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Influence of additives on the structure and microstructure of lanthanides and actinides oxalate

Influence d'additifs sur la structure et la microstructure d'oxalates de lanthanides et d'actinides

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Résumé : La conversion oxalique du plutonium, bien connue de l'industrie nucléaire, consiste à précipiter le plutonium initialement en solution avant de le calciner en oxyde. La morphologie de l'oxyde final étant fortement corrélée à celle de l'oxalate précurseur, le contrôle des propriétés structurales et morphologiques de l'oxalate dès l'étape de précipitation est essentiel. L'étude de l'influence d'additifs dans le milieu réactionnel a permis de montrer que l'utilisation d'acide nitrilotriméthylphosphonique (NTMP) permettait de modifier significativement la structure et la microstructure lors de la précipitation d'un oxalate de néodyme (III), simulant non radioactif des oxalates d'actinides (III).

Summary: Oxalic conversion is a well-known process in the nuclear industry where it is used for precipitating plutonium as an oxalate thereafter calcinated into an oxide. As there is a strong relationship between the morphology of the oxalate precursor and that of the resulting oxide, it is of interest to control the oxalate structure and microstructure during the precipitation step. The influence of additives on the precipitation of neodymium (III) oxalates, non-radioactive analogs of actinides (III) oxalates, was explored. With the use of nitrilotrimethylphosphonic acid (NTMP), the structure and microstructure of the neodymium oxalates are different from that obtained without additive.

Keywords: oxalate, lanthanide, actinide, additive, precipitation

Saving uranium resources and reducing the amount and radiotoxicity of wastes are major challenges for the nuclear industry. As valuable elements are present in the spent nuclear fuel, their recycling is considered. This requires separating the valuable elements from the solution, transforming them into a solid phase thereafter shaped to obtain new nuclear fuel pellets. Since the shaping depends on the solid phase morphology, this study aims to control it in the first step of the process.

Le recyclage des éléments valorisables du combustible nucléaire usé permet (i) d'économiser les ressources (ii) de réduire la quantité et la radiotoxicité des déchets, enjeux majeurs de l'industrie nucléaire. La re-fabrication du combustible à partir de matières recyclées impose, en amont, de séparer les éléments valorisables puis de les transformer en un solide. La morphologie du solide influant fortement la mise en forme du combustible, cette étude s'intéresse au contrôle de cette morphologie.

1 Introduction

Current researches for new generations of nuclear plants (Gen III and IV) focus on the spent nuclear fuel recycling in order, both, to reduce the radiotoxicity of ultimate wastes and to save uranium resources. Actinides which are present in the spent fuel are valuable elements that can be used to fabricate new nuclear fuel pellets or transmutation targets. In the current process the spent fuel is dissolved in nitric acid, the valuable elements are separated and purified, so two flows containing either uranium or plutonium are obtained. The transfer of plutonium from nitric solution into a solid phase is ensured by oxalic precipitation and the transformation of the so-obtained plutonium oxalate

into oxide is done by calcination. As the transformation from oxalate into oxide is pseudomorphic [1], a careful control of the oxalate morphology helps to control the final oxide microstructure. The understanding of physico-chemical parameters effects, like temperature or influence of additives, on oxalic precipitation is crucial. Indeed, from this precipitation step it is possible to drive and control the microstructural properties of the resulting oxide, which then influence the shaping of fuel pellets.

The literature reports that the use of some additives such as glycerol [2] or surfactants [3] can modify the morphology of copper or calcium oxalates. Among these studies nitrilotrimethylphosphonic acid (NTMP) is

referenced to influence the kinetic and morphology of calcium oxalate or sulfate precipitation [4][5] and to be a complexing agent for lanthanides [6]. The study aims to explore the influence of NTMP on the structure and microstructure of neodymium oxalate, used as non-radioactive analog of trivalent actinides. This paper reports the results obtained by varying the aging time for a given ratio Nd/NTMP.

2 Experimental/Methodology

The temperature was fixed at 15°C for all the experiments. Neodymium (III) oxalates were precipitated in nitric acid (3M) by adding simultaneously neodymium (III) nitrate ($\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Alfa Aesar, 99.9% reagent grade) and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, Chemlab, 99.5% reagent grade) in a vortex reactor containing a slight excess of oxalic acid. When NTMP ($\text{C}_3\text{H}_{12}\text{NO}_9\text{P}_3$, Aldrich, $\geq 97\%$ reagent grade) was used, it was added to the neodymium solution with the ratio $\text{Nd}/\text{NTMP}=2/1$ prior from adding oxalic acid. The study was extended to the influence of the aging time by varying it from 1 minute to 2 weeks. The precipitates were analyzed by X-Ray diffraction and by Scanning Electron Microscopy after filtration and drying in air, at room temperature.

3 Results and discussion

In absence of NTMP and an aging time equal to 10' (reference conditions) a two-dimensional oxalate with formula $\text{Nd}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 4\text{H}_2\text{O}$ is obtained. It crystallizes in a monoclinic system $P2_1/c$ with crystallites in form of rod-like particles 3-8 μm long [7] (fig1a). In presence of NTMP the structure and morphology of the precipitated oxalate are totally different in that spherical agglomerated particles of $\text{Nd}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 12\text{H}_2\text{O}$ ($\varnothing = 4-10 \mu\text{m}$) are obtained (fig1b, fig2a). This three-dimensional compound crystallizes with a rhombohedral symmetry in the space group $R-3$ [8].

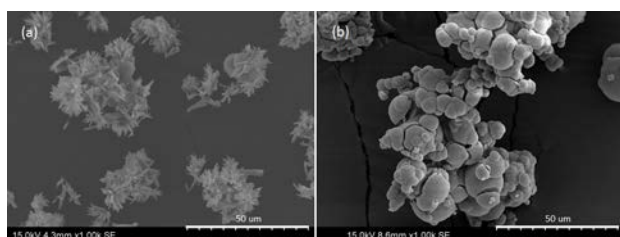


Fig. 1. SEM micrograph of neodymium (III) oxalate obtained (a) Without additive (b) In presence of NTMP

Increasing the aging time from 1' to 2 weeks in presence of NTMP leads to the formation of a mixture of $\text{Nd}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 12\text{H}_2\text{O}$ and $\text{Nd}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 4\text{H}_2\text{O}$. The morphology is also affected since rod-like particles 2-7 long start to appear beyond an aging time of a few hours (fig2b). Above three days aging, the spherical particles are completely replaced by the rod-like particles (fig2c).

Additional XRD analyses of low aged samples initially composed of $\text{Nd}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 12\text{H}_2\text{O}$ let

in air for 6 months shows that this phase progressively disappears to the benefit of $\text{Nd}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 4\text{H}_2\text{O}$, without any change in the microstructure.

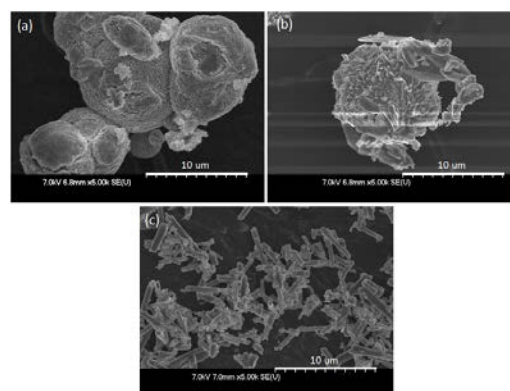


Fig. 2. SEM Micrograph of neodymium (III) oxalate precipitated with NTMP for different aging time (a) 10 minutes (b) 5 hours (c) 72 hours

These experiments have permitted to conclude that $\text{Nd}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 12\text{H}_2\text{O}$ is a metastable compound. It might form intermediately during the precipitation of neodymium oxalate thanks to the competition of NTMP and oxalate anions in complexing the neodymium (III) cations which delays the formation of $\text{Nd}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 4\text{H}_2\text{O}$.

4 Conclusions

The presence of NTMP during the neodymium oxalate precipitation modifies the structure and morphology of the precipitate. Indeed, spherical agglomerates with formula $\text{Nd}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 12\text{H}_2\text{O}$ are obtained instead of rod-like particles, $\text{Nd}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 4\text{H}_2\text{O}$. Although $\text{Nd}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 12\text{H}_2\text{O}$ is metastable, the possibility to change the morphology of a neodymium (III) oxalate with the help of additives was demonstrated. This work is currently extended to other additives and to actinides (III) oxalates.

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