Chemical Conditions of Synthesis of $Th_4(PO_4)_4P_2O_7$. Preparation of Thorium Phosphate−Hydrogenphosphate as Precursor

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Thorium phosphate−diphosphate, $Th_4(PO_4)_4P_2O_7$, is obtained, at high temperature (800−1250 °C), for a given ratio $r = PO_4/Th$ equal to $^3/_2$ from a thorium compound and a phosphating reactant whatever the chemical conditions. This compound, whose solubility is very low, can be loaded in situ and used as a host matrix for radwaste storage. One of the methods for its synthesis involves the precipitation of a precursor, thorium phosphate−hydrogenphosphate. This precursor is used as an adsorber for low concentrations of radionuclides and, after heating in air in the range 800−1200 °C, it is transformed into doped $Th_4(PO_4)_4P_2O_7$. The optimum conditions for the precipitation process have been determined. Starting from 0.5−2 M solutions of thorium nitrate or chloride and $(NH_4)_2HPO_4$ at pH = 9−9.5 at the ratio $r = ^3/_2$, a compound of general formula $Th_2(PO_4)_2HPO_4{\cdot}nH_2O$ ($n = 3-7$) is synthesized. Its physicochemical properties have also been studied.

Introduction

Starting in the 1950s[1−7] thorium phosphates have been intensively studied. Among them $Th_3(PO_4)_4$, $(ThO)_3(PO_4)_2$, $(ThO)_2P_2O_7$, β-ThP_2O_7, and $ThO_2{\cdot}0.8P_2O_5$ were reported as the most stable at high temperatures up to 1300 °C.[1] These phosphates were obtained mainly using dry chemistry methods by heating ThO_2 with a phosphating reagent: phosphoric anhydride, ammonium dihydrogen phosphate, etc. In our investigations of the system $ThO_2-P_2O_5$[7] we have proved that $Th_3(PO_4)_4$ and $ThO_2{\cdot}0.8P_2O_5$ do not exist. They form two-phase systems composed of ThO_2 and of a new compound, never mentioned in the literature up to the present, thorium phosphate−diphosphate (TPD, $Th_4(PO_4)_4P_2O_7$). The ab initio crystal structure of TPD has been determined from X-ray powder diffraction data.[7] This phosphate is synthesized as a pure phase whatever the method of synthesis, provided the mole ratio $r = PO_4/Th$ is equal to $^3/_2$.

To obtain TPD, we have applied the wet process using a thorium salt solution and phosphoric acid or ammonium phosphate solutions. When these solutions are mixed, the resulting mixture is[8−11]

(i) A gel (transparent or opaque) in acidic media (HNO_3, HCl) from pH ≈ 0 to pH ≈ 5 and for thorium concentrations in the range $10^{-2}-0.3$ M.

(ii) A solution, for acid concentrations ≥3 M (HCl or HNO_3) and thorium concentrations in the range $10^{-2}-2$ M (these solutions are transformed into transparent xerogels after evaporation of water at room temperature).[11]

(iii) A precipitate for all concentrations of thorium and for pH > 5.

After heating, first at 150 °C then at 400 °C (to evaporate water and volatile acids) and afterward at

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1100−1250 °C, all of the above solid residues finally lead to thorium phosphate−diphosphate if the *r* is fixed to $^3/_2$.

Using the same methods, i.e., mixing in situ uranium(IV) with thorium and phosphoric acid in hydrochloric medium, solid solutions of the composition $Th_{4-x}U_x(PO_4)_4P_2O_7$ have also been synthesized for $x \leq 3.0$.[12] This synthesis shows that TPD can be loaded with other cations, for example, with some radionuclides and potentially used for their storage.[13]

Alternatively, for decontamination of liquid wastes with low concentrations of radionuclides, a procedure using the adsorption method should be preferred. Adsorption and H^+ ion exchange by another cation in tetravalent hydrogenphosphates such as $Zr(HPO_4)_2$ or $Th(HPO_4)_2$ have been studied by several authors.[14−20] Amorphous zirconium hydrogenphosphate has been proposed for radioactive waste treatment for ^{137}Cs and ^{90}Sr.[20]

For nuclear waste storage, a host matrix of very low solubility and high thermal stability (because of the heat effect of radiation) is needed. Amorphous compounds cannot be used for this purpose because they are, generally, more soluble than crystallized ones. At high temperatures, hydrogenphosphates are transformed into crystallized diphosphates, for example $M_yP_2O_7$ (y = 4/valence of cation M). Diphosphates, like α-ThP_2O_7 or α-UP_2O_7[21] are more soluble than phosphates: TPD and $U_2O(PO_4)_2$.[21] Monazite type phosphates (very resistant to irradiation) seem to be good hosts for radionuclides.[22] During our investigations[23] we have found the average solubility (in distilled water and 0.1 M $NaClO_4$ solution) of thorium phosphate−diphosphate equal to 10^{-7} M (total thorium concentration), 10 times less than the solubility of monazite (La, Ce)PO_4. This work aims to synthesize and characterize a precursor of TPD. This precursor will be used as a matrix for adsorption investigations of radionuclides. Leaching of the doped TPD, obtained by calcination from the precursor, will also be studied.

Experimental Section

Thorium nitrate and chloride used for syntheses were from Rhône-Poulenc. Other chemicals were from Fluka−Aldrich.

The surface area and porosity of the precursor were measured (in nitrogen) with a COULTER SA 3100 apparatus. The density of the obtained powder was measured by means of a pycnometer.

A Pyrox MDB15 furnace was used for heat treatment (in air) of the samples in alumina crucibles at a rate of 5°C/min.

Electron Probe Microanalysis (EPMA) was performed by means of a Cameca SX 50 apparatus using 15 kV voltage and a 10 nA current beam.

X-ray powder diffraction (XRD) patterns were recorded with a Philips PW 1050/70 apparatus using the Cu Kα rays and a Ni filter. The patterns were scanned over 5−60° (2θ) with a step of 0.01°.

Infrared (IR) spectra were recorded by means of a Hitachi I-2001 spectrophotometer, with 1−2 wt % of the product in KBr.

Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) results were obtained with a SETERAM TG-DTA92 apparatus. Samples in Pt−Rh crucibles were heated to 1000 °C with a rate 5 °C min^{-1}.

All NMR experiments were performed at room temperature with a MSL 300 BRUCKER equipped with a magic angle spinning probe. The spectrometer operates at a ^{31}P frequency of 121 MHz. The high-resolution NMR spectra were obtained by spinning the samples at the magic angle at a frequency of 14.5 kHz. In such an experiment the chemical bond is characterized by its isotropic chemical shift. The 4 mm diameter rotor made of ZrO_2 was filled with powdered samples. The spectra were obtained using a phase cycling single-pulse sequence: ($\pi/2$) acquisition. The $\pi/2$ pulse width was 4 μs. To avoid the relaxation T_1 problem, a relatively long recycling time equal to 30 s was used. The spectra were recorded with a 30 kHz sweep frequency, and the number of accumulations was equal to 128 (the NMR reference is taken from 0.1 M H_3PO_4).

The solubility in 0.1 M sodium perchlorate of the synthesized products, as well of ThP_2O_7 was determined by measuring thorium concentration using PERALS (photon electron rejecting alpha liquid scintillation) spectrometry with an apparatus from ORTEC. The method is based on the total rejection of β emission (99.95%) and an efficiency of α collection near 100%, which allows the measurement of very low concentrations of α emitters. This alpha liquid scintillation method uses a mixture of an extractant (such as $Alphaexs_\alpha$ and $Thorexs_\alpha$, which contains, respectively di(2-ethylhexyl)-phosphoric acid and 1-nonyldecylamine), an energy-transfer reagent, and a scintillator. Each step of the extraction is performed according to the following procedure:

(i) Mixing a volume of aqueous solution containing the radionuclide with 1.2−1.5 cm^3 of extractant scintillator, gentle shaking for 10 min in a rotative mixer (turbula).

(ii) Separation of both aqueous and organic phases, by centrifugation at 2000 rpm for about 10 min.

(iii) Sparging of 1 cm^3 of the organic phase for 5 min with argon saturated with toluene to eliminate oxygen traces in the solution.

As the lower limit of detection for ^{232}Th was 10^{-9} M after 3 days of counting time,[24] this method enabled the determination of thorium concentrations in the range 10^{-2}−10^{-9} M. To perform this study, about 100 mg of ground samples were shaken with 10 cm^3 of distilled water for 24 h. Thereafter, the supernatant was separated by centrifugation at 13 000 rpm and the thorium ion concentration was determined in this solution.

Titration curves were obtained using a Schott pH meter.

To define the composition of the precipitate formed by mixing the two initial reactants, a 1 M solution of diammonium hydrogenphosphate is titrated with 1 M solution of thorium nitrate starting from different pH values. The titration curves are shown in Figure 1.

The solution of diammonium hydrogenphosphate is a buffer with a pH ≈ 8. When titrated with a thorium

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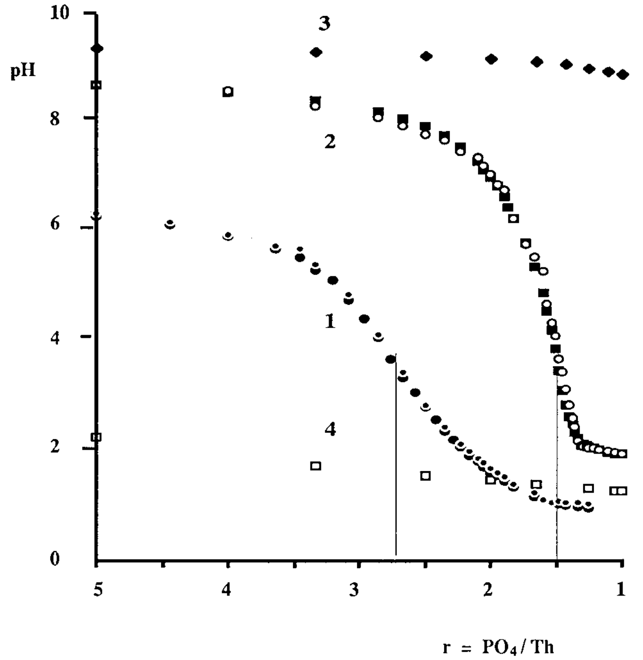

Figure 1. Titration curves in the system $(NH_4)_2HPO_4$−Th-$(NO_3)_4$ (all values $r = PO_4/Th > 5$ are omitted): 1, initial pH = 8; thorium nitrate solution as titrant 2, initial pH = 9.5; thorium nitrate solution as titrant 3, initial pH = 9.9; thorium nitrate solution as titrant 4, initial pH = 2.3; ammonium hydrogen phosphate as titrant.

salt solution (Figure 1, curves 1 and 2) a decrease of pH is observed. The equivalence point (calculated from $\Delta pH/\Delta r$) on curve 1 is found at $r = {}^8/_3$ and pH $\approx$ 3.5. When the initial diammonium hydrogenphosphate solution is brought to pH = 9.5 (concentrated ammonia was added), the equivalence point is located at pH $\approx$ 5 and the r value is equal to ${}^3/_2$. However, when the initial pH exceeds the 9.5 value, the equivalence point is not observed (curve 3). It is important to notice that during the titration the ionic strength is almost constant: it varies from 0.30 in the initial solution of diammonium hydrogenphosphate to 0.28 at the equivalence point. It should also be noticed that for the inverse titration (diammonium hydrogenphosphate as titrant) no equivalence point is observed (curve 4).

According to titration curve 2 in Figure 1 and to different concentrations of the reactants used (experiments with 0.5, 1, or 2 M solutions gave similar results, but the filtration of the formed precipitate was easier using the 0.5 M solution), the optimum conditions required to obtain a product of the composition corresponding to $r = {}^3/_2$ (the mole ratio in TPD) are the following: (i) initial pH values in the range of 8.5−9.5; (ii) final pH $\approx$ 6 (at pH $\approx$ 5 the precipitate is slightly gelatinous); (iii) concentration of the reactants equal to about 0.5 M.

It is important to start from basic solutions in order to obtain the precipitate. The pH of the initial thorium nitrate or chloride solution is equal to about 2 (hydrolysis process). Under these conditions a gelation occurs.

Following the above results the synthesis was performed by adding dropwise a thorium salt solution into a diammonium hydrogenphosphate solution taking into account the mole ratio $PO_4/Th = {}^3/_2$ and pH $\approx$ 9 (with 2% of phosphate in excess). The precipitate was filtered, washed with water to remove ammonium and nitrate ions, and then dried at 120 °C. To study its thermal behavior, samples were heated from 200 to 1100 °C in steps of 100 °C, then analyzed and characterized using the methods given above.

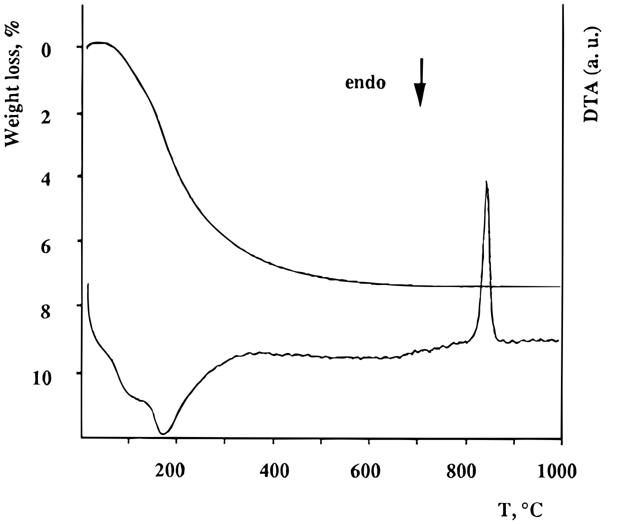

Figure 2. TGA and DTA curves for thorium phosphate-hydrogenphosphate (au arbitrary units).

Independent of the method of preparation, the mole ratio PO_4/Th of the products, obtained by electron probe microanalysis was found to be ${}^3/_2$ (1.47 ± 0.04), as was expected for the initial precipitation conditions used.

According to the TGA results (Figure 2), 7.2% of total weight loss occurs at about 400 °C. Above this temperature no decomposition is observed up to 1200 °C. On the DTA curve an endothermic process up to about 350 °C and an exothermic peak at about 860 °C are observed. This peak correponds to the crystallization temperature (in some cases the crystallization is observed even at 800 °C).

X-ray diffraction patterns (Figure 3) of precipitates heated between 120 and 700 °C show some local order, but generally the product can be considered as amorphous. The X-ray diagram characteristic of thorium phosphate−diphosphate $Th_4(PO_4)_4(P_2O_7)$[7] is obtained for temperatures higher than 800 °C. Above 1250 °C its decomposition into $(ThO)_3(PO_4)_2$ [3] and ThO_2 (JCPDS File No. 35−103) was observed.

The infrared spectra (Figure 4), recorded for samples heated from 120 to 700 °C, show a broad and strong band extending from 3500 down to 2500 cm^{-1}. This band is assigned to the O−H stretching mode which may include not only the O−H frequencies of water molecules but also the frequencies of (P)−O−H bonds.[25] The band located near 1650 cm^{-1} is characteristic for the bending mode of H_2O. These two above-mentioned bands disappear for samples heated at higher temperatures (800−1100 °C).

Bands from 1250 to 950 cm^{-1} and from 650 to 450 cm^{-1} are assigned to vibrational and deformation modes of P−O bonds of the PO_4 group.[26] These bands split into several peaks as temperature rises (Figure 4): a more

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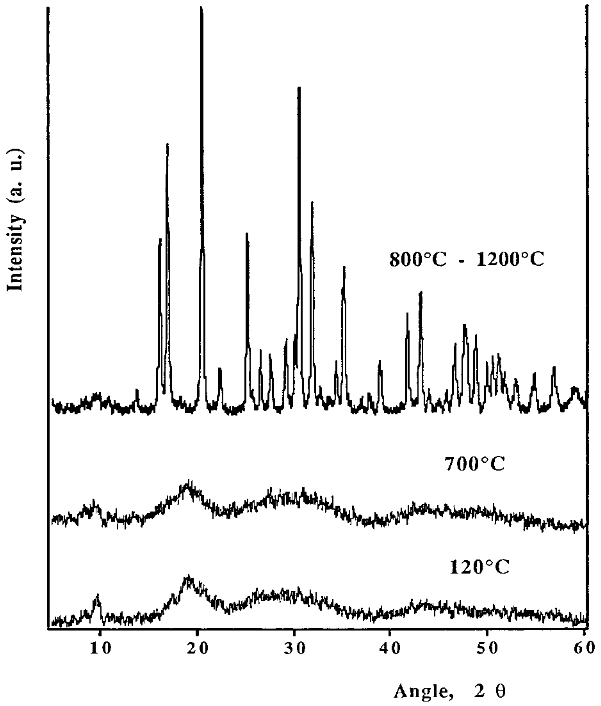

Figure 3. XRD patterns of thorium phosphate–hydrogenphosphate as a function of calcination temperature.

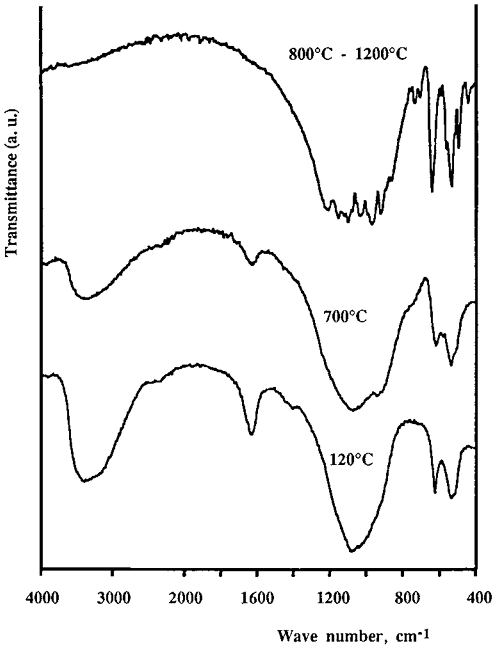

Figure 4. Infrared spectra of thorium phosphate–hydrogenphosphate as a function of calcination temperature.

complicated spectrum appears with additional bands at 950 cm^{-1} and between 750 and 730 cm^{-1}, assigned to the P–O–P bridge.[27, 28] This spectrum corresponds to the pure thorium phosphate–diphosphate.[7]

The HPO_4^{2-} group can hardly be defined from the infrared spectra because of the overlap of (P)–O–H vibrations with those of O–H and P–O. However, weak shoulders at about 2400 and 1400 cm^{-1} (spectrum for the sample dried at 120 °C) could be assigned to the (P)–O–H vibration and deformation modes, respectively.[25]

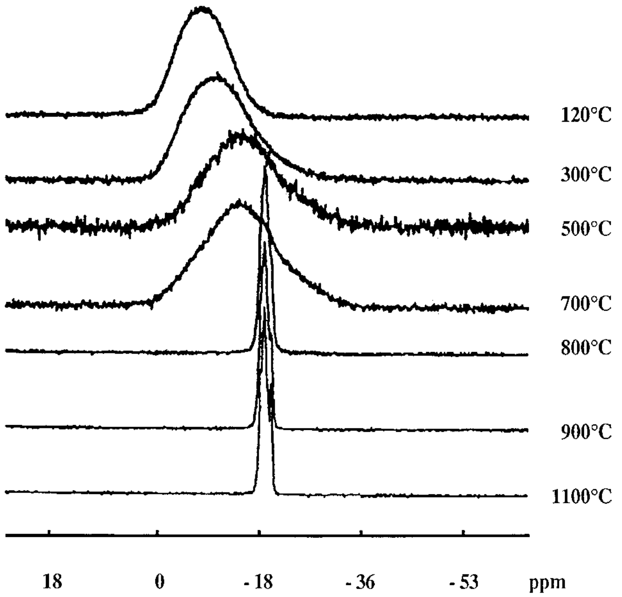

Figure 5. ^{31}P NMR spectrum of thorium phosphate–hydrogenphosphate as a function of calcination temperature (reference from H_3PO_4).

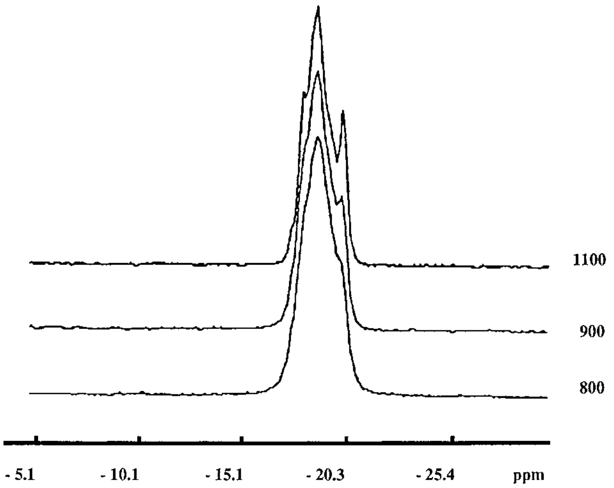

Figure 6. Evidence of ^{31}P NMR fine structure for thorium phosphate–diphosphate with an increase in the calcination temperature.

The general view of the NMR spectra obtained as isotropic chemical shifts (σ_{iso}) is given in Figure 5. For the product dried at 120 °C a relatively broad band appears at −7.5 ppm. This broadening is due to the disorder that exists in the amorphous state. The band is asymmetric and shifts toward more negative values when the temperature of calcination increases. The broadening increases for samples heated to 700 °C. For samples heated at 800 °C the spectrum exhibits a narrow band with a maximum of intensity near −18.6 ppm. Starting from 800 up to 1100 °C (temperatures of calcination) the chemical shift remains at the same position and a fine structure emerges as shown in Figure 6. This structure fine is composed of four lines whose positions are given in Table 1 (lines 3 and 4 are neglected). The resolved double band confirms the crystallinity of the compound. This double band is

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Table 1. Line Positions of the Deconvoluted NMR Spectrum Obtained from the Sample Heated at 1100 °C

line	σ_{iso} (ppm)	intensity (%)
1	−18.64	76
2	−20	16.6
3	−19.5	3.7
4	−18	3.7

assigned to two different phosphate groups: PO_4 (−18.64 ppm) and P_2O_7 (−20 ppm).

Taking into account the results of all experiments, the obtained precipitate could be defined as thorium phosphate-hydrogenphosphate (TPHP). The reaction of its formation may be written as follows:

$$2Th^{4+} + 3HPO_4^{2-} \rightarrow Th_2(PO_4)_2(HPO_4) + 2H^+ \qquad (1)$$

At high temperature (800−1200 °C) this compound is easily transformed into thorium phosphate-diphosphate according to the reaction:

$$2Th_2(PO_4)_2(HPO_4) \rightarrow Th_4(PO_4)_4P_2O_7 + H_2O\uparrow \qquad (2)$$

The weight loss calculated for reaction 2 should be 1.2% per 1 molecule of water. The 7.2% observed corresponds to $3H_2O$. Samples from different syntheses gave weight losses even up to 15%. Thus, the general formula can be given as $Th_2(PO_4)_2(HPO_4)\cdot nH_2O$ or $Th_4(PO_4)_4(HPO_4)_2\cdot 2nH_2O$ with $n = 3-7$.

An alternative formula of the precipitate may be written as $(ThOH)_2(HPO_4)_3\cdot m\ H_2O$ and its decomposition at 800−1200 °C will also give the TPD. To verify the presence of one or more hydrogenphosphate groups, a sample of the dried product was heated for 2 h with 0.1 M sodium hydroxide solution and then centrifuged, and the supernatant was titrated with 0.1 M hydrochloric acid. It appeared that the reaction ratio was equal to 1 mol of NaOH per 1 mol of HPO_4^{2-} and per 2 mol of thorium. Thus, only one hydrogen ion is exchanged. The substitution of hydrogen can be also performed using sodium nitrate or chloride solutions. Following calcination at 1000−1050 °C, the new product leads to the dithorium−sodium phosphate $Th_2Na(PO_4)_3$ mentioned in the literature (JCPDS File No. 16-812):[29−31]

$$Th_2(PO_4)_2(HPO_4)\cdot nH_2O + Na^+ + OH^- \rightarrow Th_2Na(PO_4)_3 + (n+1)H_2O \qquad (3)$$

Electron microprobe analysis shows that the mole ratio PO_4/Th in this double salt remains equal to $^3/_2$. An analogous process is observed for the Cs^+ ion.

Thorium phosphate−hydrogenphosphate is a white powder, soluble in hot 1 M acids (HCl, HNO_3, $HClO_4$, etc.). Stirred with distilled water or 0.1 M $NaClO_4$ solution for 24 h, it gives a pH value of around 5 in the supernatant and an average total thorium concentration equal to 5×10^{-6} M, which is due to its "solubility". In the same conditions "solubilities" of other thorium phosphates were found to be as follows: TPD, 10^{-7} M; α-ThP_2O_7, 3×10^{-6} M; β-ThP_2O_7, 10^{-7} M.

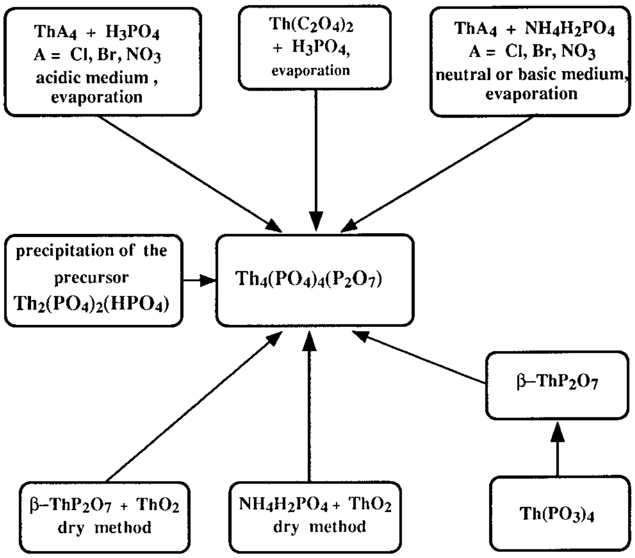

Figure 7. Methods of synthesis of thorium phosphate−diphosphate.

Using the precipitation method of synthesis of TPHP described above, a powder with the following physical properties is obtained: (i) average diameter of particles 40 μm; (ii) average surface area 150 $m^2 \cdot g^{-1}$; (iii) pore size 6−10 nm; (iv) density $d^{26}_{H_2O} = 3.7$.

We did not find in the literature any references to thorium phosphate−hydrogenphosphate. Its adsorption properties are under study. Some results already obtained for ^{241}Am, ^{152}Eu, and ^{137}Cs (for solutions containing 250−2000 Bq) lead always, under the optimum conditions, to 100% of fixed radionuclides.

The precipitate prepared with the mole ratio PO_4/Th = $^8/_3$ was also calcined at 850 °C. The obtained powder is a two-phase system of thorium phosphate−diphosphate and α-ThP_2O_7 (low-temperature form of thorium diphosphate). The latter is decomposed into TPD[7] and P_4O_{10} at 1300−1350 °C.

Conclusions

Thorium phosphate−diphosphate $Th_4(PO_4)_4P_2O_7$, previously described,[7] can be synthesized from a mixture of a thorium salt (or thorium oxide) and a phosphate reactant by dry or wet methods of chemistry. Another method of preparation of the TPD is the thermal decomposition of polyphosphates giving β-ThP_2O_7 (high-temperature form of thorium diphosphate). The latter is decomposed with evaporation of phosphoric anhydride into TPD at temperatures above 1250 °C. It is evident that for applications this method cannot be used. A summary scheme of the different ways of synthesizing TPD is presented in Figure 7.

Thorium phosphate−diphosphate is proposed for nuclear waste storage.[13] For this application only the wet method of synthesis can be used. The radionuclides are incorporated in situ into the initial mixture.[13]

Thorium phosphate−hydrogenphosphate could be used as an adsorbent for radionuclides from low concentrated solutions. Its synthesis is not complicated. To find the composition of the TPHP obtained by the precipitation procedure, the reaction between diammo-

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nium hydrogenphosphate and thorium nitrate or chloride has been studied for different initial concentrations and pH values. By titration of 0.5−2 M solutions a precipitate with a mole ratio $PO_4/Th = {}^3/_2$ is formed at final pH ≈ 6. Using these conditions an amorphous powder has been obtained with a yield near 95%. The product was characterized using EPMA, TGA, DTA, XRD, IR, and NMR methods. Considering the results of all these investigations, its general formula can be written as $Th_2(PO_4)_2(HPO_4)\cdot nH_2O$ ($n = 3-7$)−thorium phosphate−hydrogenphosphate. When heated at 800−1200 °C TPHP decomposes and transforms to well-crystallized thorium phosphate−diphosphate $Th_4(PO_4)_4P_2O_7$.

Ion exchange between hydrogen and sodium ions has been observed for TPHP using 0.1 M sodium hydroxide, sodium nitrate, or sodium chloride solutions. Heated at 1000−1050 °C, the product obtained by this reaction leads to the known dithorium−sodium phosphate $Th_2Na(PO_4)_3$.

The adsorption of some radionuclides (^{241}Am, ^{152}Eu, and ^{137}Cs) has been studied in order to test TPHP as a matrix for decontamination of radioactive effluents. Investigations on the adsorption capacity of TPHP are in progress.

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