Solubility of thorium phosphate-diphosphate†

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The solubility of the pure thorium phosphate-diphosphate, $Th_4(PO_4)_4P_2O_7$, has been measured in 0.1 M $NaClO_4$ solutions by PERALS® spectrometry (photon electron rejecting alpha liquid scintillation), ICP-MS (inductively coupled plasma-mass spectrometry) and PIXE (particle induced X-ray emission). The results obtained by the three methods are in good agreement and show that the total concentration of thorium in solution is mainly controlled by the precipitation of two compounds: $Th(HPO_4)_2$ in acidic media ($pH \leqslant 4.5$) and $Th(OH)_4$ in basic and near-neutral media.

Natural phosphate compounds (apatites, monazites, ...) are known to be stable compounds from both chemical and geological points of view.[1–3] This stability is essentially explained by their low solubility. Futhermore, we know that the mobility of thorium in soil is mainly due to organic matter; otherwise thorium is considered as a non-mobile element.[4]

In a recent study, it has been shown that a thorium phosphate, incorrectly called "orthophosphate", although its structure is not completely defined, is very insoluble in near-neutral and basic media.[5] For this reason and because of the strong capacity of phosphates to retain heavy elements, thorium phosphate could be interesting as a confining matrix for retaining radionuclides in a nuclear waste repository.

More recently, a new thorium phosphate compound has been synthesized and characterized as a single pure phase: thorium phosphate-diphosphate, $Th_4(PO_4)_4P_2O_7$. The present work deals with its solubility in aqueous phase for a relatively short time scale. A comparison with the solubility data previously obtained under similar conditions on "orthophosphate", along with that we have measured for the hydroxide $Th(OH)_4$, will be useful to interpret the results.

Experimental

Synthesis and characterization of the solids

The thorium phosphate-diphosphate $Th_4(PO_4)_4P_2O_7$. Thorium phosphate-diphosphate has been synthesized by dry or wet chemical processes.[6] The first process consists of a reaction between thorium oxide and ammonium dihydrogen phosphate with a Th : PO_4 mole ratio equal to 2 : 3. In the latter process, a concentrated thorium chloride (or nitrate) solution ($C \approx 1$ M) is mixed with 15 M H_3PO_4 solution. This mixture is then heated on a sand bath at 80–150 °C to obtain a dry residue. After grinding, this residue is heated in air at 400 °C for 2 h and then up to 900 °C (nitrate) or 1250 °C (chloride) for 12 h.

At this stage, the synthesized product is very well crystallized. A complete characterization of this compound has been performed by electron probe microanalysis (EPMA) and infrared spectroscopy. The EPMA analysis has shown that it is a pure phase, with a Th : PO_4 mole ratio equal to 0.671, while the presence of two types of phosphate groups (phosphate PO_4 and diphosphate P_2O_7) has been evidenced by IR spectroscopy. The crystal structure determination has been obtained from X-ray powder diffraction and on a single crystal. It led to the chemical formula $Th_4(PO_4)_4P_2O_7$, which is in very good agreement with the results obtained by other analytical methods.[6]

It has been verified that for a Th : PO_4 ratio of 3/4, the final product obtained after heat treatment at 1250 °C invariably leads to $Th_4(PO_4)_4P_2O_7$, the excess of phosphate being thermally decomposed into P_2O_5, which is volatilized. When the heat treatment is not complete, we can observe a two-phase mixture of $Th_4(PO_4)_4P_2O_7$ and ThO_2.

The thorium hydroxide $Th(OH)_4$. Deionized water (500 mL) containing 50 g of $Th(NO_3)_4 \cdot 5\,H_2O$ (Fluka) was added to 200 mL of a concentrated ammonia solution. The precipitate was washed, filtered, dried under vacuum at 25 °C and stored at ~4 °C. The X-ray pattern has shown a low degree of crystallinity for the powder so-obtained and the chemical formula has been confirmed by thermo gravimetric analysis (TGA).

Solubility tests

One to two hundred milligrams of fine $Th_4(PO_4)_4P_2O_7$ powder (average grain size near 9 μm) were shaken in a turbula®, at room temperature, with 5–10 mL of sodium perchlorate solution. The pH value of the equilibrated solution was in the range 1–6 in the case of PERALS® experiments and in the range 1–11 for ICP-MS ones, while the ionic strength was adjusted to 0.1 M with the $NaClO_4$ solution. Special care was brought to the preparation of the basic solutions, which were always fresh and kept under an argon atmosphere, in order to exclude the presence of carbonates in these solutions.

After 24 h (ICP-MS, PIXE) or 2–3 days (PERALS®) contact time, the two phases were separated first by centrifugation, then by ultracentrifugation at 13 000 rpm (PERALS®) or 50 000 rpm (ICP-MS, PIXE) for 1 h in order to eliminate as completely as possible the colloids unavoidably present in the supernatant. In a previous paper, it has been shown that the

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† Supplementary material available: Table of experimental "solubility" data for $Th_4(PO_4)_4P_2O_7$ obtained at various pH values by different methods. For direct electronic access see http://www.rsc.org/suppdata/nj/1999/645, otherwise available from BLDSC (No. SUP 57538, 2pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/njc).

Table 1 Detection limits of thorium for the three methods used in the present work

Method	C_{Th}/mol L^{-1}
PIXE[7]	4×10^{-6}
PERALS® [8]	$10^{-9\,a} - 3 \times 10^{-10\,b}$
ICP-MS[9]	2×10^{-13}

[a] Obtained with samples of 250 mL after 3 days of counting time.
[b] Same sample after 10 days of counting time.

presence of these nanoparticles in the solution can notably affect the solubility results, particularly when the solid compound is not very soluble.[5]

Determination of thorium concentration in leachates

Three methods have been used in the present work in order to test the validity of the solubility results. Their limits of detection are given in Table 1.

PERALS® spectrometry. Thirteen years ago, a new analytical method named PERALS® (acronyme for photon electron rejecting alpha liquid scintillation) using alpha liquid scintillation appeared.[10,11] This system, which is based on a total rejection of the beta emission (99.95%) and an efficiency of alpha collection near 100%, allows actinide concentrations at the trace level to be measured, when a good energy resolution is not needed (see Table 1). Thus, we have applied this technique for the study of the solubility of thorium phosphate-diphosphate. We first studied the optimal extraction of thorium in several media.

We present in Fig. 1 the variation of the recovery percentage as a function of pH by ALPHAEX$_\alpha$™ (which contains dialkyl phosphoric acid) and by THOREX$_\alpha$™ (which contains the primary alkyl amine nonyldecylamine) in nitric and sulfuric acid media. As observed from Fig. 1, a total extraction of thorium is obtained either by ALPHAEX$_\alpha$™ in nitric acid (0.5–2 M HNO_3), which leads to a yield of thorium extraction equal to 100 ± 4%, or by THOREX$_\alpha$™ in sulfuric acid (from pH = 5 to 3 M H_2SO_4), which gives a yield of thorium extraction of about 98 ± 4%. Due to the higher resolution obtained in ALPHAEX$_\alpha$™ medium, this extractant has been preferred for the determination of low concentrations of thorium in solution ($C < 10^{-6}$ M). For higher concentrations, both extractants are available.

A PERALS® spectrum of thorium ^{232}Th is presented in Fig. 2. The peaks of all its daughter products, that is ^{228}Th (5.423 MeV), ^{224}Ra (5.686 MeV), ^{220}Rn (6.288 MeV), ^{216}Po (6.778 MeV) and ^{212}Bi (6.051 MeV), are also observed but the small differences in the energies of alpha particles in comparison with the PERALS® resolution do not allow us to cleanly separate these peaks by deconvolution.

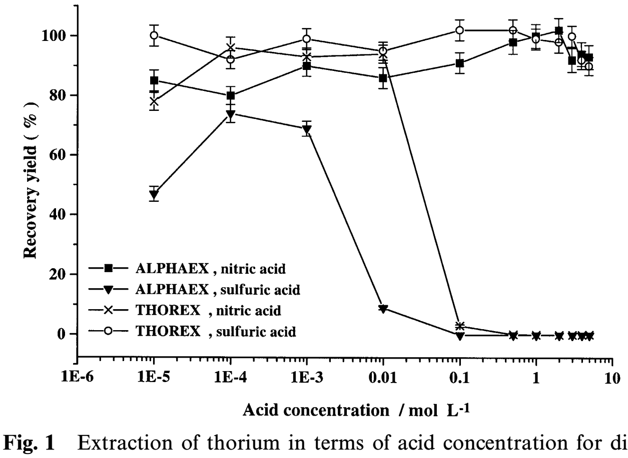

Fig. 1 Extraction of thorium in terms of acid concentration for different extractants and acid media.

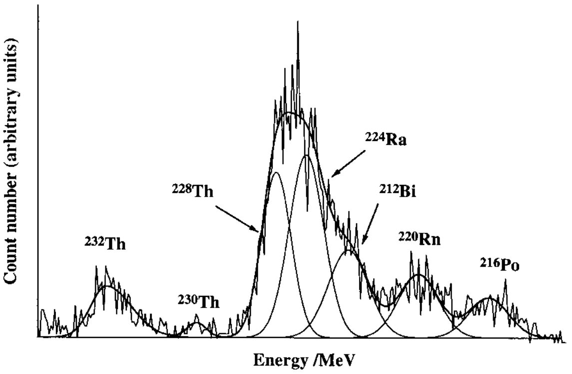

Fig. 2 PERALS® spectrum of ^{232}Th and its daughter products ($C = 1.3 \times 10^{-7}$ M, $t_c = 280\,000$ s).

ICP-MS measurements. Before their analysis, the solution samples have been acidified with HNO_3 (0.1 M) and then diluted in such a way that the salt content does not exceed 0.1 g L^{-1}, while the thorium concentration is less than 200 ppb. Two internal standards, terbium and bismuth (SPEX ICPMS internal standard, 100 ppm), have been added (10 ppb) to these samples.

A calibration curve has been first established, in the range of 10 ppb–10 ppt, using a standard thorium solution (SPEX plasma standard, 1000 ppm). Each measurement was framed by two blanks: the first one was used for correcting the total amount of thorium detected in the sample, the second one tested the sample-induced contamination.

All reagents were of high grade quality and all glass vessels were preconditioned by leaching in HNO_3 and water. The same deionized water was used for rinsing and preparing samples and standards.

The measurements were carried out in the Laboratoire Pierre Sue (CEA-CNRS, Saclay) on a VG elemental ICP-MS spectrometer, Plasmaquad Turbo 2+.

PIXE measurements. This technique has been applied to the solutions relatively concentrated in thorium (low pH values). Up to 100 ppm of rhenium (SPEX ICP internal standard, 1000 ppm) were added to these solutions prior to their analysis. This analysis was performed at the AGLAE tandem accelerator (Laboratoire de Recherche des Musées de France, LRMF, du Louvre), using the external proton beam at 3 MeV. The GUPIX code was used to calculate the C_{Th} data.[12]

Results and discussion

The solubility measurements are performed from the batch experiments described in the experimental by determining the total concentration of thorium, C_{Th}, in the leachates. As expected, this concentration is very sensitive to the pH of the solution, as shown in Fig. 3. From this figure, it can be seen that the values obtained by the three methods under consideration, PERALS, ICP-MS and PIXE (all the data with their accuracy are available as supplementary material) are in relatively good agreement. Moreover, the nature of the thorium salt used for the synthesis of $Th_4(PO_4)_4P_2O_7$, as well as the wet or dry chemistry routes, appear without effect on the solubility results. The discrepancies between the points relative to each synthesis reflect, in fact, the difficulties in reproducing both the same sample and the same analysis.

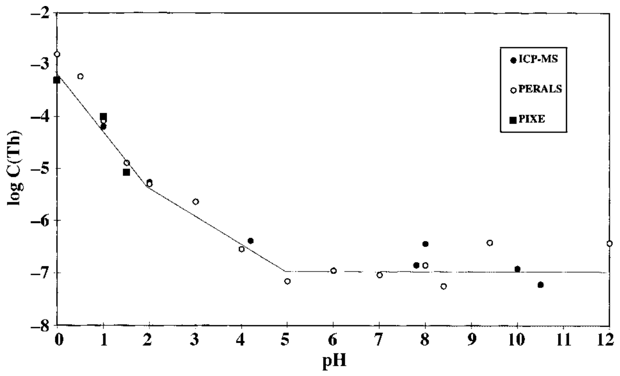

Fig. 3 Logarithmic variation of the total concentration of thorium in solution equilibrated with $Th_4(PO_4)_4P_2O_7$ *vs.* pH.

We can also observe in Fig. 3 that the $\log(C_{Th})$ *vs.* pH curve can be divided into three linear segments (characteristics given in Table 2):

(*i*) the first one corresponds to a sharp decrease (slope equal to -1.10) in acidic media ($pH \leqslant 1.5$);

(*ii*) the second one covers the range between pH 1.5 and 5 with a slope around 0.6;

(*iii*) the third one ($pH \geqslant 5$) is a plateau.

No similar variation was previously observed with the so-called "$Th_3(PO_4)_4$" labelled with ^{227}Th and investigated using the same leaching procedure.[5] In the present case, the solubility is higher and the pH effect less strong. The mechanisms involved are probably different and cannot be explained on the basis of identical hypotheses.

In order to interpret the solubility curve of Fig. 3, it is first necessary to know the form of the different dissolved species. Owing to the low concentrations of thorium and phosphate in solution, even at pH 0, only monomeric species are considered in the present work.[13] The acidity constants, K°_{a1} and K°_{a2}, of H_3PO_4 are given with a good accuracy,[14a] as well as the coefficients ε of ($H_iPO_4{}^{j-}$, Na^+) or (H^+, $ClO_4{}^-$), needed to adjust them at the correct (0.1 M) ionic strength by the SIT method.[14b] But the speciation of thorium in phosphate-containing solutions (assumed carbonate free) is based on very few thermodynamic data, which still need to be confirmed. These data, as well as the generally accepted hydrolysis constants, are summarized in Table 3.

Another difficulty comes from the fact that $Th_4(PO_4)_4P_2O_7$ cannot be formed by precipitation under oversaturation conditions. Consequently, there is no real equilibrium (*stricto sensu*) between the solid and the aqueous thorium and phosphate species. Moreover, diphosphate ions are not stable in aqueous media.[14c] They are transformed into $H_2PO_4{}^-$ or $HPO_4{}^{2-}$ ions, depending on pH and temperature. We are thus unable to interpret the solubility results in terms of a real solubility product.

Table 2 Characteristics of the apparent linear segments of the solubility curve given in Fig. 3

pH range	Slope	Linear regression coefficient
0–1.5	−1.10	0.901 (8 points)
1.5–5	−0.616	0.988 (7 points)
5–12	0	—

Table 3 Thermodynamic constants[a] used for the speciation of thorium

Ligand L	log β_1	log β_2	log β_3	log β_4	log K_S
OH^-	10.8[15,16]	21.1[15]	30.3[15]	40.1[15]	−44.7[17]
$HPO_4{}^{2-}$	15.7[18]	30.2[18]	38.68[18]		−21[19]
$H_2PO_4{}^-$	4.52[20]	8.88[20]			
H_3PO_4	1.91[20]				

[a] β_i corresponds to the equilibrium: $Th^{4+} + iL^{j-} \rightleftharpoons Th(L)^{(4-ij)+}$

Despite these thermodynamic considerations, a kinetic approach can be attempted. However, due to the low solubility observed, the time necessary to obtain significant results is very long, on the order of one year or longer. Under these conditions, we decided in a first phase to restrict our investigation to short contact times (less than a week) between the solid and the aqueous phase. We thus show that an "apparent equilibrium" is reached after 1 day of contact between the solid and liquid phases ($C_{Th} \approx$ constant over several days). For this reason, we first attempted to explain the experimental results by writing the following general reaction:

$$Th_4(PO_4)_4P_2O_7 + (1 + 4m)H_2O \rightarrow$$
$$4Th(OH)_m + 6H_iPO_4 + (2 + 4m - 6i)H \quad (1)$$

where the charges are omitted for simplification. Eqn. (1) is, in fact, the sum of 3 equilibria involving:

(*i*) the solubility of $Th_4(PO_4)_4P_2O_7$

$$Th_4(PO_4)_4P_2O_7 \rightleftharpoons 4Th^{4+} + 4PO_4{}^{3-} + P_2O_7{}^{4-} \quad (2)$$

(*ii*) the thorium hydrolysis

$$Th^{4+} + mH_2O \rightleftharpoons ThOH_m{}^{(4-m)+} + mOH^- \quad (3)$$

(*iii*) the decomposition of the P_2O_7 groups

$$P_2O_7{}^{4-} + H_2O \rightleftharpoons 2PO_4{}^{3-} + 2H^+ \quad (4)$$

If we assume the solubility as congruent, the total concentration of phosphate is related to C_{Th} by a factor of 3/2, and we can write for each pH value $[Th(OH)_m] = 2/3[H_iPO_4] = C_{Th}$, where i and m are not necessarily integers.

Taking into account eqn. (1), the above equality leads to:

$$\log C_{Th} = -(0.6i - 0.4m - 0.2)pH + Cte(m, i) \quad (5)$$

Cte(m, i) depends on the thermodynamic constant of eqn. (1) and is consequently constant for a given set of m and i values. If we neglect the complexation of the thorium aqueous species by the dissolved phosphate groups (because of a too low concentration of both thorium and phosphate), Th^{4+} and H_3PO_4 are the prevailing species to be considered at pH less than 1.5 and the parameters i and m are respectively equal to 3 and 0. A slope of -1.6 is then calculated for the $\log C_{Th}$ *vs.* pH variation, which is not in agreement with the value found experimentally.

In fact, the speciation diagram based on the complexation constants given in Table 3 shows that $Th(HPO_4)_2$ should dominate in acidic media (more than 80% for $pH \leqslant 4$ and more than 90% at $pH \leqslant 1.5$). If we take into account this complex formation, the dissolution process can be described as follows:

$$Th_4(PO_4)P_2O_7 + (m + 1)H_2O \rightarrow$$
$$3Th(HPO_4)_2 + Th(OH)_m + (m - 4)H \quad (6)$$

since the phosphate concentration is not sufficient to lead to the complete formation of $Th(HPO_4)_2$ (there are only 6 phosphate groups and not the 8 required for 4 thorium species). In this case, for each mole of thorium phosphate-diphosphate dissolved, $(m - 4)/4$ moles of protons are liberated in the solution and eqn. (5) can then be replaced by:

$$\log C_{Th} = -1 - m/4pH + Cte(m, i) \quad (7)$$

which leads to a variation of $\log C_{Th}$ *vs.* pH independent of i. In very acidic media, m is equal to 0 and the calculated slope of the $\log C_{Th}$ *vs.* pH curve is, this time, close to the experimental value: -1 compared to -1.10. Moreover, at

$pH \geqslant 4.5$, thorium ion can be considered as completely hydrolyzed ($m = 4$) in accordance with the plateau observed in Fig. 3 (slope $= 1 - m/4 = 0$). Taking into account the distribution of the (hydrolyzed or not) thorium species *vs.* pH, an average value of m can be calculated as a function of pH. Consequently, the log C_{Th} *vs.* pH curve can be simulated, using eqn. (7). This curve, which is plotted in Fig. 4 (calc. 1), is in very good agreement with the experimental points over the entire pH range. It can be compared, on the same figure, to the curve calculated on the basis of eqn. (5) (calc. 2).

However, the prevailing thorium species mentioned above, $Th(HPO_4)_2$ and $Th(OH)_4$, are not very soluble (the corresponding K_s are given in Table 3), and it is difficult not to consider the possibility of their precipitation close to the surface of the thorium phosphate-diphosphate, where the concentration of the thorium and phosphate species are the highest in the solution. For example, the solubility product of $Th(HPO_4)_2$ is such that:

$$K_S = [Th^{4+}][HPO_4{}^{2-}]^2 = S(2S)^2 = 4S^3$$

or

$$\log K_S = (\log 4 + 3 \log S) = -21$$

S being the dissolved thorium ion concentration ($[Th^{4+}]$ assimilated to C_{Th}). We deduce for S a value equal to 6.3×10^{-8} M, which is less than the concentration of thorium equilibrated with $Th_4(PO_4)_4P_2O_7$ ($C_{Th} > 2 \times 10^{-7}$ M) in acidic media ($pH < 4$). The solubility of $Th_4(PO_4)_4P_2O_7$ could thus be controlled, at least until a pH value of 4, by $Th(HPO_4)_2$ and we can write in this case:

$$Th(HPO_4)_2 + (m-4)H_2O \rightleftharpoons Th(OH)_m + 2H_iPO_4 + (m - 2i + 2)H \quad (8)$$

which replaces eqn. (1) and can be considered as a real equilibrium, owing to the oversaturation process involved. It leads to:

$$\log C_{Th} = -[(2i - m - 2)/3]pH + Cte(m, i) \quad (9)$$

if we assume again a proportionality relationship, independent of pH, between C_{Th} or $[Th(OH)_m]$ and $[H_iPO_4]$. For $i = 3$ and $m = 0$ ($pH \leqslant 1.5$), the slope of the log C_{Th} *vs.* pH curve is equal to 4/3, which is slightly higher than the experimental value. This slope value decreases with pH (i decreases and m increases correspondingly) up to $pH \approx 4.5$ and its calculation leads to the third simulated curve given in Fig. 4 (calc. 3), which fits very well the experimental data in its acidic part.

For pH values higher than 4.5, the formation of another insoluble compound is to be considered: the thorium hydroxide, $Th(OH)_4$. Owing to the formation constants and solubility products given in Table 3, $Th(OH)_4$ should prevail and consequently precipitate instead of $Th(HPO_4)_2$ in neutral and basic media. The results obtained in the present work show that this precipitation occurs from a pH value around 5, when the "plateau" is reached. As a matter of fact, the total concentration of thorium in solution is such that:

$$C_{Th} = [Th(OH)_4] = \beta_4[Th^{4+}][OH^-]^4 = \beta_4 K_S = Cte \quad (10)$$

where β_4 and K_S are the stability constant and the solubility product of $Th(OH)_4$, respectively.

From the β_4 and K_S values given in Table 3, a value of -4.6 is deduced for log C_{Th}, which is too high compared to the value around -7 observed experimentally. However, very widely different K_S values concerning the thorium hydroxide have been published in the literature (for example, $\log K_S = -54.2$).[21] Among other parameters, the K_S value could be influenced by the aging of the compound. For this reason, a fresh $Th(OH)_4$ precipitate was prepared and its solubility measured under conditions (supporting electrolyte, ionic strength, time of agitation, phase separation) similar to those used for $Th_4(PO_4)_4P_2O_7$. The obtained C_{Th} value is as expected, around 7×10^{-8} M. We also noticed that this value is much higher, around 10^{-3} M, if the solution is not ultracentrifuged prior to the thorium concentration measurement. Colloids are thus present in the solution in contact with the hydroxide. This could explain the discrepancy of the published K_S data.

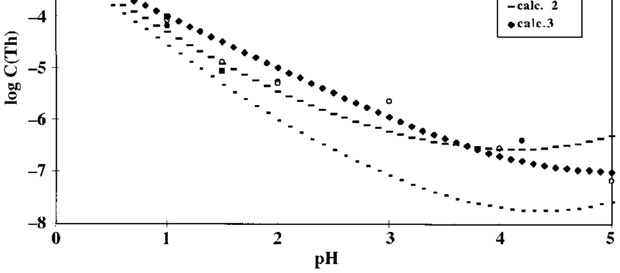

Fig. 4 Fitting curves of the solubility results for $pH \leqslant 5$. Each curve corresponds to a different hypothesis discussed in the text.

The experimental solubility curve of $Th_4(PO_4)_4P_2O_7$ can thus be explained by a combination of eqn. (9) and (10), each of them being applicable within a specific pH range, with a transition around pH 4.5. But it can also be correctly explained on the basis of eqn. (7). The thorium species involved in both interpretations are the same. The only difference is in their possible precipitation close to the surface of the $Th_4(PO_4)_4P_2O_7$ compound. This point is difficult to check. The best way would be to determine the free phosphate concentration in the solutions, which is expected to be close to zero in the former case and to vary with C_{Th} in the latter case. But the concentrations involved are too low for the usual analytical methods, and only phosphate ions labelled with ^{32}P could perhaps give some interesting results.

Nevertheless, a solubility equilibrium is justified only in the case of the precipitation in question. It seems also to be confirmed by microscopic observation.

It should also be mentioned that we tried to fit the experimental solubility data by assuming the formation of thorium phosphate compounds other than $Th(HPO_4)_2$ (*e.g.*, $Th_4(PO_4)_4(HPO_4)_2 \cdot nH_2O$), but without success.

The solubility results reported in the present work have been obtained for relatively short equilibrium times. In order to check their validity for longer time scales, leaching experiments on $Th_4(PO_4)_4P_2O_7$ in concentrated nitric acid solutions are under progress.

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