

Synthesis of uranium oxide microspheres under hydrothermal conditions as a reference material for nuclear safeguards

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ABSTRACT

Particle analyses are a key tool for safeguards verification by the International Atomic Energy Agency. Indeed, detection and measurement of the isotopic composition of nanometer- to micrometer-sized particles collected during inspection of nuclear facilities provide precious information on their activities. Because of the low number and extremely small size of the particles of interest, particles analyses are always an analytical challenge. Moreover, laboratories must possess reference materials representative of the analyzed samples, i.e. actinide oxide particles with well-known sizes, densities and isotopic compositions that can be used for optimization and qualification of analytical methods and instruments. In order to prepare such materials, several protocols have already been tested, but frequently all of them require specific equipment and cannot be easily implemented in standard chemistry labs. On this basis, we developed from several years original wet chemistry routes aiming to precipitate directly morphology-controlled actinide oxides from mixtures of solutions under hydrothermal conditions.

In the case of UO_x samples, hydrochloric solution containing tetravalent uranium (natural isotopic composition) was mixed with aspartic acid, used both as complexing and shaping agent, to yield an amorphous uranium(IV) aspartate precipitate. Solid phase and supernatant were then placed under mild hydrothermal conditions (T = 160°C) for 30 hours. A multi-parametric study allowed evidencing the impact of pH, aspartic acid concentration, and mechanical stirring. Optimizing the synthesis conditions led to precipitate monodisperse spherical particles, with an accurately size control in the 400 nm – 2.5 µm range. For all the compounds prepared, further XRD analysis attested the formation of UO₂.nH₂O samples, while TG experiments revealed the presence of residual organics and water. Nevertheless, additional heat treatments performed up to 600°C led to produce anhydrous and carbon-free dense particles without altering their initial morphology. It also enabled to control the final stoichiometry of the particles from UO_{2+x} to U₃O₈ depending on the atmosphere used. Finally, with the aim to store these samples as suspensions before use, alteration tests of the produced particles were undertaken in various media. Preliminary results revealed that only a negligible weight loss occurred after several months in ethanol, while significant modification of the general morphology was observed.

INTRODUCTION

IAEA (International Atomic Energy Agency) ensures the respect of the Treaty on the Non-Proliferation of Nuclear Weapons (NPT) [1] thanks to the inspection of nuclear facilities in various member states. The particles collected on-site are analyzed to provide isotopic information that can help checking declared activities. The samples gathered are further analyzed by a network of support laboratories [2]. In this context, the low number and the small size ($< \mu\text{m}$) of the particles of interest present in the samples still constitute an analytical challenge. The development, validation and qualification of improved analytical methods and instruments (for instance Large Geometry – Secondary Ion Mass Spectrometry, LG-SIMS) then require reference particulate materials with well-known sizes (from 100s of nm to a few μm), density, chemical form (actinide oxides) and isotopic composition [3], [4]. Currently, different methods have been reported for the synthesis of microparticles with controlled sizes and morphology. For example, Hudry *et al.* [5] prepared nanospheres between 1 and 5 nm after thermal decomposition of complexing agent (dibenzyl ether, oleic acid, oleylamine, trioctylamine, trioctylphosphine) with actinide precursor at 280°C. Kumar *et al.* [6] also reported a sol-gel method allowing to produce (U,Pu)O₂ microspheres thanks to the initial gelation of actinide nitrate solution with hexamethylenetetramine and urea followed by a thermal treatment. Last, Middendorp *et al.* [3] have recently qualified particles thanks to spray pyrolysis of a monodisperse aerosol. However, these different methods do not allow yet synthesizing particle on a wide range of sizes, along with an accurate control on the diameter. Moreover, the alteration of these particles in different storage media is still to be studied over long durations (typically several months to years). To solve these issues, we propose a hydrothermal method allowing the synthesis of spherical particles with a diameter ranging from 300 to 2500 nm, using small uranium quantities. In addition, preliminary results concerning the chemical degradation of the particles in wet conditions have been obtained through leaching tests in water and ethanol.

SYNTHESIS OF THE PARTICLES

Uranium oxide microspheres were synthesized through the hydrothermal decomposition of uranium(IV) aspartate. In this aim, hydrochloric solution containing uranium(IV) was mixed with aspartic acid in a 1:3 ratio while the pH was fixed to 2. Then, reactants were transferred in a hydrothermal reactor and heated during 30 h at 160 °C under stirring. As reported by Trillaud *et al.* [7], the stirring rate can be used to control the diameter of the oxide particles between 300 and 2400 nm (figure 1). The data reported in this work in terms of size variation versus the Reynolds number (Re_a) appeared to be in very good agreement with that obtained during previous works, thus evidencing the repeatability of the protocol. Also, Re_a values over 13000 were explored, and revealed that a plateau corresponding to a minimum diameter of about 300 nm was reached.

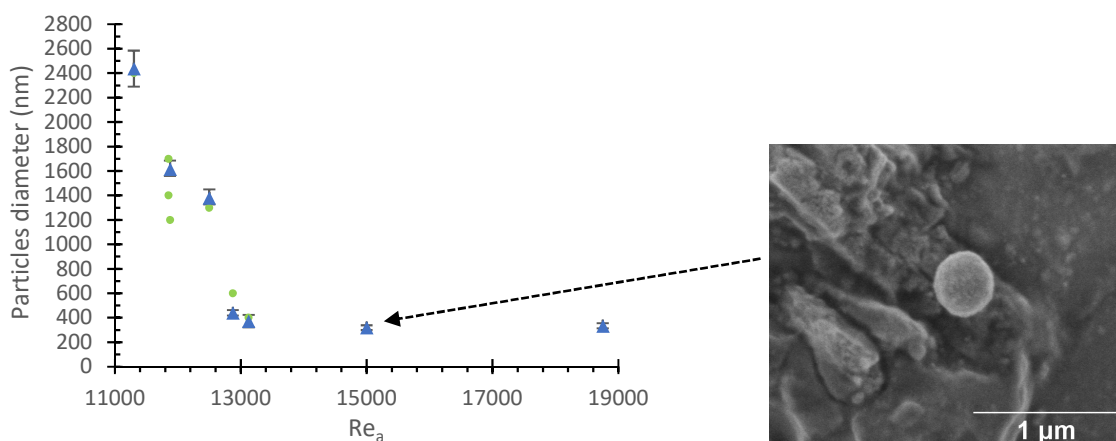


Figure 1. Variation of the particles diameter versus the Reynolds number and SEM micrograph of the particles obtained for $Re_a = 15000$. Blue triangles account for the data obtained in this work while green circles are extracted from Trillaud *et al.* [7].

In addition, with the aim to produce uranium oxide reference particles with enriched uranium isotopies, we extended the protocol with hydrothermal reactors of smaller volumes, i.e. from 23 to 10 and 5 mL. During the downscaling, the spherical morphology and diameter of the particles were preserved. For example, at $Re_a = 11300$, a good conservation of the average particle diameter for the different reactor sizes was observed, even if a slight increase of the size dispersion was noted (2400 ± 220 nm for the 23 mL reactor, 2320 ± 260 nm for 10 mL, and 2200 ± 280 nm for 5 mL). Nevertheless, these results still open the possibility to synthesize particles with small uranium quantities, as low as 25 mg.

THERMAL TREATMENT

After the synthesis of the particles, a thermal treatment step was required to eliminate organic residues and water, and to reduce the remaining porosity. Calcination was achieved at 600°C under air or Ar/H_2 4% during 1 h, resulting in the production of U_3O_8 or UO_2 particles, respectively. Whatever the atmosphere and the final chemical form of the microspheres, SEM observations showed that their general morphology was maintained. Nevertheless, a decrease of the particles diameter of approximately 10 % was evidenced, which highlighted the densification of the particles during the thermal treatment.

CHEMICAL DURABILITY

Finally, in order to forecast the long-term behaviour of the reference particles during storage as suspensions, the chemical durability of our samples was evaluated in various media. Preliminary experiments then consisted in the alteration of UO_2 and U_3O_8 particles with a diameter of 1600 nm in water and ethanol, both with the aim to test the possibility to use

such media for storage and monitor the potential formation of secondary phases following the dissolution of the particles. As it was expected, the first results demonstrate more significant alteration in water than in ethanol. Indeed, approximately 4-5 wt.% were apparently dissolved in water after 300 days against 2 wt.% in ethanol (figure 2). Nevertheless, alteration in water resulted in the quick establishment of a solubility equilibrium, with a concentration close to 0.07 g/L, which could lead to a significant underestimation of the mass dissolved. Indeed, in the same time, the SEM observations undertaken after 8 months demonstrated a total change in the particles morphology, with the formation of large aggregates composed of plate-like crystals. Additionally, XRD analyses were performed on the aged particle and showed the formation of schoepite, as already noted by Kegler *et al.* [8]. Conversely, the particles let in ethanol for more than 300 days did not evidence any change neither concerning their morphology nor their size.

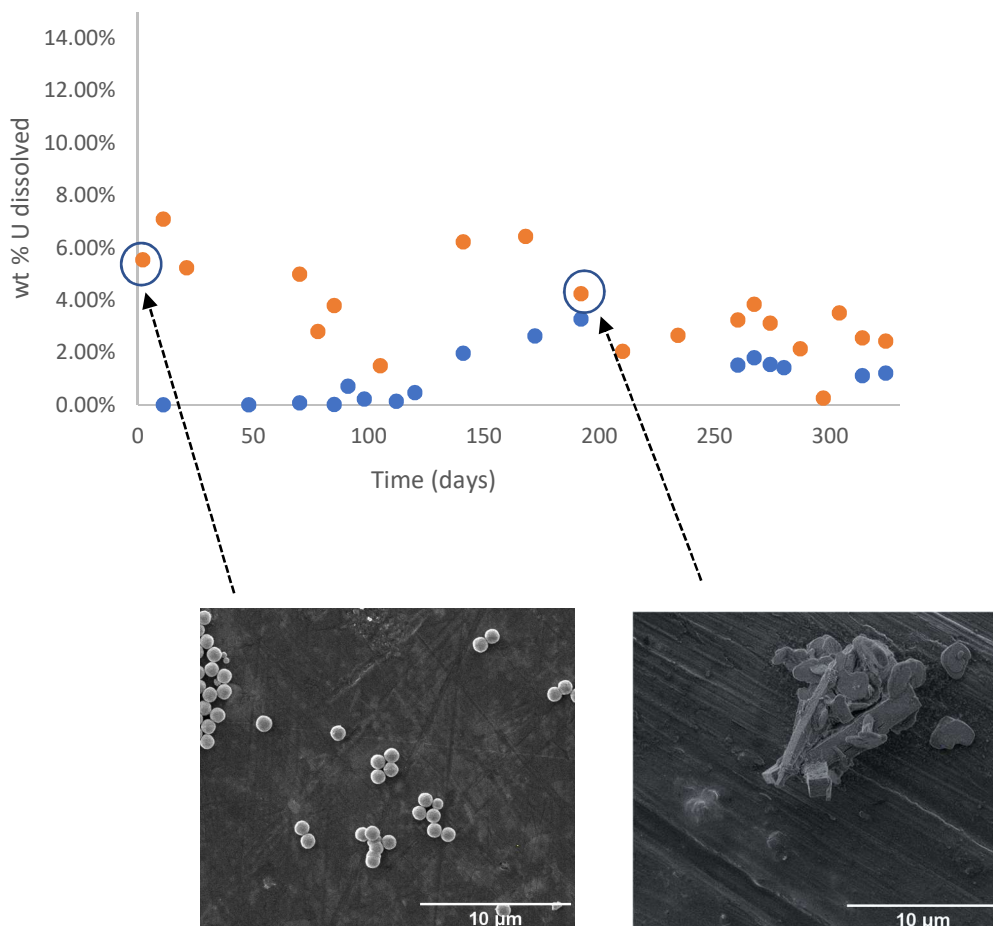


Figure 2. Evolution of the percentage of uranium dissolved during leaching tests in water (orange) and ethanol (blue). SEM micrographs showing the modification of the particles morphology during alteration in water are provided.

CONCLUSIONS

The synthesis process reported herein allowed to simply synthesize uranium oxides microspheres in mild hydrothermal conditions, starting from a mixture of uranium(IV) and aspartic acid. The particle size was controlled by stirring the reacting media, with a minimum diameter of 300 nm reached for $Re_a > 13000$. Moreover, such protocol was validated for different uranium amounts involved, typically from 25 to 100 mg, which paves the way to work with ^{235}U -enriched isotopes. After synthesis, a calcination step at $T = 600^\circ\text{C}$ allowed the elimination of organic residues and the reduction of remaining porosity. Depending on the atmosphere considered, it was also possible to tune the oxide chemical form, from UO_2 to U_3O_8 , without any change of the spherical morphology. Finally, the particles alteration in different media showed a faster alteration in water than in ethanol. The SEM analysis also revealed a strong morphology modification after 8 months in water, associated with the formation of schoepite. These results demonstrate that water is not suitable as a storage medium, and that ethanol has to be preferred, at least for short time periods (i.e. several weeks to several months).

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