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The stability of uranium microspheres for future application as reference standard in analytical measurements

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Abstract

The monitoring of fuel-cycle facilities provides a tool to confirm the compliant operation, for example with respect to emissions into the environment or to supervise non-proliferation commitments. Hereby, anomalous situations can be detected in a timely manner and responsive action can be initiated to prevent an escalation into an event of severe consequence to society. In order to verify non-nuclear weapon states' compliance with the non-proliferation treaty (NPT), international authorities such as the International Atomic Energy Agency (IAEA) conduct inspections at facilities dealing with fissile or fertile nuclear materials. One measure consists of collection of swipe samples through inspectors for later analysis of collected nuclear material traces in the laboratory. Highly sensitive mass spectrometric methods provide a means to detect traces from nuclear material handling activities that provide indication of undeclared use of the facility. There are, however, no relevant (certified) reference materials available that can be used as calibration or quality control standards. Therefore, an aerosol-generation based process was established at Forschungszentrum Jülich for the production of spherical, mono-disperse uranium oxide micro-particles with accurately characterized isotopic compositions and amounts of uranium in the picogram range. The synthesized particles are studied with respect to their suitability as (certified) reference material in ultra-trace analysis. Several options for preparation and stabilization of the particles are available, where preparation of particles in suspension offers the possibility to produces specific particle mixtures. In order to assess the stability of particles, dissolution behavior and isotope exchange effects of particles in liquid suspension is studied on the bulk of suspended particles and also via micro-analytical methods applied for single particle characterization. The insights gained within these studies will form the basis on the choice of the further route towards preparation of uranium particle reference standard and certification as a reference material.

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1. Introduction

Fuel-cycle facilities handling nuclear materials are subject to tight regulation by a number of national and international authorities and measures are implemented to confirm the compliance of the facility with various applicable laws and treaties. Non-nuclear weapon states signatory to the non-proliferation treaty (NPT) are required to subject all nuclear material and nuclear facilities to so-called safeguards administered by the International Atomic Energy Agency (IAEA). The IAEA conducts regular inspections during which on-site measurements are combined with sampling and analysis in dedicated laboratories to confirm nuclear material inventories and transfers declared by the states. Although these inspections provide confidence on the declaration of the facility, undeclared activities might not be detected. Swipe sampling followed by particle analysis provides a tool for the detection of such undeclared activities. Swipe samples taken in facilities are sent to specialized laboratories of the IAEA's network of analytical laboratories (NWAL) in which the samples are scanned for fissile and fertile microparticles and where, if found, the individual particles are measured by dedicated techniques to provide information about the collected material.

In most cases, identified particles containing fissile or fertile material are analyzed with accurate mass spectrometric methods, such as thermal ionization mass spectrometry (TIMS) or secondary ionization mass spectrometry (SIMS) in order to determine the isotopic composition of the particle[2]. Although these methods have proven to provide reliable results, quality control measures are required to ensure the validity of the measurement results. In general four types of quality control measurements are required; (1) calibration, (2) method validation, (3) regular quality control measurements and (4) participation in interlaboratory comparisons[3]. For each of these measures dedicated materials are required, generally in the form of reference materials (RM's). Such materials have a high degree of homogeneity and stability with respect to one or more property values[4]. If a true value is important, for example for calibration, the material is described as a certified reference material (CRM). For such a material, not only the true value is determined accurately, also the stability and inhomogeneity of this value is quantified and included in the expanded uncertainty of the value.

As no suitable reference materials in the form of uranium microparticles exist presently, a particle production process and a dedicated setup was developed able to produce uranium microspheres with a nominal diameter around 1 μm with a specified uranium isotopic composition. Aside from the isotopic composition, the uranium content of a single microparticle is of interest towards optimization of analytical methods. As the produced particles may be well suited for calibration, it is intended to certify the isotopic composition and elemental content and to be able to provide such particles as a CRM. An important parameter in the certification process is the stability of particle properties, which depends on the particle properties but also the way in which kind of packaging the particles are provided.

Nomenclature

α	Degree of reaction
α_C	Predictive detachment factor
β	Void fraction in cluster
η	Dynamic viscosity
ρ	Density
P_C	Void collapse pressure
R_P	Particle radius
t	Time
W_A	Work of adhesion
$X(t)$	$^{235}U/^{238}U$ mass ratio at time t. Subscripts l denotes the liquid phase
x_0	Layer thickness

2. Particle production and characterization

The production of micrometer sized uranium particles is described in detail elsewhere[5,6]. In short, an aerosol is produced from an uranyl nitrate solution with a known isotopic composition. This aerosol is dried and heated to 500 °C in which the formed uranyl nitrate particles are expected to decompose to β-UO_3[7,8]. The particles are collected using a single-stage inertial impactor on either a glass-like carbon disk or a silicon wafer. Although the collected microparticles can be analyzed without further handling, additional processing steps are considered to produce mixtures of particles of various isotopic compositions. The most suitable method to produce such mixtures is by transferring microparticles into a suspension. Although such suspensions also provide advantages towards the homogeneity of the elemental content, the stability of the isotopic composition and uranium content might be decreased. Therefore, a number of preliminary experiments have been performed to examine the suitability of various solutions as matrix for particle suspensions.

In order to determine the stability of the microparticles in a suspension, basic knowledge on the chemical composition and crystal structure of the microparticles is required. Therefore, powder X-ray diffraction (XRD) and X-ray absorption near-edge spectroscopic (XANES) measurements have been performed at the microXAS beamline (PSI, Switzerland). The measurements have been performed on microparticles impacted directly on Kapton foil coated with a thin layer of Apiezon L grease. XRD measurements have been performed using a micro-focused beam (4×1.5 µm) with a photon energy of 17.200 keV (72.08 pm). XANES measurements have been performed with a diffuse 300×300 µm beam at the uranium L3 edge.

The combined XRD patterns (Fig. 1) show a polycrystalline, orthorhombic U_3O_8 phase with some nanocrystalline domains. Other than the orthorhombic U_3O_8 phase, no uranium containing phases have been identified. The reflex at 13.4° is due to the adhesive used for particle collection. XANES measurements yielded spectra with a similar shape to U_3O_8 reference powder. A total of three measurements have been performed over the sample, all of which yielded a similar shape and absorption energy to the U_3O_8 reference. The obtained spectra are shown graphically in Fig. 2. The maximum absorption of all measurements and of the U_3O_8 reference powder was found at 17.180 keV.

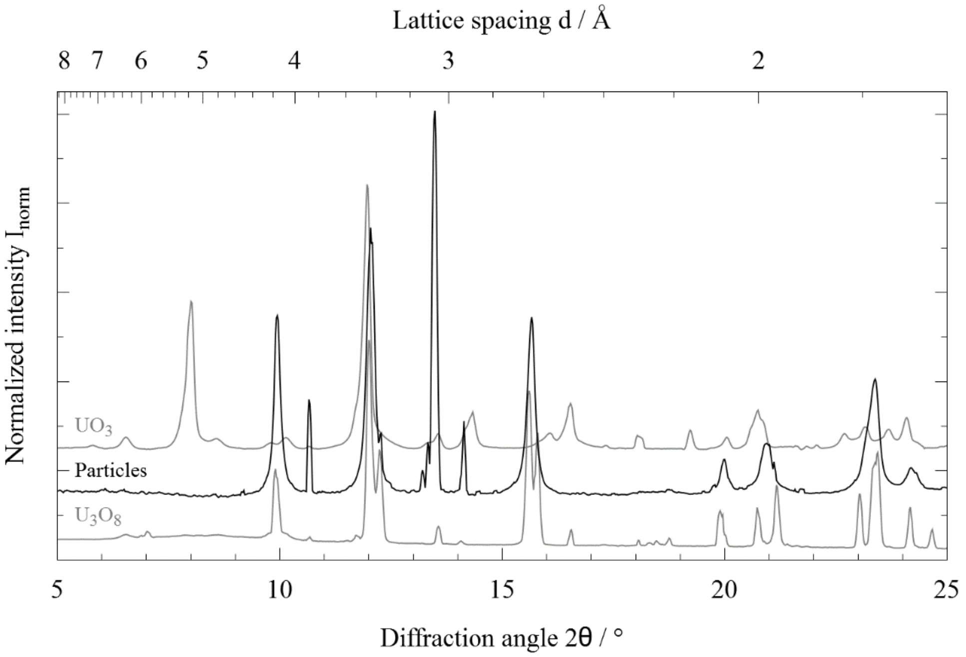


Fig. 1. Integrated XRD patterns of 17 individual microparticles.

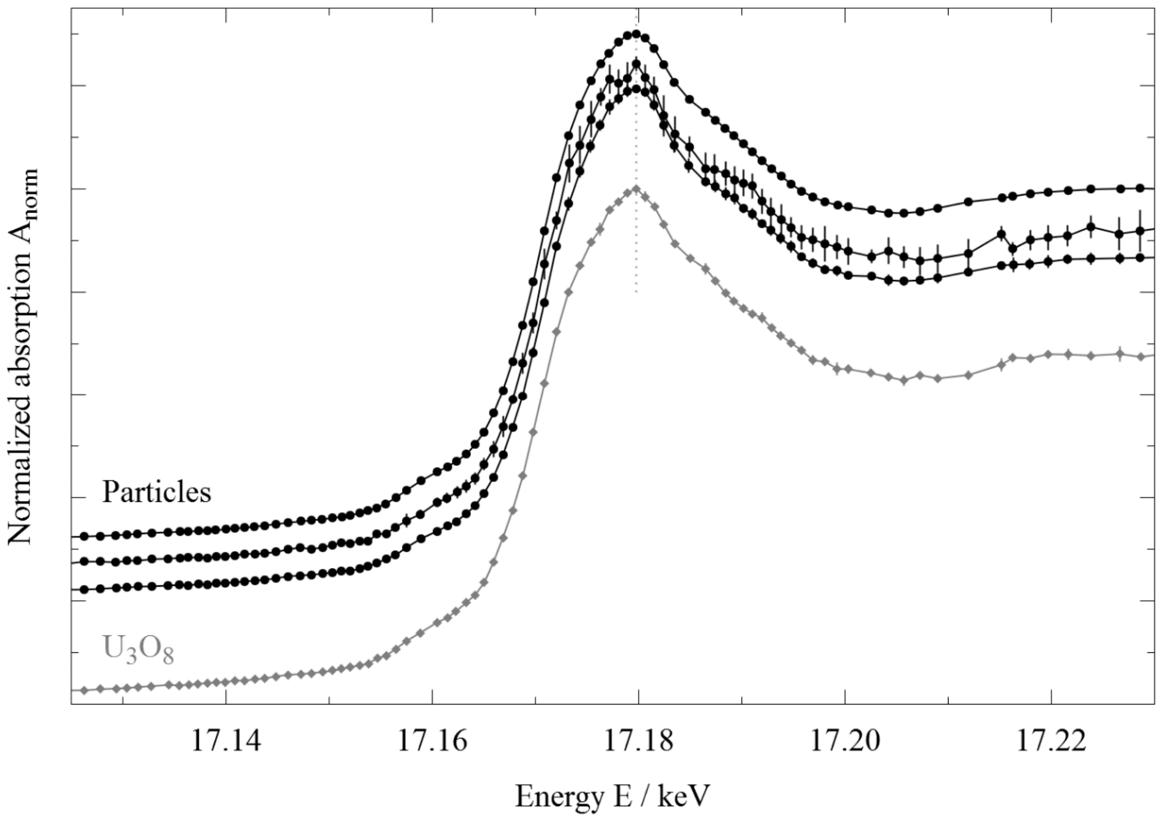


Fig. 2. XANES spectra of uranium microparticles compared with U_3O_8 reference powder.

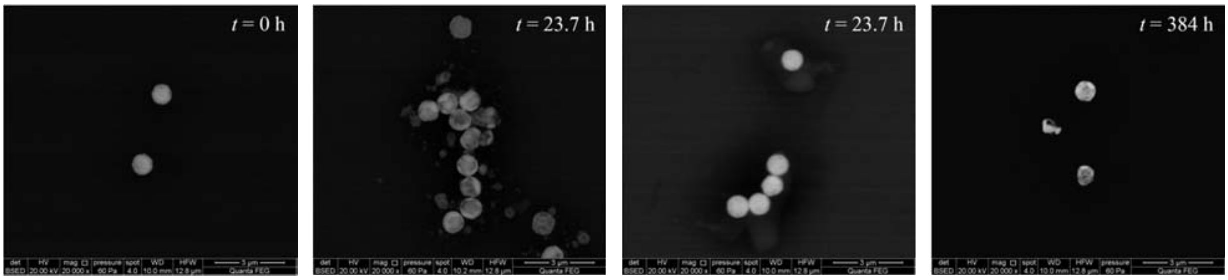
Based on both the XRD and XANES results, it is concluded that the microparticles consist of orthorhombic U_3O_8 instead of monoclinic β-UO_3. This difference from bulk material is most likely caused by the small volume of material and the high surface area, compared to bulk materials. The presence of the U_3O_8 phase instead of UO_3 is an advantage towards the stability of the particles of suspension, as U(VI) is less stable than the mixture of U(VI) and U(V) present in the U_3O_8 phase.

3. Microparticle behavior in suspension

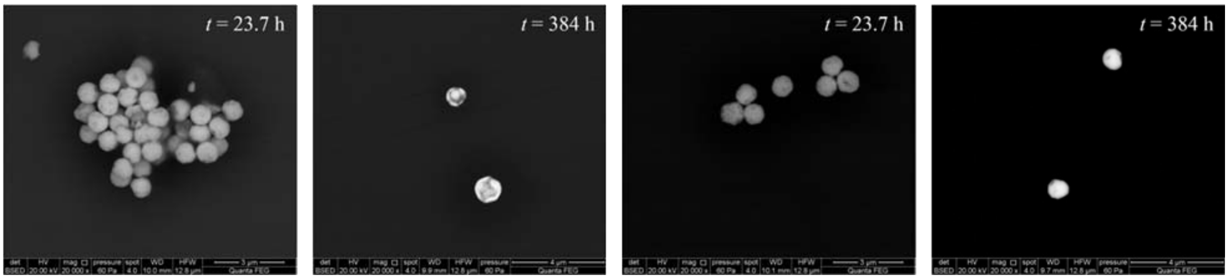
3.1. Particle dissolution

When microparticles are dispersed in a suspension, partial dissolution is likely to occur in a relative short time-frame especially due to the high surface area. To determine the suitability of various solvents, microparticles impacted on a silicon wafer have been stored in various solvents for 23.7 h and 384 h. After storage and drying, the silicon wafers have been investigated using a scanning electron microscope (SEM, FEI Quanta 200f) equipped with a backscatter electron detector (BSED) to study the integrity of the particles after storage. A select number of the micrographs collected are shown in Fig. 3.

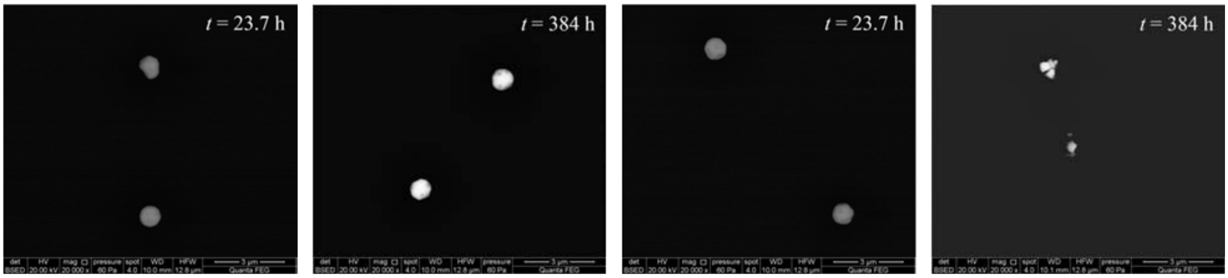
After 23.7 h, other than nitric acid, no significant alteration of the particles has been observed. The particle stored in nitric acid show that the inner part of the microparticles seems to dissolve at a higher rate and shells remain. As FIB/SEM investigations showed an increased porosity at the particle core, such dissolution behavior indicates that the density of the outer shell is insufficient to protect the particle core from solvent intrusion. After storage for 384 h some alteration has been observed. In the case of water, both with and without surfactant, the particle core has dissolved and shells remain, similar to storage in nitric acid for 23.7 h. For both ethanol and n-decane no alteration has been observed and these solvents seem to be suitable for short-term storage and handling. In dimethyl formamide the particles seem to have broken up into fragments. As no clear shell structure can be observed, it is likely that no significant dissolution took place. Although the experiments have been performed on particles still deposited on a silicon wafer, the results provide some insight into suitable dispersion media for particles produced in our process.



(a) Initial (b) Nitric acid (1%) (c) Water



(d) PVP-10000 in water (e) Ethanol



(f) n-Decane (g) Dimethyl formamide

Fig. 3. SEM micrographs of uranium microparticles stored in various solvents.

In order to detach the particles from the substrate, ultrasonification in an ultrasonic bath is deemed the most efficient technique. However, during some tests it was observed that in n-hexane almost no particles were detached whereas in ethanol most particles were removed from the silicon wafer. According to Awad and Nagarajan[9], the predictive fraction of particles removed from a substrate α_C can be calculated according to equation (1). Although a number of parameters are unknown, the detachment fraction for different solvents is expressed by two factors; the density ρ and viscosity η. Using estimated constants for the other parameters, the detachment fraction has been calculated for a number of common solvents. The determined fraction normalized to water is shown in Fig. 4. The plot shows that the detachment fraction for n-hexane is much lower compared to ethanol, which is in agreement with the initial observation. Of the alkanes, only n-dodecane has a higher detachment fraction than ethanol. However, due to the high boiling point of 216 °C the usage of n-dodecane is considered impractical.

$$\alpha_C = \frac{\eta x_0 R_P{}^2 \sqrt{\dfrac{P_C}{\rho\beta(1-\beta)}}}{1.5W_A} \tag{1}$$

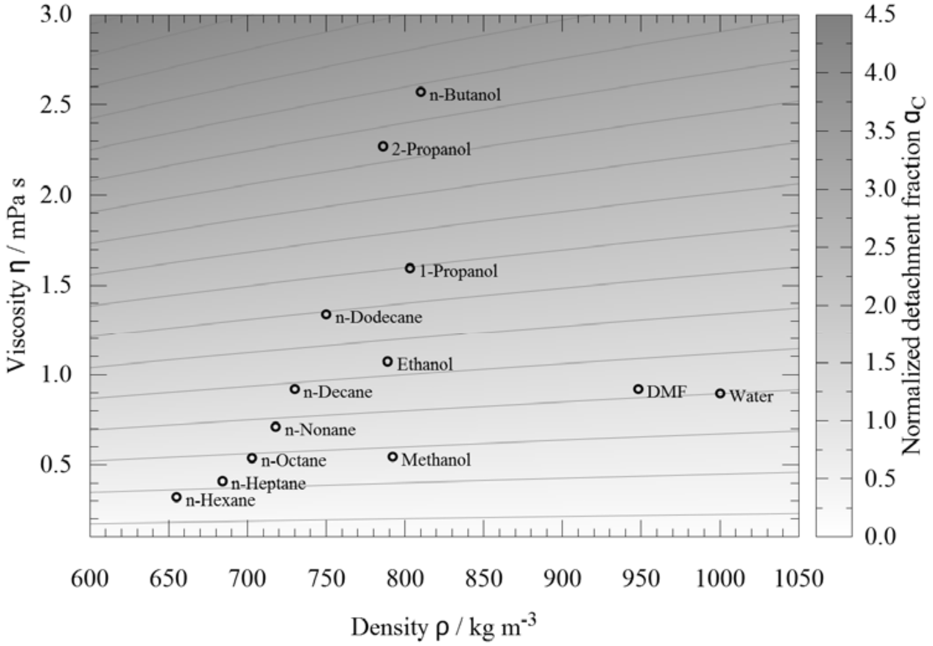


Fig. 4. Normalized detachment fraction for particles in various solvents (x_0=10 mm, R_P=0.5 µm, P_C=1003 MPa, β=0.01, W_A=3×10^{-11}).

3.2. Uranium isotope exchange

Although partial dissolution is important for the uranium content of single microparticles, the property value of highest importance is the uranium isotopic composition. If microparticles are dispersed in a suspension which contains traces of uranium with a different isotopic composition, exchange of uranium between the microparticles and the solvent might significantly alter the composition of the microparticles. In general, two reaction mechanisms can be expected to occur, surface reactions and diffusion[10]. Diffusion of uranium in U_3O_8 has been studied by various authors at elevated temperature. Leme and Matzke[11] determined a diffusion constant of 2.0×10^{-21} m^2.s^{-1} at 800°C. Even with the small particle size, at room temperature no significant effect due to diffusion is expected. On the other hand, surface reactions generally have a much higher rate compared to diffusion and due to the high surface area of the microparticles, this mechanism is expected to be the major contributor. At present, no exchange rates between aqueous solutions containing traces of uranium and solid uranium oxides have been published. Johnston et al.[12] measured the exchange of ^{18}O between water and various uranium oxides, including U_3O_8. Experiments involving U_3O_8 were performed at 360°C, during which up to 57.3% of equilibrium was achieved after 2.0 h.

In order to obtain first indicative information about the exchange of uranium between solid U_3O_8 and uranium in aqueous solution, U_3O_8 powder was prepared by heating depleted uranyl nitrate hexahydrate at 800°C. A solution containing traces of low enriched uranium was prepared by storing β-UO_3 in ultra-pure water (18.2 MΩ.cm, Elga PURELAB Ultra) for two weeks at 90 °C followed by a few days at room temperature. A second solution was prepared by addition of a few drops of dilute nitric acid (1%) before storage to increase the amount of uranium dissolved. Aside from U_3O_8, experiments were conducted with β-UO_3 as the exchange in β-UO_3 is expected to proceed at a faster rate compared to U_3O_8. About 5 mg powder was added to 20 ml solution and stored at room temperature. Aliquots of 50 µl were removed for Q-ICP-MS measurement (PerkinElmer/SCIEX Elan 6100 DRC). The obtained mass ratios of ^{235}U to ^{238}U have been corrected for isotope fractionation, solid phase dissolution and aliquot removal. The degree of reaction was calculated using equation (2), in which $X(t)$ is the determined mass ratio at time t, $X(0)_l$ is the initial mass ratio of the liquid phase and $X(\infty)$ is the expected mass ratio at equilibrium.

$$\alpha = \frac{X(t) - X(0)_l}{X(\infty) - X(0)_l} \qquad (2)$$

The first solution, with a pH of 6.27(15) has a uranium content 35.40(59) µg.g^{-1}. For both β-UO_3 and U_3O_8 a significant decrease of the $m(^{235}U)/m(^{238}U)$ ratio was measured in the solution. Plotting the degree of reaction against time (Fig. 5) shows a trend following first-order kinetics. Due to dissolution effects at the start of the experiment, a deviation from 0 has been observed. As only relative values have been used for further calculations, this effect has been neglected. Based on the measurements, reaction rates of $34.9(13)\times10^{-3}$ h^{-1} and $474(37)\times10^{-6}$ h^{-1} have been determined for β-UO_3 and U_3O_8, respectively. The faster reaction rate of β-UO_3 compared to U_3O_8 is in accordance with the results for oxygen exchange as reported by Johnston et al.[12] and the general increased stability of the U_3O_8 phase compared to UO_3. The second solution, with a pH of 3.95(15) has a higher uranium content of 193.9(37) µg.g^{-1} but shows no significant exchange. These results indicate that the exchange reaction most likely involves the formation of hydrates as intermediate product. As more uranyl hydrates tend to be produced at neutral conditions compared to acidic conditions, the exchange rates are expected to increase with increasing pH, similar to the effect observed by Szabó et al.[13].

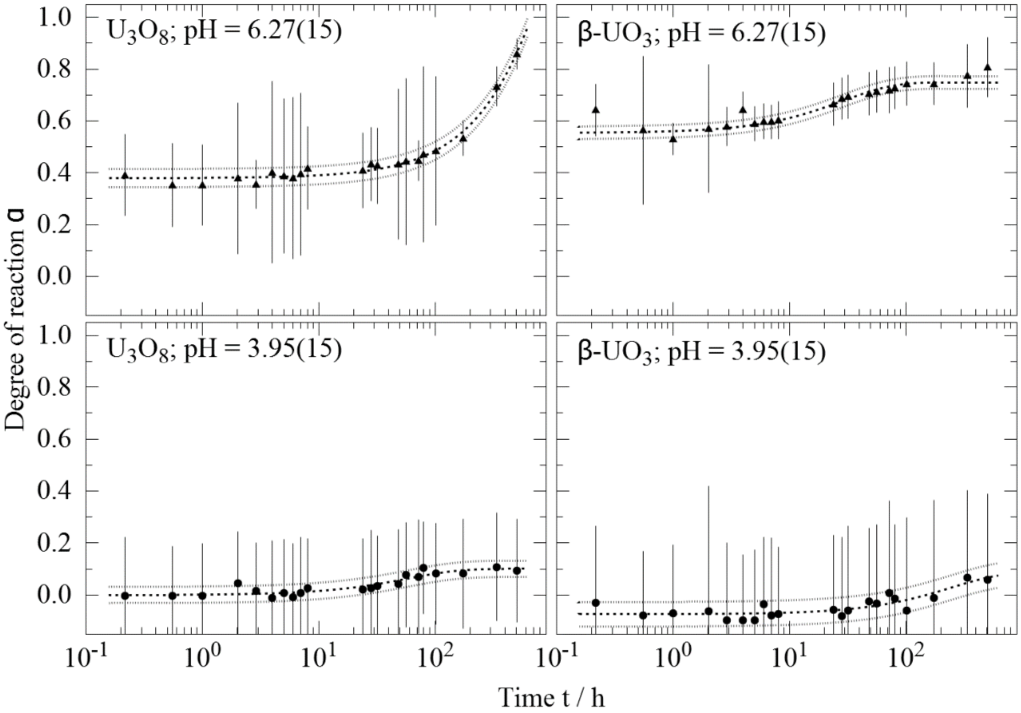


Fig. 5. Isotope exchange between solid U_3O_8 or β-UO_3 and aqueous uranium solutions.

4. Summary and outlook

Monodisperse microspheres with a nominal diameter of 1 µm have been prepared which consist of a specified uranium isotopic composition. The microparticles have been investigated using XRD and XANES, both methods confirmed the presence of an orthorhombic U_3O_8 phase in all observed particles. Although different from literature data on bulk materials, the presence of such a phase provides advantages towards the microparticle stability in suspension.

The suitability of a number of solutions for a microparticle suspension has been determined qualitatively. During these investigations, it was observed that particle dissolution seem to occur dominantly at the particle core. This effect indicates that the density of the shell is insufficient to prevent solvent penetration inside the particle, strongly increasing the reactive surface area. Although both ethanol and n-hexane did not indicate dissolution after 16 days, particle detachment by ultrasonification in n-hexane is inefficient. Based on these results, ethanol is considered the most suitable solution for particle suspension. Further investigations will be performed to determine the suitability of ethanol for longer timeframes and provide quantitative results on the particle stability.

Exchange of uranium between U_3O_8 and uranium in aqueous solution was measured to be significant at neutral conditions. The absence of exchange at more acidic conditions indicates that exchange proceeds by the formation of uranyl hydrates as intermediate product. Further investigations will be performed using better characterized materials and in ethanol solutions instead of aqueous solutions.

Acknowledgements

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