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From Nd(III) and Pu(III) Oxalates to Oxides: Influence of NitriloTris(MethylenePhosphonic acid) on Chemical Composition, Structure and Morphology.

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ABSTRACT:

Neodymium oxalate structure and morphology were modified by adding a phosphonate, NTMP, during the oxalic precipitation step. Spherical agglomerates of neodymium oxalate $Nd_2(C_2O_4)_3(H_2O)_6\cdot 12H_2O$ composed of thin hexagonal rods were precipitated instead of decahydrated oxalate $Nd_2(C_2O_4)_3(H_2O)_6\cdot 4H_2O$ with rod-like particles usually obtained in absence of additive. Despite some differences in the complexation with NTMP and complexity from redox, the use of NTMP was successfully transposed to the plutonium system. Spherical agglomerates of plutonium(III) oxalate were so obtained, leading to spherical agglomerates of PuO₂ plutonium oxide after thermal treatment.

Oxalic conversion is a well-known process to obtain metal oxide from cations in solution^{1,2,3}. In nuclear field, the recovery of valuable actinides requires, first, to dissolve the spent fuel, then to partition the elements, and finally to recover the valuable actinides into a solid form by means of a conversion step which can be achieved by oxalic precipitation. This process leads to the precipitation of solid actinide oxalates used as oxide precursors⁴. As oxalates keep their morphology when calcined into oxides through pseudomorphic transformations, controlling of the size, structure and morphology of the oxalate particles is a key factor to optimize the conception of new fuels^{5,6,7,8}.

In the past decades, some ways have been found to control actinide oxalate size, structure and morphology^{9,10,11,12}. Increasing crystallization temperature of tetravalent actinides $An(C_2O_4)_2.6H_2O$ (An = Pu or Np) has, for example, a significant influence on particles size and shape^{13,14,15}. Considering the strong correlation between the particles shape and the crystal structure, another way to influence the final morphology of the oxalate is to target its crystal structure by varying chemical conditions of crystallization^{16,17,18,19,20,21,22,23,24,25,26,27,28}. Few studies were dedicated to the influence of additives on actinide oxalates structure and morphology. However, influence of some additives on oxalic precipitation was studied on other systems as calcium oxalate, primary constituent of human kidney stones, or copper oxalate, which permits to obtain copper oxide, used for bulk and thin films applications. For example, polymers, such as hydroxypropyl methylcellulose (HPMC), are able to act as surface capping agents to cover the surface of crystals and lead to the formation of rods for copper oxalate²⁹. Moreover, complexing agents of metallic cations should also be considered. By competing oxalic acid they could influence the kinetic of precipitation and the structure of the precipitated oxalate, so that microstructural modification can be expected.

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Among the different chelating reagents, nitrilotris(methylenephosphonic acid) N[CH₂PO(OH)₂]₃ (hereinafter referred as NTMP), is used in numerous technical and industrial applications such as corrosion, scale inhibitor, in waste water treatment, selective noble or toxic metals recovery³⁰. It is also referenced to be a kinetic inhibitor of crystal growth for calcium oxalate³¹, calcium sulfate³² and calcium phosphate such as hydroxyapatite³³ and a strong complexing agent for lanthanides³⁴ and actinides³⁵. The present study focuses on the impact of this phosphonate additive on plutonium oxalate crystallization. When in contact with metal ions, phosphonates form stable and water soluble complexes as hybrid inorganic–organic frameworks^{36,37}. This property was used here to modify plutonium (III) oxalate crystalline nucleation and growth, and, therefore, its morphology.

A preliminary work was first carried out on neodymium (III) oxalate, in order to anticipate, to a certain extent by analogy, plutonium oxalate behavior before assessing it. Reference experiments - without NTMP - were also systematically performed for easiest comparison.

EXPERIMENTAL SECTION

Precursors

Because of the radioactive nature of actinides, especially plutonium, the experiments involving this element were carried out in glove boxes with very restrictive protocols. Plutonium(IV) and plutonium(III) solutions were prepared using the following specific procedures. The Pu(IV) solution was prepared by dissolving PuO₂ oxide in concentrated HNO₃. The Pu(III) solution was synthesized by reducing the Pu(IV) solution by hydrazinium nitrate (N₂H₅⁺, NO₃⁻) at 50 °C. Hydrazinium nitrate was also used as an anti-nitrous agent to stabilize the trivalent oxidation state of plutonium.

The concentration of plutonium in these solutions is $1 \text{ mol} \cdot \text{L}^{-1}$ and that of hydrazinium cations, in the plutonium(III) solution, is $0.2 \text{ mol} \cdot \text{L}^{-1}$. The concentration, purity and oxidation state of plutonium in these primary solutions were essentially determined by UV-visible spectroscopy.

Neodymium nitrate salt (Aldrich, 99.9% Reagent Grade Nd(NO₃)₃·6H₂O) was used when appropriate to prepare Nd(III) solutions to simulate Pu(III) solutions in pseudo-active experiments, on considering the analogies between Ln(III) and An(III) ions^{26,38,39}. NTMP (Aldrich, >97 %) and oxalic acid (Aldrich, 98 %) were used as received, without further purification.

Oxalate precipitation experiments

Solutions A were first prepared by adding various amounts of NTMP ([NTMP]/[Nd]=0, 0.167, 0.33, 0.5, 0.67, 1 and [NTMP]/[Pu]=0, 0.33, 0.5) to an acidic solution (1M) of neodymium (III) or plutonium (III) (0.16 M). As NTMP tends to precipitate with neodymium and even more with plutonium, the acidity of solutions A was adjusted with various amounts of nitric acid, so as to prevent this precipitation. The nitric acid concentration (mol/L) in each solution versus the ratio [NTMP]/[Nd] or [NTMP]/[Pu] is summed up in table 1. With plutonium, the NTMP-Pu precipitation could not be completely prevented by higher acidification. The solutions A containing plutonium were therefore filtered off before using.

Neodymium (III) and plutonium (III) oxalates were precipitated at around 20 °C, by adding simultaneously the considered solution A and a nitric solution of oxalic acid (solution B- $[H_2C_2O_4] = 0.54 \text{ M} - [HNO_3] = 1\text{ M}$) into a nitric solution containing a slight excess of oxalic acid (solution C - $[H_2C_2O_4] = 0.15 \text{ M} - [HNO_3] = 1\text{ M}$), in order to maintain a constant

 oxalic concentration in the vortex during the precipitation. Time of addition and aging were both fixed at 10 minutes as the reference.

For [NTMP]/[Nd]=0.5, the influence of aging time (1 min to 24 hrs) and temperature (5 to 35°C) was also investigated.

Table 1: Nitric acid concentrations (mol/L) in solutions A versus the [NTMP]/[cation]

ratio and sum up of the structure and morphology of the precipitated solids.

	[NTMP]/[cation]	[HNO ₃] _A	Structure	Morphology
Nd	0	1	$Nd_2(C_2O_4)_3(H_2O)_6 \cdot 4H_2O$	Rod-like particles
	0.167			
	0.33		$Nd_2(C_2O_4)_3(H_2O)_6\cdot 4H_2O$	Spherical
	0.5	3.8	+	agglomerates
	0.67		$(Nd_2(C_2O_4)_3(H_2O)_6 \cdot 12H_2O)_6 \cdot 12H_2O$	
	1	3.8		Small particles
	1	5.0	amorphous	without defined shape
Pu	0	1		Rod-like particles
	0.33	3.8		Sphere-like
	0.55			agglomerates
	0.5	2		Sphere-like
	0.5			agglomerates

After 10 minutes of precipitation by mixing solutions A, B and C, followed up by 10 min of maturation, fine pale purple powder of neodymium compounds and blue to green/blue powder of plutonium compounds are obtained (Figure 1). Those powders are filtered off on a Buchner funnel under vacuum and then dried during 24 hours at room temperature.





Figure 1: Neodymium oxalate (a) and plutonium oxalate (b) powders obtained without additive

Thermal conversion

In some cases, a heat treatment of the as-obtained oxalates was carried out in a tubular furnace. The samples were calcined at 1098 K under flowing air, at a heating rate of 10° .min⁻¹.

UV-visible analysis

The acidified solutions A were analyzed by UV-vis spectroscopy to study the complexation of neodymium or plutonium by NTMP, using a spectrophotometer Cintra 10^e CBG. For neodymium, the analysis is direct (PMMA UV-cuvette, 1 cm optical path), whereas for plutonium, the optical signal is transmitted through optical fibers (10 m length, Hellma) from the disposable UV-cuvette (PMMA, 0.2 cm optical path) inside the glove-box to the spectrophotometer placed outside. Solution is scanned from 350 to 900 nm with a speed of 270 nm/min, a measuring range of 0.479 nm and a gap width of 1.5 nm. Additional ratios of [NTMP]/[Nd] and [NTMP]/[Pu] compared to ratios chosen for the precipitation experiments were studied, in order to get a sufficient number of data to simulate the spectra by

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chemiometry, following an algorithm developed by Pochon *et al.*⁴⁰. This method gives information about the number of species in solution and complex constants.

XRD acquisition

After precipitation, compounds were characterized by X-ray powder diffraction (XRD). XRD data were obtained with a BRUKER D8 Advanced diffractometer (LynxEye detector) in Bragg Brentano θ - θ mode using Cu-K α radiation (λ =1.5418 Å). Each powder pattern was recorded within an angular range of 5°-60° in 2 θ , with steps of 0.02° and a counting time of 0.5 s per step.

The stripping of the K α 2 radiation according the Rachinger method as well as the baseline and angle shift corrections were done using empirical calculations and DIFFRAC^{plus} EVA software⁴¹. Plutonium oxalates were mixed with an epoxy resin to prevent contamination spreading. Silicon was added to the samples as an internal standard to calibrate the angular positions of the observed XRD lines.

In order to study the broadening of some peaks, powder patterns of some neodymiumcontaining oxalates were recorded with a RIGAKU-SMARTLAB X-ray diffractometer in θ – θ mode using Cu–K_a radiation within the angular range 5°-50° in 2 θ , with steps of 0.01° and a counting time of 0.3 s per step. Refinement was realized using the powder option of JANA 2006⁴².

SEM analysis

The SEM analyses of neodymium compounds were performed on a Hitachi-S3400N microscope, equipped with a tungsten filament (acceleration voltage = 15 kV, secondary electron mode, working distance = 5 to 10 mm). Plutonium compounds were studied on a

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Zeiss Supra 55/55VP field-emission scanning electron microscope (acceleration voltage = 5 kV, secondary electron mode, working distance 5 to 10 mm, diaphragm= 30 μ m). When EDS analyses were performed, the following conditions were chosen: acceleration voltage = 15 kV, working distance 8.6 mm, diaphragm= 240 μ m. Both with neodymium and plutonium based samples, powders were coated with gold prior to the analysis.

Infrared spectroscopy

The neodymium solids were analyzed by IR spectroscopy using a Perkin Elmer Spectrum Two, equipped with a single reflection attenuated total reflectance, between 4000 and 400 cm⁻¹ with a 1 cm⁻¹ resolution.

Thermogravimetric analysis

For neodymium oxalates, the thermogravimetric analyses (TGA) were carried out on a thermoanalyser 92 SETARAM TGA up to 700 °C, with a platinum crucible, under air conditions and with a heating rate of 5°C.min⁻¹. Thermogravimetric analyses of plutonium precipitates were performed on a NETZSCH STA 409C thermal analysis system with an alumina crucible up to 950°C, under argon flow and with a heating rate of 20°C min⁻¹. The normalized weight loss is calculated considering the mass/final oxide mass ratio (normalized weight loss = 1 for final oxide).

Specific Surface area (BET)

The specific surface area was measured at 77 K by the BET method with a MICROMERITICS ASAP 2020 (surface area and porosity analyser).

RESULTS

Characterization of solutions A (neodymium/plutonium + NTMP in nitric acid medium)

Neodymium -NTMP interactions

UV-vis analyses performed on Nd(III)-NTMP nitric acid solutions (solutions A) revealed the complexation of neodymium by NTMP (Figure 2). Indeed, the Nd characteristic spectrum evolves as NTMP concentration increases, evidencing modifications of the cation coordination. For example, absorption bands at 740 and 795 nm are shifted toward higher wavelengths, which are characteristic of ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$ and ${}^{4}I_{9/2} \rightarrow {}^{4}F_{3/2}$ transitions, respectively⁴³.

The UV-visible spectra were analyzed and interpreted by modeling factor analysis (MFA) techniques coupled with principal components analysis (PCA). PCA evidenced the formation of a single anionic complex in the form $M(H_{6-n}L)^{n-}$, where M stands for neodymium and L for NTMP. In the pH range studied, H_5L^- and H_4L^{2-} forms of NTMP coexist⁴⁴ and the coordination mode of NTMP in these neodymium complexes could be either monodentate or bidentate³⁴.



Figure 2: UV-vis study of neodymium complexation by NTMP

Plutonium -NTMP interactions

 In Pu(III)-NTMP nitric acid mixtures (solutions A), high acidification up to nearly 4M and NTMP presence did not affect Pu(III) stability. A slight complexation of plutonium(III) by NTMP was shown by UV-vis spectroscopy but the chemiometric study could not give further information on the nature of the complex, due to the fact that even slight amounts of plutonium precipitate with NTMP into the disposable UV-cuvette during the analysis (Figure 3).



Figure 3: UV-vis study of plutonium(III) complexation by NTMP, after removal of the Pu-NTMP precipitate

Oxalic precipitation experiments

Influence of the NTMP content

Without NTMP, in reference precipitation conditions, the expected rod-like neodymium oxalate Nd₂(C₂O₄)₃(H₂O)₆·4H₂O⁴⁵, crystallizing in the monoclinic P2₁/c space group, was obtained as a pure phase (Figure 4a and Figure 5) whereas in presence of NTMP with [NTMP]/[Nd] ratios equal to 0.167, 0.33, 0.5 and 0.67 the additional neodymium oxalate Nd₂(C₂O₄)₃(H₂O)₆·12H₂O⁴⁶, crystallizing in the rhombohedral R $\overline{3}$ space group, was observed (Figure 5). Increasing the [NTMP]/[Nd] ratio decreases the Nd₂(C₂O₄)₃(H₂O)₆·4H₂O content

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to the benefit of Nd₂(C₂O₄)₃(H₂O)₆·12H₂O until reaching [NTMP]/[Nd]=1 for which a X-Ray amorphous compound was obtained (Figure 5). The oxalic precipitation from complexed neodymium, with [NTMP]/[Nd] ratios equal to 0.167, 0.33, 0.5 and 0.67, led to spherical agglomerates of about 8 μ m in diameter made of the radial agglomeration of thin hexagonal rods assumed to be the neodymium oxalate Nd₂(C₂O₄)₃(H₂O)₆·12H₂O⁴⁶ (Figure 4b-e). Some XRD peaks of Nd₂(C₂O₄)₃(H₂O)₆·12H₂O, such as those located at 2θ = 13.9 (2-21) and 15° (211), are very broad compared to the others, indicating a strong anisotropy of either crystallite size or microstrains (or both) within the observed sample. For the ratio [NTMP]/[Nd]=1, the pattern is characteristic of an amorphous phase, and related to small particles without defined shape on SEM images (Figure 4f).



Figure 4: SEM analyses of neodymium oxalates precipitated with various amounts of NTMP: [NTMP]/[Nd] = a) 0, b) 0.167, c) 0.33, d) 0.5, e) 0.67 and f) 1



Figure 5: Powder X-Ray Diffraction analyses of neodymium samples precipitated with various amounts of NTMP ([NTMP]/[Nd] = 0, 0.167, 0.33, 0.5, 0.67, 1). Peaks under dashed lines correspond to $Nd_2(C_2O_4)_3(H_2O)_6 \cdot 12H_2O^{46}$. Other peaks belong to the $Nd_2(C_2O_4)_3(H_2O)_6 \cdot 4H_2O^{45}$.

The anisotropic line broadening of X-ray peaks was thoroughly investigated for the [NTMP]/[Nd]=0.5 sample. Full powder pattern matching refinement was done considering the two phases with Le Bail method⁴⁷. The peak profile of Nd₂(C₂O₄)₃(H₂O)₆·4H₂O was modeled using a conventional Pseudo-Voigt function, whereas the peak profile of Nd₂(C₂O₄)₃(H₂O)₆·12H₂O was refined using a [001] broadened Pseudo-Voigt function. After deconvolution of the broadening due to the instrument (estimated using a LaB₆ NIST standard), Williamson-Hall analysis was performed and lead to platelets with sizes along a and b around 140 nm to compare to 6 nm in the perpendicular direction, i.e. a very anisotropic size, as expected. Refined cell parameters for this phase are a=31.204(4) and c=7.317(13) Å (space group R3), and a=11.197(6) b=9.640(4), c=10.272(6) Å and β=114.40(4) (space group P2₁/c), for Nd₂(C₂O₄)₃(H₂O)₆·4H₂O. The X-ray pattern, as well as a scheme of the obtained morphology is reported Figure 6.



Figure 6 : Final LeBail plot of the sample precipitated for [NTMP]/[Nd]= 0.5 and platelets scheme. Observed data points are indicated as circles; the best-fit profile and the difference are drawn as upper trace and lower blue trace, respectively. Vertical bars indicate the angular positions of the allowed Bragg reflections for $Nd_2(C_2O_4)_3(H_2O)_6.4H_2O$ (lower bars) and $Nd_2(C_2O_4)_3(H_2O)_6.12H_2O$ (upper bars) phases.

The FTIR spectra of the different precipitates are quite similar and characteristic of oxalate compounds (Figure 7). Indeed, the broad absorption band around 3240 cm⁻¹ corresponds to stretching vibration of O-H bonds of coordinated water molecules, whereas the intense peak at 1605 cm⁻¹ is due to the combined effects of distortion vibrations in the water molecules plane and of asymmetric stretching vibration of C=O bonds of oxalate groups⁴⁸. The 1360 and 1316 cm⁻¹ peaks correspond to symmetric O-C-O stretching vibration. Finally, the metal-oxygen bonds are confirmed by the presence of peaks at 800 and 490 cm^{-1 49}. The main differences between these spectra are observed in the 1250-800 cm⁻¹ range and for a [NTMP]/[Nd] ratio of 1, large peaks at 1169, 1038 and 885 cm⁻¹ are observed whereas for other ratios these absorption bands are weak. These bands don't match with spectra of neodymium oxalates but with the stretching mode of phosphorus-oxygen bonds⁵⁰ and indicate the presence of phosphorous in the precipitated solid, coming the most probably from NTMP or NTMP degradation products. The amount of phosphorous is higher in the precipitate obtained for [NTMP]/[Nd] ratio of 1.



Figure 7: IR analyses of neodymium powders precipitated with various amounts of NTMP ([NTMP]/[Nd] = 0, 0.167, 0.33, 0.5, 0.67, 1). Peaks in dashed boxes correspond to the phosphorus-oxygen bonds.

Influence of the temperature

For the ratio ([NTMP]/[Nd]=0.5), for which spherical agglomerates are obtained, the influence of temperature was further investigated by precipitating powders at 5, 20 and 35 °C. At the lowest temperature, the Nd₂(C₂O₄)₃(H₂O)₆·12H₂O phase is obtained as a major phase containing small amounts of Nd₂(C₂O₄)₃(H₂O)₆·4H₂O (Figure 8). The powder X-Ray patterns exhibit the as previously described broadening of the peaks located at 13.9° and 15.1°. As the temperature increases, the amount of Nd₂(C₂O₄)₃(H₂O)₆·4H₂O increases and the relative intensities of the powder XRD pattern of the Nd₂(C₂O₄)₃(H₂O)₆·12H₂O phase tend to be similar to that expected from the calculated diagram. The structural changes are accompanied by microstructural modifications in that the smooth spheres observed at 5°C disappear to give rise to thin hexagonal rods at 35°C.



Figure 8: XRD analyses of neodymium powders precipitated with an amount of [NTMP]/[Nd] = 0.5 for various precipitation temperatures (5, 20, 35 °C). Peaks under dashed lines correspond to $Nd_2(C_2O_4)_3(H_2O)_6 \cdot 12H_2O^{45}$. Other peaks belong to $Nd_2(C_2O_4)_3(H_2O)_6 \cdot 4H_2O^{46}$.

Influence of the aging time

Same effects are observed by varying the aging time. At the first step, a X-ray amorphous compound forms. When precipitation is carried out within a few minutes to 5 hours, smooth spheres of $Nd_2(C_2O_4)_3(H_2O)_6\cdot 12H_2O$ are precipitated. A longer aging time increases the crystallinity of $Nd_2(C_2O_4)_3(H_2O)_6\cdot 12H_2O$ and replaces the spheres by isolated thin rods corresponding, at 24 hours, to a mixing of $Nd_2(C_2O_4)_3(H_2O)_6\cdot 4H_2O$ and $Nd_2(C_2O_4)_3(H_2O)_6\cdot 12H_2O$ (Figures 9 and 10). X-Ray fluorescence combined with XRD and SEM analyses show evidence that a high phosphorus content is maintained as long as the X-ray amorphous compound and the spheres of $Nd_2(C_2O_4)_3(H_2O)_6\cdot 12H_2O$ are found in the solid phase. X-Ray fluorescence analyses support that the amount of NTMP decreases as maturation proceeds (Figure I, SI).

Therefore, the structure, composition and microstructure of neodymium oxalate synthesized with NTMP evolve with the aging time as if NTMP was initially inhibiting the crystal growth of $Nd_2(C_2O_4)_3(H_2O)_6\cdot 4H_2O$ to the benefit of the metastable $Nd_2(C_2O_4)_3(H_2O)_6\cdot 12H_2O$ neodymium oxalate, characterized by sphere shape particles, which progressively transforms into rod-like particles of $Nd_2(C_2O_4)_3(H_2O)_6\cdot 4H_2O$ neodymium oxalate. Under ambient conditions, the metastable $Nd_2(C_2O_4)_3(H_2O)_6\cdot 12H_2O$ neodymium oxalate evolves towards $Nd_2(C_2O_4)_3(H_2O)_6\cdot 4H_2O$ neodymium oxalate.



Figure 9: XRD analyses of neodymium powders precipitated with an amount of [NTMP]/[Nd] = 0.5 for various aging times (1 min, 4 min, 8 min, 30 min, 5h and 24 h). Peaks under dashed lines correspond to the $Nd_2(C_2O_4)_3(H_2O)_6$ ·12H₂O phase⁴⁶. Other peaks marked by squares belong to $Nd_2(C_2O_4)_3(H_2O)_6$ ·4H₂O phase⁴⁵.



Figure 10: SEM analyses of neodymium powders precipitated with an amount of [NTMP]/[Nd] = 0.5 in function of aging time (1 min, 8 min, 30 min, 5h and 24 h)

Influence of the trivalent element

As for neodymium(III), the oxalic precipitation of plutonium(III) in an aqueous solution acidified by HNO₃ leads to the formation of $Pu_2(C_2O_4)_3(H_2O)_6\cdot 4H_2O$ exhibiting a rod-like morphology (Figures 11a and 12).

By oxalic precipitation of NTMP- plutonium(III), sphere-like agglomerates of about 20 µm diameter were obtained (Figure 11 b-c). However, in this case, they are heterogeneous in terms of morphology and composition.

Regardless of the [NTMP]/[Pu] ratio, two morphologies are visible within the sphere-like agglomerates. They are mainly composed of thin needles (Figure 11b) and of some small particles (Figure 11c). According to XRD analysis, the spherical agglomerates mainly consist of $Pu_2(C_2O_4)_3(H_2O)_6$ ·4H₂O, but deviation of the baseline reveals the presence of an amorphous compound (small particles). For [NTMP]/[Pu]=0.5, a third morphology is also visible in the powder, based on tabular particles (Figure 11b) and corresponding to a third phase, which does not match to any phase referenced in the literature (Figure 12). The

corresponding XRD peaks were indexed in a monoclinic symmetry by the McMaille software⁵¹, and its unit cell parameters were refined with a=17.658(3) Å, b=9.862(2) Å, c=8.623(1) Å and β =112.48(1) °, corresponding to a cell volume of 1387.5(3) Å³. The lack of information about this phase does not permit to solve the structure from the XRD powder pattern.





Numbers correspond to the three identified morphologies: 1=needles, 2=small particles, 3= tabular particles



Figure 12: XRD analyses of plutonium powders precipitated in various conditions:
a) [NTMP]/[Pu] = 0, [HNO₃]A = 1 mol/L ; b) [NTMP]/[Pu] = 0.5, [HNO₃]A = 2 mol/L ;
c) [NTMP]/[Pu] = 0.33, [HNO₃]A = 3.8 mol/L.
Peaks under dashed lines topped by squares correspond to Pu₂(C₂O₄)₃(H₂O)₆·4H₂O, peaks under dashed lines topped by triangles correspond to the unknown phase.

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Calcination of oxalates into oxides

Spherical agglomerates of neodymium oxalate synthesized for [NTMP]/[Nd]=0.5 were converted into oxides by heating at 800 °C in air. During this thermal treatment, spherical morphology of the oxalate precursor was kept (Figure 13). At the same time, the specific area of the neodymium oxide increased from 2.5 m^2/g for the rod-like particles (obtained from oxalate synthesized without NTMP) to 12 m^2/g for the spherical particles.

In parallel, TG analyses were performed on this sample (Figure 13). Its thermal decomposition exhibits one main difference with the reference-sample (without NTMP), i.e. a higher initial dehydration. This can be explained by the presence of the dodecahydrate phase $Nd_2(C_2O_4)_3(H_2O)_6\cdot 12H_2O$ which contains a higher amount of non-coordinated water molecules than $Nd_2(C_2O_4)_3(H_2O)_6\cdot 4H_2O$. The second step of decomposition is similar to the one observed for the reference compound and corresponds to the departure of the oxalate groups at around 400 °C, accompanied by the release of CO and CO₂. In agreement with the XRD analyses, Nd_2O_3 is accompanied with small amounts of Nd_3PO_7 which indicates that phosphorous remains in the compound despite the thermal treatment (Figure II SI).



Figure 13: TG analyses under air of neodymium powder precipitated for [NTMP]/[Nd] = 0.5 at 20 °C and SEM pictures of the oxalate precipitate and the resulting oxide after thermal treatment.

Concerning the Pu system, the thermal conversion into oxides was performed by heating the precipitated oxalates, in air. The oxides XRD analyses indicate that PuO_2 is accompanied with small amounts of $PuPO_4$, which confirms that as for neodymium system, some amount of phosphorous remains in the oxides despite the thermal treatment (Figure III, SI). As for neodymium, the spherical morphology of the plutonium oxalate synthesized with [NTMP]/[Pu]=0.33 and $[HNO_3]A=3.8$ M was kept during its thermal transformation into oxide (Figure 14).



Figure 14 : SEM analyses of plutonium oxalate synthesized with [NTMP]/[Pu] = 0.33 and a nitric acid concentration of 3.8 M in solution A, at 25 °C, and of the oxide resulting from its calcination at 950 °C under air.

Precipitation of sphere-like agglomerates of neodymium oxalate

In regard of the reported results and a previous work on the template free synthesis of zinc oxide hollow spheres⁵², a growth mechanism of neodymium oxalate in presence of NTMP is proposed. This envisaged mechanism is summarized Figure 15.

Firstly, when contacting the neodymium and NTMP, a Nd-NTMP complex is formed. This acts the most probably as a nanoreservoir of neodymium, which slowly releases its neodymium content, when the solution is put into contact with oxalate. This initial complex formation strongly modifies the Nd-oxalate nucleation step and leads to the formation of a X-ray amorphous submicronic compound made of neodymium, phosphonate and oxalate which composition evolves in contact of oxalate ions in solution to the dodecahydrate oxalate Nd₂(C₂O₄)₃(H₂O)₆·12H₂O then to the decahydrate oxalate Nd₂(C₂O₄)₃(H₂O)₆·4H₂O. The input of neodymium from the inside to the surface of the first nuclei and the subsequent crystallizations of Nd₂(C₂O₄)₃(H₂O)₆·12H₂O and Nd₂(C₂O₄)₃(H₂O)₆·4H₂O are accompanied by the formation of hollow spheres successively composed of an assembly of dots, hexagonal platelets and, finally, thin rods with hexagonal section.

At first, the slow diffusion of neodymium may limit the kinetic of reaction and favor the formation of small particles of $Nd_2(C_2O_4)_3(H_2O)_6 \cdot 12H_2O$ which agglomerate into a spherical structure. At this stage, the crystal growth of $Nd_2(C_2O_4)_3(H_2O)_6 \cdot 12H_2O$ is confined in the [001] direction and the particles are allowed to grow in two directions, leading to thin hexagonal plates. This two-dimensional growth, which leads to the strong anisotropy visible on the XRD patterns, can be explained by the inhibition of the (001) faces by NTMP which precludes the crystal growth in this direction.

Once NTMP starts to be released, the hydrated oxalate is allowed to grow in the third direction, and hexagonal plates give rise to rods with hexagonal section.

When growth is favored by an increase of either the precipitation temperature or the precipitation time, the rods would finally break away from the initial amorphous support. However, even a small disturbance of the precipitation conditions (local supersaturations, kinetic changes...) would preferentially lead to the crystallization of the most stable phase, that is to say the decahydrate $Nd_2(C_2O_4)_3(H_2O)_6\cdot 4H_2O$. Even if no evidence supports strongly this interpretation, it provides the advantage of suggesting a mechanism in quite good agreement with the experimental results concerning the morphology of the precipitated compounds.



Figure 15: Proposed mechanism for the growth of hollow spheres of Nd₂(C₂O₄)₃(H₂O)₆·12H₂O in presence of NTMP

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Precipitation of sphere-like agglomerates of plutonium oxalate

The thorough study on the neodymium surrogate system enabled to propose a mechanism based on the same principle for spherical plutonium oxalate precipitation. The complexation of plutonium by NTMP in solution A, prior to the oxalic precipitation, would enable the formation of an amorphous compound with oxalic acid and could then delay the release of plutonium during the oxalic precipitation. However, if the dodecahydrate phase $Nd_2(C_2O_4)_3(H_2O)_6\cdot12H_2O$ was obtained with neodymium, for plutonium system, an unknown monoclinic phase with parameters a=17,658(3) Å, b=9,862(2) Å, c=8,623(1) Å, β =112,48(1)° was precipitated. The appearance of this unknown monoclinic phase could be favored by the slow release of plutonium in presence of NTMP but an additional explanation can be proposed since the plutonium system is more complex than the neodymium one. Indeed, the tetravalent form of plutonium is stable in nitric acid medium whereas the stabilization of trivalent plutonium requires the presence of hydrazinium ions. These monovalent cations might be involved, with plutonium and oxalate, in the precipitation of the original monoclinic compound.

Also, the complexation of tetravalent elements by NTMP is very strong, it is therefore possible that the presence of small amounts of Pu(IV) in solution leads to the formation of insoluble NTMP-Pu precipitates which would explain the small particles observed in the final solid.

Finally, the plutonium system is more sensitive to supersaturation and temperature or acidity variations, which could explain that $Pu_2(C_2O_4)_3(H_2O)_6\cdot 4H_2O$ precipitation is favored and that the intermediate stage of crystallization is hard to observe.

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In this study, we firstly managed to modify neodymium oxalate structure and morphology by adding a phosphonate, NTMP, into the precipitation medium. Depending upon the NTMP/Nd ratio and/or aging different crystallinity, morphology, particles size distributions of precursor oxides were found starting from submicronic particles to spherical agglomerates composed of dots, hexagonal platelets or thin hexagonal rods instead of the rodlike particles usually obtained in absence of additive. The formation of hollow sphere can be explained by a two-steps process of nucleation/growth involving the formation of complex as metastable intermediate which favors formation an the of a compound, $Nd_2(C_2O_4)_3(H_2O_6) + 12H_2O_6$. This approach of solution phase synthesis of oxide precursor is quite interesting in that the morphology obtained the precipitation stage is kept during the calcination process.

Despite some differences in the complexation with NTMP and complexity from redox, the use of NTMP was successfully transposed to the plutonium system. Spherical agglomerates of plutonium(III) oxalate were so obtained, leading to spherical agglomerates of PuO_2 plutonium oxide after thermal treatment. The PuO_2 squared particles commonly synthetized by oxalic route are replaced by spherical agglomerates. Then, varying the conditions of oxalic precipitation, it is possible to obtain unusual morphologies of PuO_2 , highlighting the flexibility of this conversion method.

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SUPPORTING INFORMATION

The X-Ray fluorescence analysis of the precipitate versus the aging time and XRD powder patterns of the Nd

and Pu oxides are available in the supporting information. This information is available free of charge via the

Internet at http://pubs.acs.org.

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From Nd(III) and Pu(III) Oxalates to Oxides: Influence of NitriloTris(MethylenePhosphonic acid) on Chemical Composition, Structure and Morphology.

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SYSNOPSIS TOC

The chemical composition, structure and morphology of neodymium and plutonium oxalates have been modified by adding a complexing agent (NTMP) in the precipitation medium. The Nd/Pu complexation has been evidence by UV-visible spectroscopy and leads to sphere-like agglomerates precipitation instead of rod-like particles.

