



KINETIC STUDY OF THE THORIUM PHOSPHATE - DIPHOSPHATE DISSOLUTION

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ABSTRACT

The thorium phosphate-diphosphate $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ (TPD) structure allows the replacement of large amounts of thorium by tetravalent actinides leading to the formation of solid solutions. This compound was obtained in powdered or sintered form after pressing at room temperature at 300-800 MPa then heating at 1250°C for 10-30 hours. The resistance of this material to aqueous corrosion was determined by varying several parameters such as surface, leaching flow, acidity or temperature. It was thus possible to independently determine the influence of each parameter on the leaching rate provided that the saturation of the solution was not obtained. In acidic media, the partial order related to $[\text{H}_3\text{O}^+]$ was found to be in the 0.31-0.35 range while, in basic media, the partial order related to $[\text{OH}^-]$ was almost the same (0.45). The activation energy (42 kJ/mol) was determined between 4°C and 120°C. Moreover, the addition of phosphate in the leachate slightly increased the TPD dissolution rate. When the saturation of the solution is reached, a gelatinous precipitate controls the thorium and phosphate concentrations. The complete characterization of this solid led to the proposed general formula $\text{Th}_2(\text{PO}_4)_2(\text{HPO}_4) \cdot n \text{H}_2\text{O}$ which conventional solubility product (at $I=0\text{M}$) is very low : $K_{S,0}^{\circ*} = 10^{-66.6 \pm 1.2}$ even in very acidic media.

INTRODUCTION

We already mentioned that the thorium phosphate-diphosphate $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ (namely TPD) could be used for the immobilization of actinides coming from an advanced reprocessing or for the final disposal of the excess plutonium from dismantled nuclear weapons (1,2). This compound can be synthesized whatever the chemical way of synthesis (using wet and dry chemistry methods) after heating between 1100 and 1350°C. Its characterization and the replacement of Th^{4+} by large amounts of U^{4+} , Np^{4+} or Pu^{4+} in the structure leading to the formation of solid solutions $\text{Th}_{4-x}\text{M}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$ were extensively reported (1,3,4).

Since water is the main vector for the nuclides migration for deep underground disposal storage, we evaluated the TPD resistance to aqueous corrosion by determining the influence of several parameters on the TPD leaching rate. Owing to the very low dissolution rate of this solid, a systematic study was undertaken in very corrosive conditions varying surface, temperature, phosphate concentration and leaching flow.

SYNTHESIS AND CHARACTERIZATION

The TPD samples were prepared from a mixture of concentrated thorium nitrate (1.5 –2 M) and phosphoric acid (5M) solutions in the mole ratio $r = \text{Th}/\text{PO}_4 = 2/3$. The final solid was obtained after heating at 1100°C-1350°C for 10-30 hours in air with a heating rate equal to 2-5°C/min. It is well-crystallized, homogeneous and single phase (the mole ratio Th/PO_4 and the elementary wt. % were verified by electron probe microanalysis (EPMA) for all the powdered and sintered samples). After grinding, the average grain size was equal to about 10 μm and the specific area reached 0.2 - 0.4 m^2/g .

Sintered samples of TPD were obtained from the residue prepared by evaporation of the mixture then heating at 400°C during 2 hours. This residue was pressed via a uniaxial pressing at 100-800 MPa at room temperature then heated at 400°C for 2 hours and up to 1250°C for 10-30 hours with a heating rate equal to 2°C/min. The density of the samples was determined in terms of the initial pressure used (2) using helium, xylène and water pycnometries. From 200 to 800 MPa, it varied from 92 to 99 % of the calculated value ($d_{\text{calc}} = 5.19$).

DISSOLUTION STUDY

Several studies dealt with the mineral dissolution especially in the case of weathering conditions. For several authors, all the parameters are macroscopic (5,6). The authors agreed that for most of the minerals, the dissolution (or leaching) rate is controlled by surface reactions at the solid-solution interface with the decomposition of an activated complex. These heterogeneous reactions involve the adsorption of fluid species onto the surface, the reaction of these adsorbed species with the atoms present at the surface of the solid then the desorption of the product species formed at the surface.

EXPERIMENTAL SECTION

Several leaching tests were performed for TPD (pure or doped with ^{241}Am or ^{244}Cm). Samples of 50 mg – 1.4 g of powdered (or sintered) TPD were put into 5-10 mL of solution (distilled water, acidic or basic solutions). The separation of both phases was obtained by centrifugation at 2000 – 13000 rpm then a part of the leachate (100 μL – 3mL) was taken off at regular intervals and renewed with fresh solution. The activity of thorium (or actinide) released in the solution was measured by α -liquid scintillation (PERALSTM spectrometry). PTFE (Polytetrafluoroethylene) containers were chosen for the leaching experiments at 90°C while for lower temperatures they were in high-density polyethylene. In these conditions, less than 1% of the total dissolved elements is adsorbed onto the surface of the containers.

DEFINITION OF THE NORMALIZED LEACHING AND NORMALIZED LEACHING RATE

The leachability of the element i from a mineral can be described by its normalized leaching, $N_L(i)$ (g/m^2) defined as follows:

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

where m_i corresponds to the total amount of i measured in the solution (g); f_i is the mass ratio in the solid and S the surface area of the solid.

For a congruent dissolution, the leaching rate $R_L(i)$ ($\text{g}/(\text{m}^2.\text{d})$) can be written:

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

It is usually expressed in $\text{g}/(\text{m}^2.\text{d})$ and noted R_H in acidic media and R_{OH} in basic media. It corresponds to the slope obtained when drawing the normalized leaching as a function of time as mentioned by several authors for washed minerals (7). For unwashed minerals, a higher release was observed during the first days of dissolution because of the surface heterogeneity (minor phases,...) (7). This problem was avoided in corrosive media.

EXPRESSION OF THE TPD DISSOLUTION RATE

We calculated the leaching rates from the quantity of dissolved thorium, considering that the dissolution of the solid is congruent. It was verified in 5M HNO_3 since the mole ratio Th/PO_4 remains equal to 2/3 in the leachate as a function of the leaching time (Table I).

Table I. Evolution of the thorium and phosphate concentrations measured in the leachate (5M HNO₃, $\theta = 25^\circ\text{C}$)

Leaching time (hours)	C _{Th} (M)	C _{PO₄} (M)	Mole ratio Th/PO ₄
24	$(3.7 \pm 0.2) 10^{-4}$	$(5.4 \pm 0.3) 10^{-4}$	0.68 ± 0.04
55	$(5.3 \pm 0.2) 10^{-4}$	$(7.6 \pm 0.3) 10^{-4}$	0.70 ± 0.04
128	$(5.8 \pm 0.3) 10^{-4}$	$(8.7 \pm 0.3) 10^{-4}$	0.66 ± 0.03
175	$(6.0 \pm 0.3) 10^{-4}$	$(8.8 \pm 0.4) 10^{-4}$	0.68 ± 0.04

INFLUENCE OF THE SOLID SURFACE AREA

The apparent dissolution rate of a mineral, r (g/d) can be expressed as a function of the reactive surface area S as follows (5):

$$r = \frac{dm}{dt} = R_L \times S \quad (3)$$

This study was performed on powdered TPD in 5M HNO₃ at 25°C considering several conditions (50 mg -1.4 g of solid with various surface areas). We clearly observed that dm/dt increases linearly with the reactive surface area S as shown from Table II and Eq. 4:

$$\frac{dm}{dt} = 1.84(8) \times 10^{-2} S + 3(1) \times 10^{-4} \quad (4)$$

It is coherent with Eq. 3 since the slope corresponds to the R_H value measured in 5M HNO₃ at 25°C (Table IV) and the intercept is near to zero. So, the species measured in solution are under saturation conditions (absence of secondary phases).

Table II. r dependence on the surface for TPD (5M HNO₃, $\theta = 25^\circ\text{C}$)

Surface (m ²)	S/V (cm ⁻¹)	dm/dt (g/d)
0.012	24	$(6.9 \pm 0.3) \times 10^{-4}$
0.025	50	$(1.11 \pm 0.07) \times 10^{-3}$
0.049	98	$(1.51 \pm 0.06) \times 10^{-3}$
0.146	290	$(2.9 \pm 0.1) \times 10^{-3}$
0.196	390	$(3.7 \pm 0.3) \times 10^{-3}$
0.247	490	$(4.9 \pm 0.2) \times 10^{-3}$
0.346	690	$(6.9 \pm 0.3) \times 10^{-3}$

Influence of the leaching flow

The influence of the leaching flow on the normalized leaching rate was also studied to confirm that no secondary phases are formed in these conditions. The leaching tests were performed with powdered TPD in 5M HNO₃ at 25°C for leaching flows varying from 0.02 to 20 mL/(m².d). The experimental data (Table III) showed that R_H remains almost constant during the first 50 days of leaching time in this medium even for the higher leaching flows studied.

Table III. R_H dependence on the leaching flow for TPD (5M HNO₃, $\theta = 25^\circ\text{C}$)

Leaching flow (mL/(m ² .d))	R_H (g/(m ² .d))
0.02	$(2.4 \pm 0.3) \times 10^{-2}$
0.4	$(2.3 \pm 0.2) \times 10^{-2}$
0.99	$(2.8 \pm 0.1) \times 10^{-2}$
2.0	$(2.4 \pm 0.3) \times 10^{-2}$
7.0	$(3.5 \pm 0.3) \times 10^{-2}$
20	$(3.7 \pm 0.2) \times 10^{-2}$

Influence of the temperature

The normalized leaching rate usually depends on the temperature considering the Arrhenius law:

$$R_L = k \times e^{\left(-\frac{E_{\text{app}}}{RT}\right)} \quad (5)$$

where k is the normalized leaching rate constant independent on the temperature (g/(m².d)) and E_{app} is the activation energy of the mineral dissolution (kJ/mol) (6). This study was performed on powdered TPD between 4°C and 120°C in 5M HNO₃ keeping constant all the other parameters. The E_{app} value was determined considering the slope of the straight line obtained by studying the variation of $\ln(R_H)$ as a function of the reciprocal temperature. The slope obtained from the linear regression was found to be (-5045 ± 360) K which leads to $E_{\text{app}} = (42 \pm 3)$ kJ/mol.

Table IV. R_H dependence on the temperature for TPD (5M HNO₃, $\theta = 25^\circ\text{C}$)

Temperature (K)	R_H (g/(m ² .d))
277	$(4.5 \pm 0.1) \times 10^{-3}$
298	$(1.93 \pm 0.08) \times 10^{-2}$
323	$(5.3 \pm 0.1) \times 10^{-2}$
343	$(2.5 \pm 0.3) \times 10^{-1}$
363	$(4.0 \pm 0.3) \times 10^{-1}$
393	$(7.6 \pm 0.4) \times 10^{-1}$

Leaching tests of solid solutions $\text{Th}_{4-x}\text{Pu}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$ were also performed in distilled water between 25°C and 90°C using high leaching flow in order to avoid any formation of neoformed phases. They led to $E_{\text{app}} = (41 \pm 1)$ kJ/mol which is coherent with the previous value and indicates that E_{app} seems to be independent on the leachate acidity and on the presence of tetravalent plutonium in the structure. Both E_{app} values are in good agreement with those reported for others minerals (40-80 kJ/mol) (6).

Influence of $[\text{H}_3\text{O}^+]$

Many authors already investigated the influence of pH on the normalized leaching rate. They showed that the dissolution rates of most of the minerals increase with the proton activity if the pH is lower than 7 as follows (8):

$$R_H = k' \times (a_{\text{H}_3\text{O}^+})^n \times e^{\left(-\frac{E_{\text{app}}}{RT}\right)} = k'_T \times (a_{\text{H}_3\text{O}^+})^n \quad (6)$$

where k' is the normalized leaching rate constant for proton-promoted dissolution ($\text{g}/(\text{m}^2 \cdot \text{d})$); k'_T is the apparent normalized leaching rate constant (dependent on temperature); $a_{\text{H}_3\text{O}^+}$ is the proton activity and n , the partial order related to the proton activity.

For several minerals, the n value was found between 0 and 1 (6). This parameter depends on the dissolution mechanism but does not correspond to the number of protons involved in the dissolution reaction. Some authors tried to interpret this value in terms of surface species concentrations (they found an integer partial order related to the protons adsorbed on the solid surface) (9). The influence of pH on R_H was explained by the decomposition of an activated complex which surface concentration depends on the dissolved proton concentration.

Owing to the precipitation of thorium as a thorium phosphate hydrogenphosphate for $\text{pH} \geq 1$ as reported in the following sections, we determined the influence of pH on the TPD leaching rate for samples doped with trivalent actinides (^{241}Am or ^{244}Cm) between $\text{pH}=1$ and 4 (2). The ionic strength was fixed to $I = 0.1\text{M}$ by addition of NaClO_4 or NaNO_3 . The R_H values were measured for several pH (Table V) and allowed the determination of n and $k'_{298\text{K}}$.

The R_H value strongly decreases in 10^{-4}M HClO_4 (for TPD doped with ^{244}Cm) and in 10^{-4}M HNO_3 (for TPD doped with ^{241}Am) due to the precipitation of curium (or americium) phosphate hydrate as already reported (2). For this reason, we determined the n value between $\text{pH}=1$ and $\text{pH}=3$. Moreover, the TPD dissolution slightly increases with the proton activity. Indeed, the n values are lower than that reported for several minerals in the literature (6,10) which indicates that the TPD resistance to aqueous corrosion is quite good even in acidic media.

Table V. Normalized dissolution rate of TPD in acidic solutions ($\theta = 25^\circ\text{C}$)

$[\text{H}_3\text{O}^+]$	R_H ($\text{g}/(\text{m}^2 \cdot \text{d})$) ^a	R_H ($\text{g}/(\text{m}^2 \cdot \text{d})$) ^b
10^{-1}M	$(1.2 \pm 0.1) \times 10^{-5}$	$(5.9 \pm 0.1) \times 10^{-6}$
10^{-2}M	$(6.0 \pm 0.2) \times 10^{-6}$	$(1.84 \pm 0.04) \times 10^{-6}$
10^{-3}M	$(2.9 \pm 0.2) \times 10^{-6}$	$(1.18 \pm 0.04) \times 10^{-6}$
10^{-4}M	$(4.4 \pm 0.6) \times 10^{-9}$	$(6.5 \pm 0.6) \times 10^{-8}$
n	0.31 ± 0.01	0.35 ± 0.04
$k'_{298\text{K}}$	$(2.4 \pm 0.1) \times 10^{-5} \text{g}/(\text{m}^2 \cdot \text{d})$	$(1.2 \pm 0.3) \times 10^{-5} \text{g}/(\text{m}^2 \cdot \text{d})$

^a leaching tests of TPD doped with ^{244}Cm in HClO_4

^b leaching tests of TPD doped with ^{241}Am in HNO_3

Influence of $[\text{OH}^-]$

We were also interested in the same study in basic media by performing the leaching tests in 10^{-1}M - 10^{-4}M NaOH under inert conditions (Ar). In these operating conditions, thorium precipitated rapidly (probably as a thorium hydroxide hydrate) while the phosphate concentration increased linearly with the leaching time. For this reason, the R_{OH} values (Table VI) were determined from the variation of the phosphate concentration in the leachate considering Eq. 7:

$$R_{\text{OH}} = k''_T \times (a_{\text{OH}^-})^m \quad (7)$$

where k''_T is the apparent normalized leaching rate constant for hydroxide-ion-promoted dissolution (expressed in $\text{g}/(\text{m}^2 \cdot \text{d})$), and m , the partial order related to $[\text{OH}^-]$.

Table VI. Normalized dissolution rate of TPD in basic solutions ($\theta = 25^\circ\text{C}$)

[OH ⁻]	R _{OH} (g/(m ² .d))
10 ⁻¹ M	$(3.5 \pm 0.2) \times 10^{-5}$
10 ⁻² M	$(1.7 \pm 0.2) \times 10^{-5}$
10 ⁻³ M	$(5.8 \pm 0.9) \times 10^{-6}$
10 ⁻⁴ M	$(1.6 \pm 0.6) \times 10^{-6}$
<i>m</i>	0.45 ± 0.04
<i>k''</i> _{298K}	$(1.1 \pm 0.3) \times 10^{-4}$ g/(m².d)

The partial order related to [OH⁻] ($m = 0.45$) is of the same order of magnitude than the partial order related to [H₃O⁺] in acidic media ($n = 0.31-0.35$) and remains rather low. That confirms the good resistance of TPD to aqueous corrosion by comparison to other minerals.

We also verified that the TPD dissolution was slightly influenced by the phosphate concentration because they are probably involved in the formation of the activated complex at the surface of the solid. This study was performed in 5M HNO₃ at 25°C for phosphate concentrations varying from 10⁻² M to 0.89 M. We found that the normalized leaching rate slightly increases with the phosphate concentration. Nevertheless, this increase is very low and becomes significant only for concentrations higher than 0.1M.

CHARACTERIZATION OF THE PHASE NEOFORMED AT SATURATION

Several leaching tests were performed in 5M HNO₃ at 90°C for very long leaching times in order to get the complete dissolution of TPD and to characterize the phase neoformed when the saturation of the solution is reached (for example in 10⁻¹M-10⁻⁴M HNO₃). During these experiments, the normalized leaching related to thorium first increases linearly with the leaching time then strongly decreases after 30 days and reaches a plateau (the dissolution becomes incongruent). The first step corresponds to a kinetic process while the second step was assigned to the formation of a gelatinous-precipitate, which controls the thorium and phosphate concentrations in the leachate. We verified that in all the acidic media studied, the mole ratio Th/PO₄ remained equal to 2/3 in the leachate (i.e. the stoichiometry of the initial TPD) which confirms that the dissolution is stoichiometric in these conditions. Consequently, the stoichiometry of the neoformed phase should be equal to 2/3 too.

The solid obtained after the complete dissolution of TPD was characterized by several methods. The XRD pattern showed diffraction lines which do not correspond to TPD (Fig. 1.). The TEM study revealed that this residue was a polyphase system composed of amorphous and crystallized phases. The EPMA analysis (Table VII) of the residue obtained after removal of the supernatant (#1) or after the direct evaporation of the mixture at 90°C (#2) led to a mole ratio Th/P equal to 0.69 (which is very close to 2/3 found in the TPD). The total wt. % is far from 100% due to the very small grain size which leads to difficult analyses. Moreover, the results obtained are in very good agreement with that obtained for the thorium phosphate-hydrogenphosphate Th₂(PO₄)₂(HPO₄) . H₂O synthesized using hydrothermal conditions (#3). All the vibration modes corresponding to water and PO₄ group were observed in the infrared spectrum of the residue. A weak shoulder (located at 2400 cm⁻¹) was assigned to the (P)-O-H vibration mode. The band observed at 1234 cm⁻¹ was assigned to the symmetric stretching mode of (P)-O-H of HPO₄²⁻ groups in the plane deformation according to the literature (11). In these conditions, it was possible to propose the formula Th₂(PO₄)₂(HPO₄) . *n* H₂O (TPHP) for the neoformed solid. Indeed, the XRD diagrams of both samples (#1 and #2, Fig. 1b) are identical to that of Th₂(PO₄)₂(HPO₄) . H₂O (#3, Fig. 1c). The water amount contained in the solid was determined from TGA results.

Table VII. Results of EPMA analysis of leached TPD and $\text{Th}_2(\text{PO}_4)_2(\text{HPO}_4) \cdot \text{H}_2\text{O}$

Weight %	Calc. ^a	Exp. (#1)	Exp. (#2)	Exp. (#3)
Th	62.6	52.7 ± 4.0	55.0 ± 2.2	54.6 ± 2.2
P	12.6	10.1 ± 0.8	10.7 ± 0.5	11.1 ± 0.8
O	24.8	20.3 ± 1.6	21.4 ± 0.8	22.0 ± 1.6
Total	100	83.1 ± 6.4	87.1 ± 3.5	87.9 ± 4.7
Th / P	0.667	0.69 ± 0.03	0.68 ± 0.02	0.66 ± 0.07

^a calculated considering the formula $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$

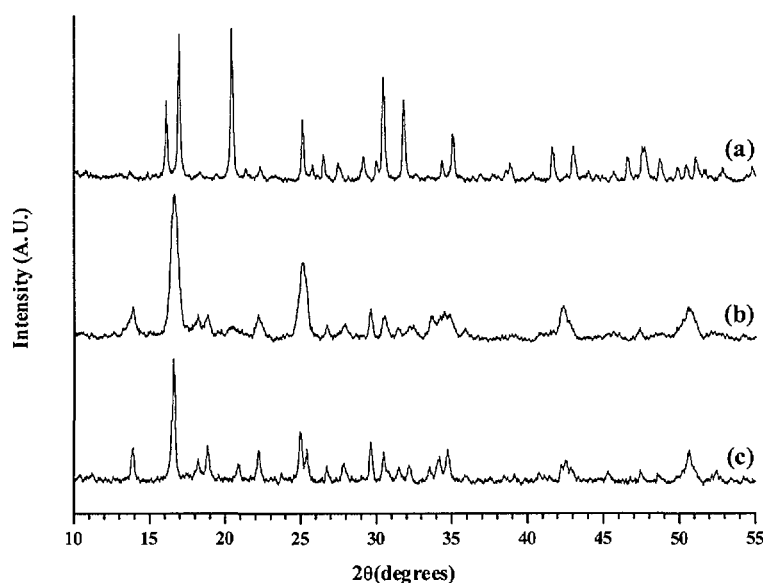


Fig. 1. XRD diagram of unleached (a) and leached (b) TPD (5M HNO_3 , 90°C) – XRD of TPHP obtained using hydrothermal conditions (c)

DETERMINATION OF THE SOLUBILITY PRODUCT OF $\text{Th}_2(\text{PO}_4)_2(\text{HPO}_4) \cdot n \text{H}_2\text{O}$

The conventional solubility product of the TPHP, $K_{S,0}^{\circ*}$ (calculated for $I=0\text{M}$), was determined from the results obtained when leaching the TPD in $10^{-1} - 10^{-4}\text{M}$ HNO_3 at 25°C taking into account the following equation :

$$K_{S,0}^{\circ*} = [\text{Th}^{4+}]^2 \times [\text{PO}_4^{3-}]^2 \times [\text{HPO}_4^{2-}] \times (\gamma_{\text{Th}^{4+}})^2 \times (\gamma_{\text{PO}_4^{3-}})^2 \times (\gamma_{\text{HPO}_4^{2-}}) \quad (8)$$

The Specific Interaction Theory was used to determine the ion activity coefficients. The speciation of thorium and phosphate species was determined using the CHES software (12). The results are reported in Table VIII. They are consistent (average value : $K_{S,0}^{\circ*} = 10^{-66.6 \pm 1.2}$) and confirm the very low solubility of the neoformed TPHP : $\text{Th}_2(\text{PO}_4)_2(\text{HPO}_4) \cdot n \text{H}_2\text{O}$.

Table VIII. Values of $K_{S,0}^{o*}$ obtained for $\text{Th}_2(\text{PO}_4)_2(\text{HPO}_4) \cdot n \text{H}_2\text{O}$

Leachate	$C_{\text{Th}^{4+}}$	$[\text{Th}^{4+}]$	$C_{\text{PO}_4^{3-}}$	$[\text{HPO}_4^{2-}]$	$[\text{PO}_4^{3-}]$	$\text{Log}(K_{S,0}^{o*})$
10^{-1}M HNO_3	$7.3 \times 10^{-5} \text{ M}$	$6.9 \times 10^{-5} \text{ M}$	$1.1 \times 10^{-4} \text{ M}$	$1.2 \times 10^{-11} \text{ M}$	$2 \times 10^{-22} \text{ M}$	- 68,5
10^{-2}M HNO_3	$8.5 \times 10^{-6} \text{ M}$	$5.7 \times 10^{-6} \text{ M}$	$1.5 \times 10^{-5} \text{ M}$	$6.2 \times 10^{-11} \text{ M}$	$1 \times 10^{-20} \text{ M}$	- 66,6
10^{-3}M HNO_3	$1 \times 10^{-6} \text{ M}$	$5.4 \times 10^{-7} \text{ M}$	$1.5 \times 10^{-6} \text{ M}$	$7.5 \times 10^{-11} \text{ M}$	$1,2 \times 10^{-19} \text{ M}$	- 66,4
10^{-4}M HNO_3	$4 \times 10^{-7} \text{ M}$	$9 \times 10^{-8} \text{ M}$	$6 \times 10^{-7} \text{ M}$	$1.4 \times 10^{-10} \text{ M}$	$2,2 \times 10^{-18} \text{ M}$	- 65,2
10^{-3}M HClO_4	$1 \times 10^{-6} \text{ M}$	$4 \times 10^{-7} \text{ M}$	$2 \times 10^{-6} \text{ M}$	$1.0 \times 10^{-10} \text{ M}$	$1,6 \times 10^{-19} \text{ M}$	- 66,3

CONCLUSION

All the experimental data obtained showed that the TPD is very resistant to aqueous corrosion even in acidic (and basic) media. The influence of several parameters (such as temperature, leachate acidity) on the normalized leaching rate were independently determined in under-saturation conditions. The activation energy ($42 \pm 3 \text{ kJ}\cdot\text{mol}^{-1}$) as well as the partial orders related to $[\text{H}_3\text{O}^+]$ ($n = 0.31 - 0.35$) and $[\text{OH}^-]$ ($m = 0.45$) were found to be lower than that reported for several minerals or matrices. When the saturation of the solution is reached, a gelatinous-precipitate controls the thorium and phosphate concentrations in the leachate. It was identified as a thorium phosphate hydrogenphosphate hydrate in which the mole ratio Th/PO_4 remains equal to 2/3 (same ratio than in TPD). The corresponding conventional solubility product $K_{S,0}^{o*}$ is equal to $10^{-66.6 \pm 1.2}$ which confirms the very low solubility of this neoformed phase.

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