can be explained by several chemical properties of plutonium in aqueous media: (i) disproportionation of Pu(IV) and Pu(V)[40] in Pu(III) and Pu(VI) for $C_{HNO_3} < 0.5$ M and (ii) formation of hydrogen peroxide due to radiolysis of aqueous phase through the α-radioactivity of Pu isotopes for $C_{HNO_3} < 0.5$ M.[41]

First, the disproportionation of Pu(IV) and Pu(V) and the reduction of Pu(VI) and Pu(IV) by H_2O_2 in acidic solution[40,42] could be responsible for the presence of trivalent plutonium in the leachate. However, because of the partial oxidation of Pu(III) by oxygen or nitrate ions, an equilibrium between Pu(IV) and Pu(III) is always observed in low acidic media. Moreover, it is well-known that trivalent actinides are hydrolyzed for higher pH than tetravalent actinides (see Figure 2).[32,40]

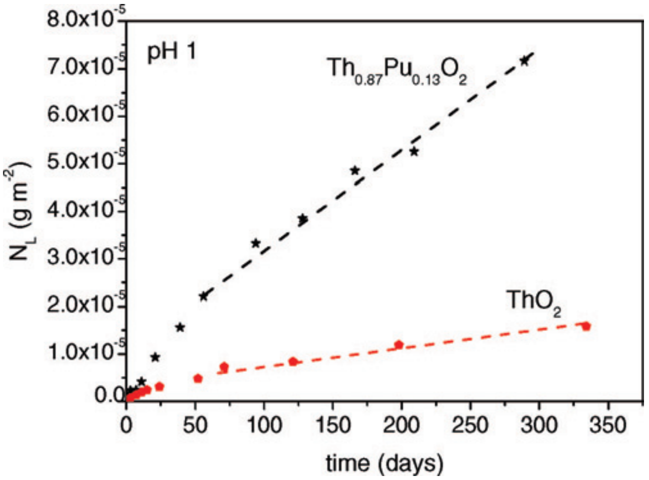

Figure 9. Evolution of N_L(Pu) during the dissolution of $Th_{0.87}Pu_{0.13}O_2$ compared to that for ThO_2 (N_L(Th)) in 10^{-1} M HNO_3.

Second, it is well-known that Pu(IV) is stabilized in aqueous solution by H_2O_2 because of the formation of peroxo complexes with a stoichiometry of 2:2 and 2:1.[37] It is worth noting that the precipitation of peroxo plutonium complexes with stoichiometry 1:2 is only observed for very high concentration of H_2O_2 in acidic media.

Although the thorium concentration could not be measured, the results obtained from the plutonium concentration measurement, indicate that the behavior of $Th_{0.87}Pu_{0.13}O_2$ solid solution dissolution is more complicated than that of ThO_2, because of the complex chemical behavior of plutonium: hydrolysis behavior, plutonium redox reactions, and complexation of tetravalent plutonium with hydrogen peroxide formed from the water radiolysis. Although more experimental data are needed, we consider that the presence of Pu(III) in the leachate can explain that Pu does not precipitate at pH 3 (i.e., observation of the linear variation of log N_L versus log $a_{H_3O^+}$ until pH 3) and that the plutonium concentration measured in the leachate at pH 3 is higher than that we could expect from the solubility data associated to $Pu(OH)_4$. As a matter of fact, the extraction process by ALPHAEX in absence of redox cycle yields only 70% of Pu extracted, which can be explained by the presence of trivalent plutonium in the leachate.

Dissolution of $Th_{0.87}Pu_{0.13}O_2$ in Nitric Media at pH 1. Comparison with ThO_2. As already mentioned, leaching tests of $Th_{0.87}Pu_{0.13}O_2$ were performed in 10^{-1} M HNO_3 in the same conditions as for ThO_2. The evolution of the normalized leaching, N_L(Pu), obtained at pH 1 was compared to that determined for ThO_2, N_L(Th), (Figure 9). Considering that plutonium dissolves congruently with thorium as already shown for other $Th_{1-x}U_xO_2$ solid solutions for pH < 3, we observed a significant increase of the normalized leaching of the $Th_{0.87}Pu_{0.13}O_2$ solid solution compared to that for ThO_2. The normalized dissolution rate R_L(Pu), deduced from the linear regression (1.9×10^{-7} g m^{-2} day^{-1}), is about five times as large as that of ThO_2 (3.9×10^{-8} g m^{-2}day^{-1}).

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(40) Cleveland, J. M. *The Chemistry of Plutonium*; American Nuclear Society: La Grange Park, IL, 1979..

(41) Savel'ev, J. I.; Ersoya, Z. V.; Vladimirova, M. V. *Radiochemistry* **1967**, *9*(2), 244249..

(42) Maillard, C.; Adnet, J. M. *Radiochim. Acta* **2001**, *89*, 485–490.

Considering the speciation of Pu(IV) in comparison with that of Th(IV) at pH 1, one should expect the presence of hydrolyzed species for Pu(IV) in the leachate ($PuOH^{3+}$, $Pu(OH)_2^{2+}$, and $Pu(OH)_3^{+}$), in addition to $PuNO_3^{3+}$.

Although the thorium concentration could not be measured and with consideration of the increase of the release of ThO_2 in presence of only 10^{-2} M H_2O_2, as well as the probable congruent dissolution of $Th_{1-x}M_xO_2$ solid solution, the increase of the dissolution of the $Th_{0.87}Pu_{0.13}O_2$ solid solution, can be attributed in part by the production of few amount of hydrogen peroxide in the leachate formed by radiolysis. Moreover, the redox properties of plutonium in acidic aqueous media, like the disproportionation of Pu(IV) and Pu(V) and the reduction of Pu(VI) and Pu(IV) in Pu(III) by H_2O_2, probably increase the dissolution of plutonium. Indeed, these assumptions need to be strenghtened, by further experiments, confirming the presence of Pu(III) in the solution and the congruence of the solid solution dissolution. However, the dissolution experiments performed with $Th_{0.87}Pu_{0.13}O_2$ solid solution at pH 3 indicate no precipitation, unlike ThO_2, and the extraction procedure yield for Pu analytical measurement confirms the presence of Pu(III). In the case of $Th_{1-x}U_xO_2$ solid solution with $x > 0.50$, the congruence of the dissolution was always observed, although the oxidation of U(IV) in U(VI) occurs in the leachate.

Conclusion

The parameters describing the dissolution kinetic law (n and k', the partial order and the partial dissolution rate constant, respectively) were first determined in hydrochloric and nitric solution for ThO_2.

Then, the influence of various inorganic ligands such as perchlorate, chloride, nitrate, sulfate, and hydrogen peroxide was studied for various proton concentrations during several months. At constant pH and ionic strength (pH = 1, $I = 0.1$ M), the same behavior is observed for most of the ligands. A fast initial leaching process is followed by a slower release of the elements from the solid. After one month, a linear variation of the mass loss is observed. However, the normalized dissolution rate is enhanced in the presence of complexing inorganic ligands; $\log(R_L(i))$ increases quite linearly with the logarithm of the Th-ligand stability constants. Since, the rate controlling steps in the dissolution of oxides are mainly surface reaction processes, the normalized dissolution rates depend on the concentration of species at the surface, which increases with that of the complex in the solution. It suggests that the formation constant of the surface complexes increases with the stability constant of the complex formed in the solution. The formation of surface complexes at the surface weakens the metal–oxygen bonding, enhancing the detachment of the metal.

Finally, the effect of hydrogen peroxide in the leachate, which is formed through water radiolysis, was also evaluated in comparison with other ligands, ClO_4^- and HSO_4^-/SO_4^{2-}. In presence of H_2O_2, the normalized dissolution rate is increased by 2 orders of magnitude, in comparison with the values obtained in the non-complexing perchloric solution. It is even larger than the dissolution rate in the most-complexing ligand HSO_4^-/SO_4^{2-}. This enhancement confirms the strong affinity of the hydrogen peroxide with respect to thorium and demonstrates that the normalized dissolution rate of ThO_2 is dependent on the nature of the leachate, as far as saturation is not reached in the solution. It is all the more important since groundwater from the French repository contains large amount of complexing anions, as well as radiolytic products.

The dissolution curves of $Th_{0.87}Pu_{0.13}O_2$ solid solution were also obtained in nitric solutions at various pH. The parameters describing the dissolution kinetic law were compared to that of ThO_2. The partial order, as well as the normalized dissolution constant, is larger for $Th_{0.87}Pu_{0.13}O_2$ than that of ThO_2. At pH 1, the dissolution curve of $Th_{0.87}Pu_{0.13}O_2$ solid solution is even larger than that of ThO_2 in presence of H_2O_2. The larger kinetic dissolution parameters of the solid solution could be partly attributed to the formation of small amount of hydrogen peroxide resulting from the radiolysis effect.

In contrast to ThO_2, for which precipitation of hydrous thorium oxide occurs at pH 3, no precipitation is observed from $Th_{0.87}Pu_{0.13}O_2$ solid solution at pH 3. Taking into account the complexity of the chemical behavior of plutonium, several assumptions can explain this behavior. The disproportionation of Pu(IV) and Pu(V) in Pu(III) and Pu(VI) for $C_{HNO_3} < 0.5$ M and the formation of hydrogen peroxide because of radiolysis of the aqueous phase through α-radioactivity of Pu isotopes may be the most important parameter influencing the dissolution behavior observed until pH 3. Indeed, further experiments are needed to confirm these assumptions: measurement of Th release from the solid solution, comparison of the dissolution behavior of both oxide and solid solution in presence of H_2O_2, and influence of the concentration of Pu in $Th_{1-x}Pu_xO_2$ solid solution, on the dissolution behavior. These studies are under investigation.

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