

## Decontamination of liquid radioactive waste by Thorium Phosphate.

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**Abstract** – In the field of the complete reexamination of the chemistry of thorium phosphate and of the improvement of the homogeneity of Thorium Phosphate Diphosphate (TPD,  $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ ) prepared at high temperature, several crystallized compounds were prepared as initial powdered precursors. Due to the very low solubility products associated to these phases, their use in the field of the efficient decontamination of high-level radioactive liquid waste containing actinides (An) was carefully considered. Two main processes (called “oxalate” and “hydrothermal” chemical routes) were developed through a new concept combining the decontamination of liquid waste and the immobilization of the actinides in a ceramic matrix (TPD). In phosphoric media (“hydrothermal route”), the key-precursor was the Thorium Phosphate HydrogenPhosphate hydrate ( $\text{Th}_x(\text{PO}_4)_2(\text{HPO}_4) \cdot \text{H}_2\text{O}$ , TPHP, solubility product  $\log(K_{s,0}^\circ) \sim -67$ ). The replacement of thorium by other tetravalent actinides (U, Np, Pu) in the structure, leading to the preparation of  $\text{Th}_{2-x}\text{An}_x(\text{PO}_4)_2(\text{HPO}_4) \cdot \text{H}_2\text{O}$  solid solutions, was examined. A second method was also considered in parallel to illustrate this concept using the more well-known precipitation of oxalate as the initial decontamination step. For this method, the final transformation to single phase TPD containing actinides was purchased by heating a mixture of phosphate ions with the oxalate precipitate at high temperature.

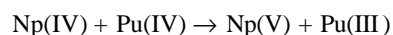
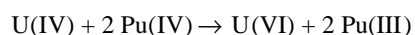
### INTRODUCTION

The immobilization of tetravalent actinides: U(IV), Np(IV) and Pu(IV) in the Thorium Phosphate Diphosphate (TPD,  $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ ) structure was already established few years ago [1,2]. More recently, some wet chemistry methods of preparation of TPD (or associated solid solutions) were developed from room-temperature crystallized precursors. Due to the very low solubility products associated to the precursors precipitated, these chemical ways of preparation could be applied for the efficient decontamination of radioactive liquid waste. Both methods are based on a two-step procedure involving first, the decontamination of the liquid waste by precipitation of the initial precursors (oxalate or phosphate compound) then their conversion to the final TPD (and associated solid solutions) by heating at high temperature. Two original chemical routes (called “oxalate” and “hydrothermal”) were especially considered to study the feasibility of this concept and to evidence the successive chemical steps leading to the simultaneous or individual incorporation of tetravalent actinides in the TPD structure. With a view of developing decontamination processes, a particular attention was given to the control of the oxidation states of the actinides during these successive steps considering

concentrated actinide solutions prepared in nitric acid as initial media.

### SYNTHESIS AND CHARACTERIZATION OF THE PRECURSORS

In nitric medium, uranium, neptunium and plutonium can not usually coexist in the tetravalent oxidation state mainly due to the following reactions:



So, if both ways of synthesis involved the individual incorporation of each actinide at the tetravalent oxidation state, the quantitative simultaneous precipitation of the three actinides was reached considering first their reduction to the lowest stabilized oxidation state (Table I).

TABLE I. Oxidation states of actinides.

	Stabilized oxidation state	Lowest stabilized oxidation state
U	VI	IV
Np	IV, V & VI	IV
Pu	IV & VI	III

### “Oxalate” Chemical Route

For this first way of synthesis, called “oxalate method”, mixed oxalate of thorium and tetravalent actinide (An = U, Np or Pu) were prepared from nitric solutions of U(IV), Np(IV) or Pu(IV) in optimized conditions to guarantee their quantitative precipitation (2M HNO<sub>3</sub> – 0.2M An(IV) solution with several initial An/Th mole ratios). After adding phosphoric acid and homogenizing the mixture, a paste was obtained. It was transformed into powder by gentle drying under argon stream. At this stage of the preparation, the initial powder was found to be a mixture of several crystallized phases or was partly amorphous. A thermal treatment of this mixture at high temperature was first used to prepare the final TUPD (Th<sub>4-x</sub>U<sub>x</sub>(PO<sub>4</sub>)<sub>4</sub>P<sub>2</sub>O<sub>7</sub>), TNpPD (Th<sub>4-x</sub>Np<sub>x</sub>(PO<sub>4</sub>)<sub>4</sub>P<sub>2</sub>O<sub>7</sub>) or TPuPD (Th<sub>4-x</sub>Pu<sub>x</sub>(PO<sub>4</sub>)<sub>4</sub>P<sub>2</sub>O<sub>7</sub>) solid solutions. The global scheme of this chemical route is given in Fig. 1.

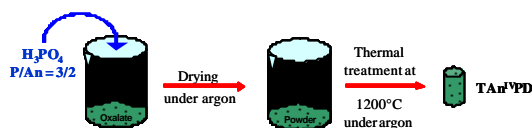


Fig. 1. Preparation of TAn<sup>IV</sup>PD through the “oxalate” method.

The purity of the final products prepared was found to be independent of the atmosphere considered during the heating treatment (air or argon), except for uranium which was significantly oxidized when firing in air leading to a polyphase system. The samples were extensively characterized by XRD, IR and UV-Visible techniques. They confirmed the presence of each actinide in the tetravalent oxidation state in the final samples prepared.

Other solid solutions of general formula Th<sub>4-x</sub>An<sub>x</sub><sup>IV</sup>(PO<sub>4</sub>)<sub>4</sub>P<sub>2</sub>O<sub>7</sub> (TAn<sup>IV</sup>PD, An = U, Np and/or Pu) containing simultaneously U, Np and Pu, were also prepared through *via* this “oxalate route”. With a view of controlling the speciation of the distinctive actinides and obtaining quantitative precipitation yields, the actinides were initially reduced to their lowest oxidation states and the precipitation conditions slightly adapted. Initial Pu(III) was found to be oxidized only partially to Pu(IV) during thermal treatments and consequently plutonium incorporates only partially the TPD phase. A secondary minor phase, Pu(III) monazite, was then encountered in the final product. It represents however no significant limitation

since this secondary phase appears as a low-soluble ceramic often reported for the immobilization of An(III) (An= Pu, Am and Cm).

### “Hydrothermal” Chemical Route

Recently, in order to improve the homogeneity of the samples, pure and single phase crystallized Thorium Phosphate-Hydrogen Phosphate hydrate, Th<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(HPO<sub>4</sub>) · H<sub>2</sub>O (TPHP) was synthesised, as a precursor of TPD, when heating a mixture of thorium nitrate (or chloride) solution and concentrated phosphoric acid in closed PTFE container at 90-160°C [3]. The global scheme of this chemical route is given in Fig. 2.

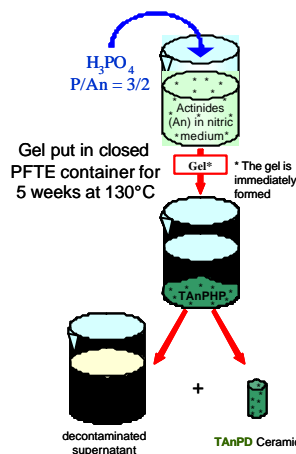


Fig. 2. Preparation of TAn<sup>IV</sup>PD through the “hydrothermal” method.

In the aim to prepare Th<sub>2-x/2</sub>An<sub>x/2</sub>(PO<sub>4</sub>)<sub>2</sub>(HPO<sub>4</sub>) · H<sub>2</sub>O (TAnPHP) solid solutions, the replacement of thorium by smaller tetravalent actinide in this key-precursor was examined. Several solid solutions based on TPHP with tetravalent uranium (TUPHP), neptunium (TNpPHP) or plutonium (TPuPHP) were prepared by the same way of synthesis in autoclaves at 90-130°C for about 1 month. After separation of the solid from the supernatant by centrifugation, washing, drying then grinding, the powdered samples were characterized by TGA/DTA experiments, XRD, UV-visible and IR spectroscopy. Moreover, the unit cell parameters were refined for each tetravalent actinide (Tables II & III for Np- and Pu-bearing compounds, respectively) considering the monoclinic unit cell reported recently for pure TPHP (monoclinic system,  $a = 6.697(2) \text{ \AA}$ ,  $b = 7.028(2) \text{ \AA}$ ,  $c = 11.210(4) \text{ \AA}$ ,  $\beta = 107.35(2)^\circ$ , e.g.  $V = 503.6 \text{ \AA}^3$ ) [4].

TABLE II. Unit cell parameters of TNpPHP.

	$x = 0.8$	$x = 2.0$	$x = 4.0$
$a$ (Å)	6.675(3)	6.628(5)	6.57(2)
$b$ (Å)	7.006(3)	6.985(6)	6.94(1)
$c$ (Å)	11.162(6)	11.130(14)	11.05(2)
$\beta$ (°)	107.38(4)	107.4(1)	107.38
$V$ (Å <sup>3</sup> )	498.0(8)	492(3)	482(3)

TABLE III. Unit cell parameters of TPuPHP.

	$x = 0.8$	$x = 1.6$	$x = 2.0$
$a$ (Å)	6.669(4)	6.63(1)	6.62(1)
$b$ (Å)	6.996(4)	6.965(7)	6.97(2)
$c$ (Å)	11.154(6)	11.13(2)	11.10(3)
$\beta$ (°)	107.36(5)	107.4(1)	107.3(1)
$V$ (Å <sup>3</sup> )	497(1)	491(3)	488(3)

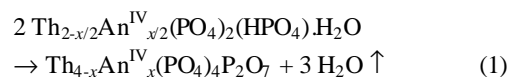
The unit cell parameters and volume decreased linearly when increasing the amount of tetravalent actinide in the sample (Table IV) which agrees well with the replacement of thorium by smaller cation in the TPHP structure and confirmed the preparation of the expected solid solutions. Moreover, the variations observed for tetravalent neptunium and plutonium are consistent with that reported for  $\text{Th}_{2-x/2}\text{U}_{x/2}(\text{PO}_4)_2(\text{HPO}_4) \cdot \text{H}_2\text{O}$  samples already described in literature [5].

TABLE IV. Variation of the unit cell parameters of  $\text{TAn}^{\text{IV}}\text{PHP}$  solid solutions

Actinide	U [5]
$a$ (Å)	$6.693(2) - 0.024(1) \times x_{\text{U}}$
$b$ (Å)	$7.027(2) - 0.017(1) \times x_{\text{U}}$
$c$ (Å)	$11.206(2) - 0.039(1) \times x_{\text{U}}$
$V$ (Å <sup>3</sup> )	$503.1(2) - 4.7(1) \times x_{\text{U}}$
Np	
$a$ (Å)	$6.702(4) - 0.034(2) \times x_{\text{Np}}$
$b$ (Å)	$7.026(2) - 0.021(1) \times x_{\text{Np}}$
$c$ (Å)	$11.195(4) - 0.036(2) \times x_{\text{Np}}$
$V$ (Å <sup>3</sup> )	$502.8(5) - 5.3(2) \times x_{\text{Np}}$
Pu	
$a$ (Å)	$6.705(3) - 0.044(3) \times x_{\text{Pu}}$
$b$ (Å)	$7.024(2) - 0.031(6) \times x_{\text{Pu}}$
$c$ (Å)	$11.194(6) - 0.045(5) \times x_{\text{Pu}}$
$V$ (Å <sup>3</sup> )	$503.3(1) - 7.7(1) \times x_{\text{Pu}}$

Several solid solutions containing simultaneously U(IV), Np(IV) and Pu(IV) were also synthesized from nitric solution of U(IV), Np(IV) and Pu(III) stabilized by adding reducing and antinitrous agents. After gelation then precipitation, the three actinides were significantly incorporated in the structure even though some amounts of U(VI) and Np(V), resulting from the oxidation of both actinides, were found in the supernatant.

Due to a high specific area value (10-20 m<sup>2</sup>/g) [5], TPHP (and associated solid solutions) are transformed into TPD (and associated solid solutions) above 950°C, according to the following reaction:



Consequently to the dehydration of the samples then to the condensation of hydrogenphosphate groups into diphosphate entities, only water molecules are eliminated during this calcinations step which appears as a main advantage of this process compared to that involving the "direct evaporation" of the acidic mixture. As already reported for the samples prepared through the "oxalate" chemical route, the three actinides studied were found individually or simultaneously in the tetravalent oxidation state in the final solid solutions prepared, i.e.  $\text{Th}_{4-x}\text{An}_x^{\text{IV}}(\text{PO}_4)_4\text{P}_2\text{O}_7$  (with An = U, Np and/or Pu) after heating the precipitates at 1100-1200°C in air or under inert atmosphere.

More generally the sintering properties of pure TPD and associated solid solutions with uranium were already examined through the "direct evaporation" of the initial mixture or *via* the precipitation process [6,7]. Very dense pellets were prepared by both ways after a two-step procedure involving a uniaxial pressing at room temperature then a heating treatment at 1250°C. In these conditions, the rather good immobilization of tetravalent actinides in the final dense and low-soluble ceramic could be guaranteed.

### EVALUATION OF THE PERFORMANCES OF THE PROCESSES

The global scheme of the decontamination processes is reported in Fig. 3.

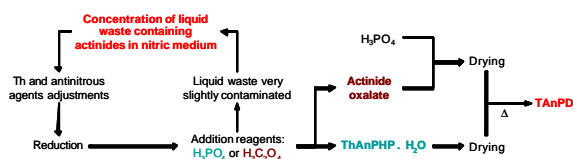


Fig. 3. Global scheme of the decontamination processes.

The efficiency of both processes was evaluated through the determination of the decontamination factor (DF) for each actinide studied (Table V) taking into account the following expression:

$$DF = \frac{\text{Initial actinide amount in nitric medium}}{\text{Actinide amount in the resulting supernatant}} \quad (2)$$

Taking into account the satisfying results obtained for uranium, neptunium and plutonium, both processes could be considered for the efficient removal of these actinides from high-level radioactive liquid waste after only few decontamination steps then could guarantee the good immobilization of these actinides in the final TPD (and in the associated solid solutions prepared).

TABLE V. DF values obtained by both decontamination processes

	"Oxalate route"	"TPHP route"
DF (Th)	> 2500	1500
DF (U)	> 120	> 140
DF (Np)	470	800
DF (Pu)	2300	340

For the simultaneous incorporation of the three actinides, the DF values obtained through the "oxalate" route are reported in table VI while that determined from the "hydrothermal" must be reconsidered after optimizing the precipitation step (especially by reducing the precipitation time or by increasing the corresponding temperature).

TABLE VI. DF values obtained by "oxalate" process

DF (Th)	1600
DF (U)	> 120
DF (Np)	500
DF (Pu)	2800

## CONCLUSIONS AND PROSPECTS

A new concept combining the decontamination of actinide-containing liquid waste and the immobilization of the actinides in a ceramic matrix (TPD) was evaluated via the study of two chemical methods called "oxalate" and "hydrothermal".

For both routes, studies were performed using U, Np and/or Pu-bearing liquid synthetic wastes in order to describe and adjust precisely the successive chemical steps. The satisfying obtained results led to propose two new processes.

Prospects of this preliminary study include:

- subsequent optimizations of the decontamination step ("hydrothermal" route);
- tests with a real high-level radioactive liquid waste to evaluate the process robustness ;
- the consideration of the presence of An(III) (An = Am or Cm) with the corresponding needed adjustments for both processes.

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