Formation of Stable Uranium(VI) Colloidal Nanoparticles in Conditions Relevant to Radioactive Waste Disposal

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ABSTRACT: The favored pathway for disposal of higher activity radioactive wastes is via deep geological disposal. Many geological disposal facility designs include cement in their engineering design. Over the long term, interaction of groundwater with the cement and waste will form a plume of a hyperalkaline leachate (pH 10−13), and the behavior of radionuclides needs to be constrained under these extreme conditions to minimize the environmental hazard from the wastes. For uranium, a key component of many radioactive wastes, thermodynamic modeling predicts that, at high pH, U(VI) solubility will be very low (nM or lower) and controlled by equilibrium with solid phase alkali and alkaline-earth uranates. However, the formation of U(VI) colloids could potentially enhance the mobility of U(VI) under these conditions, and characterizing the potential for formation and medium-term stability of U(VI) colloids is important in underpinning our understanding of U behavior in waste disposal. Reflecting this, we applied conventional geochemical and microscopy techniques combined with synchrotron based in situ and ex situ X-ray techniques (small-angle X-ray scattering and X-ray adsorption spectroscopy (XAS)) to characterize colloidal U(VI) nanoparticles in a synthetic cement leachate (pH > 13) containing 4.2−252 μM U(VI). The results show that in cement leachates with 42 μM U(VI), colloids formed within hours and remained stable for several years. The colloids consisted of 1.5−1.8 nm nanoparticles with a proportion forming 20−60 nm aggregates. Using XAS and electron microscopy, we were able to determine that the colloidal nanoparticles had a clarkeite (sodium−uranate)-type crystallographic structure. The presented results have clear and hitherto unrecognized implications for the mobility of U(VI) in cementitious environments, in particular those associated with the geological disposal of nuclear waste.

INTRODUCTION

Many countries including the U.K., USA, and former Soviet Union have significant legacies of radioactive waste materials due to their long history of nuclear power generation and military activities. Typically, the long-term strategy for nuclear waste management of higher activity materials is containment in a geological disposal facility (GDF) within the deep subsurface.1 Currently, in many nations, GDF designs are at a generic stage and will be developed as site selection proceeds. Essentially, the design of a GDF is focused on limiting the mobility and migration of radionuclides.2 Typically, the mobility of radionuclides, and particularly uranium, in the subsurface is governed by solubility and adsorption to geological materials.3 In addition, colloidal transport has the potential to significantly enhance radionuclide migration in geodisposal relevant conditions.3,4 However, it is not known whether stable U(VI) colloids form under geochemical conditions relevant to radioactive waste disposal in GDFs.

Most scenarios for intermediate level waste (ILW) disposal in a GDF utilize cementitious materials. For example, ILW is typically grouted with Portland cement and emplaced in steel drums, and engineering of any subsurface disposal facility will require use of structural cement.5,6 In addition, some GDF designs are likely to utilize cementitious backfill.5,7,8 Post closure, groundwater will resaturate the GDF and interact with the cementitious material forming hyperalkaline leachate (pH 10−13) with elevated concentrations of K, Na, and Ca.9 Specifically, during the initial stages of the evolution of a GDF,
the pH of the hyperalkaline leachate may reach values in excess of 13 due to dissolution of sodium and potassium hydroxide phases present in the cementitious materials used. During operation, the GDF will be open to the atmosphere and hence will be aerobic. Chemically reducing conditions are expected to dominate post closure as iron corrosion will consume any oxidants. Typically, within ILW, uranium will be the most significant radionuclide by mass. Furthermore, the ILW will contain uranium in both oxidation states, i.e., U(VI) and U(IV). However, it is noteworthy that under alkaline and slightly reducing conditions U(VI) is expected to be relatively stable and may exist within a GDF for a significant period post closure.

The benefit of using cementitious materials in the design of a GDF is that U(VI) is expected to exhibit low solubility in the resulting hyperalkaline environment. At the pH values of cement leachates (pH 10–13), aqueous U(VI) concentration in equilibrium with, i.e., alkali/alkaline-earth uranates (e.g., Na(UO2)O(OH)(H2O)0−1 and Ca(UO2)2 will be very low (∼10−9 M).11,12 Furthermore, U(VI) adsorbs strongly to the surfaces of many solid phases (e.g., iron oxides,13–15 silicates,14,16 and cement related phases7,18) which will be ubiquitous in the GDF. These factors are predicted to significantly reduce the concentration of aqueous U(VI) in a cementitious GDF. Furthermore, even though the aqueous concentration of carbonate is expected to be low in the deep subsurface, it is noteworthy that the presence of carbonate could significantly enhance U(VI) mobility through the formation of soluble uranium(VI)–carbonate and calcium– uranium(VI)–carbonate complexes.12–14,19

Significantly, U(VI) mobility could also be enhanced by colloids formed within or transported through the GDF.20 Depending on the physical and chemical state of these colloidal nanoparticles (e.g., surface charge) and the prevailing geochemical conditions, colloids could facilitate the transport of U(VI) into the geosphere. Previous studies have identified cement and sediment derived colloidal particles with complexed radionuclides and intrinsic radionuclide colloids (e.g., ThO2 and Pu(OH)4) as potentially important transport vectors.3,4 Recently, complexation of uranium and plutonium to iron oxides has been implicated in their migration in groundwater.22 Furthermore, uranates, among other U(VI) colloids, have been identified as a potential transport vector,23 and plutonium(IV) colloidal transport has been inferred at the Nevada Test Site, Nye County, NV, USA.24,25

Despite the widely recognized relevance of colloidal transport in radioactive waste disposal and the potential significance of U(VI) in waste disposal, few studies have focused on the formation of colloidal U(VI) nanoparticles. As a result, the aim of this study was to explore the potential for colloidal U(VI) nanoparticle formation in a hyperalkaline synthetic cement leachate (pH > 13) representative of the early stages of the evolution of a GDF. Additionally, where colloidal nanoparticles were found to be present, their characteristics and stability were then determined by conventional chemical and microscopy techniques combined with synchrotron based in situ small-angle X-ray scattering (SAXS) and X-ray adsorption spectroscopy (XAS).

## METHODS

To investigate the speciation of U(VI) in conditions relevant to cementitious GDFs, a synthetic cement leachate (pH ∼ 13.1) was prepared by dissolving KOH (0.19 mol), NaOH (0.19 mol), and Ca(OH)2 (0.27 mmol) (all AnalR grade) in 2 L of degassed, deionized water.9,17,18 Prior to use, this was filtered through a 0.22 µm polyvinylidene fluoride (PVDF) syringe filter in a CO2 controlled (<1 ppm of CO2) anaerobic chamber where all subsequent manipulations were performed. A 2.52 mM U(VI)O2(NO3)2 stock solution (pH ∼ 2.3) was used to spike the cement leachate to 4.2, 42, and 252 µM U(VI), after which the pH of 13.1 was confirmed. A time point series of samples were then taken up to 32 months. At each time point, separate samples were filtered using 0.22 µm (PVDF), 0.10 µm (PVDF), and 0.02 µm (Anoprot) syringe filters, and one sample was unfiltered and undisturbed. The resulting samples wereacidified to 2% HNO3 and analyzed for total U using ICP-MS (Agilent 7500cx).

PHREEQC26 calculations were performed to determine the equilibrium concentrations of U(VI) in the synthetic cement leachate when a single U(VI) phase precipitated. These phases included the minerals clarkeite (Na(UO2)O(OH)(H2O)0−1), becquerelite (Ca–(UO2)O4(OH)6(H2O)4), compregiacite (K2(UO2)O2(OH)4· (H2O)2), and several Ca/Na uranate phases. The PHREEQC calculations were performed using the SIT (specific ion activity) database, which includes thermodynamic information on clarkeite, becquerelite, and compregiacite from Gorman-Lewis et al.12 and sodium and calcium uranates from O’Hare et al.23 The thermodynamic equilibrium constants of uranyl hydroxide complexes as determined by Zanontolo et al.28 were also included.

### Small Angle X-ray Scattering

SAXS was used to characterize suspended/colloidal particles in the 42 µM U(VI) experiments, as described earlier, using beamline I22 at Diamond Light Source. All analyses were performed using a monochromatic X-ray beam at 12 keV and a 4 or 10 m camera length. Scattering patterns were collected using a 2D PILATUS 2 M detector.29 Two sets of experiments were performed. First, samples aged for 1 week, 20 months, and 32 months were characterized. Here, the samples were injected into a quartz capillary in line with the X-ray beam and SAXS patterns were collected. Second, in situ time-resolved SAXS analyses were performed to study the formation of colloidal U(VI) nanoparticles. These experiments were performed at the I22 experimental hutch by spiking the synthetic cement leachate to a final concentration of 42 µM U(VI). The solution was then stirred for ~15 s, injected into a quartz capillary in-line with the X-ray beam, and sealed. SAXS measurements were started concurrently to the U(VI) spike. Typically, the first full scattering frame was acquired at ~2 min after the injection of the U(VI) spike. Scattering patterns were collected for up to 7 h at a 1–10 s/frame collection rate.

### SAXS Data Analyses

The scattering patterns from the aged samples, collected using the 4 and 10 m camera lengths, were combined to form a single scattering pattern with a large scattering vector (q) range. All SAXS patterns were modeled using the Irena macro for Igor Pro.30 Additionally, the SAXS patterns from the in situ time-resolved experiments were analyzed to determine the invariant (Q) and I(0),31 described in detail in the Supporting Information (SI). In short, Q and I(0) are a function of the scattering volume and the density of the scatterers and I(0)/Q is a function of the particle volume (eq 1; Vp).31,32 Additionally, separate Q and I(0), and thus I(0)/Q, can be estimated for particle populations with different particle volumes in a dilute suspension34 to track the evolution of different particle populations.

\[
\frac{I(0)}{Q} \approx V_p
\]  

### Solid Characterization

At selected time points, suspended particles were captured on either carbon coated (Agar Scientific) or positively charged C-SMART PLUS (Dune Sciences) transmission electron microscope (TEM) grids and the supernatant was removed using isoamyl alcohol to minimize the effect of drying on the solids formed during the experiments. TEM images were taken using a Philips CM200 field emission electron gun transmission electron microscope (FEG-TEM). Chemical composition of the solids was analyzed using energy dispersive X-ray spectroscopy (EDX) with an Oxford Instruments 80 mm X-Max SD detector running the AZTEC
software, TEM images were analyzed using image processing software ImageJ.35 X-ray absorption spectroscopy (XAS) analyses were performed at beamline B18 at Diamond Light Source, at the U LIII-edge using a Si(111) monochromator at liquid nitrogen temperature. Two samples were analyzed; first, a solid sample from the 252 \( \mu \text{M} \) U(VI) experiment was prepared by centrifuging at 2600 g over 28 days. Conversely, the unfiltered (and undisturbed) solution samples from the 252 \( \mu \text{M} \) U(VI) experiment aged for 1 month was analyzed in fluorescence mode. XAS data analyses were performed using Athena and Artemis from the Demeter software package using FEFF6.36

### RESULTS AND DISCUSSION

During the 252 \( \mu \text{M} \) U(VI) experiments a yellow precipitate formed and solution analyses showed that the U(VI) concentration in all of the filtered samples decreased to 1.4 \( \mu \text{M} \) (Figure 1a) over 28 days. Conversely, the unfiltered (and undisturbed) solution samples only showed a minor decrease in the U(VI) concentration to \( \sim 200 \mu \text{M} \) U(VI) (Figure 1a) suggesting the presence of a colloidal U(VI) component with particle size > 0.22 \( \mu \text{m} \) in the 252 \( \mu \text{M} \) U(VI) experiment. Interestingly, the 42 and 4.2 \( \mu \text{M} \) U(VI) experiments did not show any visible precipitation or removal of U(VI) from solution during filtration up to 32 months (Figure 1b). This is in contrast to the thermodynamic modeling using PHREEQC,26 which showed the solutions were (highly) supersaturated with respect to several calcium and sodium uranate phases (Table 1). It is worth noting that the introduction of carbonate (including Ca–UO2–CO3 complexes15) due to the dissolution of calcite had no significant effect on the equilibrium concentrations in Table 1. These results indicated that, in the 42 and 4.2 \( \mu \text{M} \) systems, U(VI) was either dissolved in a supersaturated metastable state or that stable colloidal U(VI) nanoparticles (\( \leq 0.02 \mu \text{m} \)) were present.

**Small Angle X-ray Scattering.** SAXS patterns of the aged solutions from the 42 \( \mu \text{M} \) U(VI) experiments are presented in Figure 2a. The observed scattering intensity suggests that colloidal U(VI) was present in the 42 \( \mu \text{M} \) U(VI) experiments. The best fit to the SAXS patterns using the Irena fitting package consisted of a two particle population model: Smaller/primary particles (high q values) were modeled using a form factor for spherical particles, and larger particles (low q values), presumptively aggregates of the primary particles, were modeled using the form factor for algebraic globules.37,38 In all cases the scattering patterns were modeled as dilute systems reflecting the (relatively) low concentration of U(VI). Fits to the respective scattering patterns are shown in Figure 2a, and the fit parameters are given in Table 2. Briefly, by 2.3 h, the primary particles reached a mean diameter of 1.54 ± 0.05 nm and 57 ± 12% of the scattering solids formed aggregates with a mean diameter of 22.4 ± 2.8 nm (Table 2). Beyond 2.3 h, there was little significant change in the particle populations over 32 months, with a primary particle diameter of 1.60–1.82 nm and between 33–57% of the scattering solids within aggregates of 42.2–60.0 nm. The only significant change in the particles over the observation period was an increase in the mean aggregate diameter from 22.4 to 56.0 nm between 2.3 h and 1 week. The results from the SAXS patterns were supported by TEM images of 1 h and 1 month samples from parallel experiments, with evidence for 1–2 nm primary particles which formed aggregates to 20–60 nm in size (Figure 2b). The aggregate morphology observed by TEM was consistent with the algebraic globules form factor used in the SAXS modeling approach. It should however be noted that air drying nanoparticle suspensions for TEM analysis could alter aggregate morphology,39 however, due to the consistency between the SAXS and TEM analyses we are confident that the TEM images are a representation of the in situ colloidal nanoparticles. Overall, the SAXS analyses indicate that the U(VI) in this system was present as colloidal U(VI) nanoparticles and underwent very little change from 2.3 h up

### Table 1. PHREEQC26 Calculations on the Concentration of U(VI) in Equilibrium with Selected Phases in the Cement Leachate

<table>
<thead>
<tr>
<th>exp (( \mu \text{M} ) U(VI))</th>
<th>mead U(VI) concn (( \mu \text{M} ))</th>
<th>U(VI) concn (( \mu \text{M} )) in equilibrium with solid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Comp&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>252</td>
<td>1.88 ± 0.02&lt;sup&gt;e&lt;/sup&gt;</td>
<td>180</td>
</tr>
<tr>
<td>42</td>
<td>44.7 ± 2.9</td>
<td>42.0</td>
</tr>
<tr>
<td>4.2</td>
<td>4.27 ± 0.05</td>
<td>4.20</td>
</tr>
</tbody>
</table>

<sup>a</sup>Note that when the concentrations calculated are identical to the input concentrations, these phases are below saturation in the corresponding experiment. 

<sup>b</sup>Compregnacite: \( K_2(UO_2)_3O_4(OH)_2(H_2O)_7 \). 

<sup>c</sup>Calcium uranate trihydrate: \( CaUO_2(H_2O)_6 \). 

<sup>d</sup>Becquerelite: \( Ca(UO_2)_3O_4(OH)_6(H_2O)_8 \). 

<sup>e</sup>Clarkeite: \( Na(UO_2)O(OH)(H_2O)_{10} \).

<sup>f</sup>The printed values are the averages of all filtered samples and their standard deviation.

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Figure 1. Solution data from the 252 \( \mu \text{M} \) U(VI) experiment (a) and the 42 and 4.2 \( \mu \text{M} \) U(VI) experiments (b). The error bars on the data from the 42 \( \mu \text{M} \) U(VI) experiment are the standard deviation of triplicate experiments; the results from filtering the solutions through 0.1 and 0.22 \( \mu \text{m} \) filters from the 42 and 4.2 \( \mu \text{M} \) U(VI) experiments showed no differences compared to the plotted results and are given in Figure 2 in the SI.
to 32 months. Interestingly, the 0.02 μm filtration samples from the 42 μM U(VI) experiment showed no removal from solution (Figure 1) even though TEM and SAXS analysis suggest the presence of aggregates > 20 nm (Figure 2 and Table 2). This suggests artifacts from filtration and/or facile disaggregation of colloidal nanoparticles upon forced filtration through 20 nm pores.

Time-resolved I(0) data from the in situ 42 μM U(VI) experiments (4 and 10 m camera length) are shown in Figure 3a. The above background I(0) in the first scattering pattern collected (at ~2 min; Figure 3a) suggested particle formation prior to ~2 min. Between 2 min and 2.3 h, I(0) increased 10-fold (Figure 3a, dashed vertical line). After this initial increase, I(0) decreased slightly (Figure 3a) possibly due to aggregate growth (Table 2).

Fitting (Irena) the SAXS patterns from the 42 μM U(VI) experiments yielded time-resolved size information for the aggregates, but due to the low intensity of the scattering patterns at high q values, fitting of the primary particle model was not achieved. However, it was possible to determine I(0) and Q for each particle population. Figure 3b shows the I(0)/Q (which relates to particle volume; eq 131−33) for the aggregates and primary particles, and aggregate volume, calculated from the size determined using Irena. The aggregate volume (Irena) and I(0)/Q values as a function of time are consistent (Figure 3b), giving confidence that I(0)/Q reflects particle volume trends in the 42 μM U(VI) experiment. The aggregate diameter increased up to ~22.4 nm (Figure 3b and Table 2) during the first 1.5 h of the experiment (Figure 3b, vertical line) and then remained constant. This initial growth of the aggregates was presumably due to primary particle aggregation and/or nucleation of particles on the aggregate surface. Between ~1.5 and ~2.3 h the aggregate size did not increase, while I(0) increased about 3-fold (Figure 3). This indicates that continuous formation of colloidal nanoparticles/aggregates occurred after the aggregate size reached a maximum. The I(0)/Q for the primary particles remained constant (Figure 3b), indicating that the primary particles formed at ~1.5 nm (Table 2) in diameter and did not change in size. Thus, the formation mechanism of the primary particles was likely nucleation dominated, with no significant particle growth occurring (e.g., ripening).40,41

The persistence of a significant fraction of unaggregated primary particles (Table 2) could have been caused by the high pH. The pH at the point of zero charge for several uranyl oxyhydroxides is 4−4.42 It is thus clear that U(VI) (oxyhydr)oxide nanoparticles would have a highly negative surface charge at pH 13.1. Thus, electrostatic repulsion would minimize (further) particle aggregation consistent with our observations and potentially reduce the interaction of U(VI) with materials present in a cementitious GDF system.

**Solid Characterization.** HR-TEM images of the colloidal nanoparticles (1 day and 1 month) from the 42 μM U(VI) experiment are shown in Figure 4b,d. The 1−2 nm nanoparticles collected after 1 h (Figure 2b) lacked any resolvable lattice fringes, suggesting an amorphous character. By contrast, the nanoparticles from 1 day to 1 month had visible lattice fringes (emphasized by circles, Figure 4b,d) which were spaced at 3.0−3.3 Å. Reflecting on this, the primary particles in the 42 μM U(VI) experiments initially formed as amorphous nanoparticles, potentially due to the aggregation of stable prenucleation clusters akin to the observed dynamically ordered liquid-like oxy-anion polymers (DOLLOP) observed during the process.

**Table 2. Results of the Fits from the SAXS Patterns from the 42 μM U(VI) Experiments**

<table>
<thead>
<tr>
<th>sample name</th>
<th>primary particles</th>
<th>aggregates</th>
<th>fraction of aggregated particles $\left[\frac{V_{agg}}{V_{agg} + V_{prim}}\right] \times 100$ (%)$^{a,c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3 h</td>
<td>1.54 ± 0.05</td>
<td>22.4 ± 2.8</td>
<td>57 ± 12</td>
</tr>
<tr>
<td>1 week</td>
<td>1.60 ± 0.26</td>
<td>56.0 ± 18.2</td>
<td>34 ± 15</td>
</tr>
<tr>
<td>20 month</td>
<td>1.82 ± 0.22</td>
<td>42.2 ± 11.6</td>
<td>44 ± 16</td>
</tr>
<tr>
<td>32 month</td>
<td>1.75 ± 0.16</td>
<td>60.0 ± 30.0</td>
<td>57 ± 14</td>
</tr>
</tbody>
</table>

$^{a}$The errors were evaluated by calculating the range less 1.05 times the minimum $\chi^2$. $^{b}$The polydispersity is defined as the standard deviation of the log-normal distribution of the particles. $^{c}$V$_{prim}$ and V$_{agg}$ represent the calculated volumes for the primary particles and aggregates respectively.
formation of amorphous calcium carbonate. Furthermore, the amorphous uranium nanoparticles became nanocrystalline during the course of a day. The crystallinity of the nanoparticles is also emphasized by visible polycrystalline rings in the selected area electron diffraction patterns (SAED, Figure 4c) collected from the 1 day sample. Additionally, the EDX analyses of the nanoparticles formed during the 42 μM U(VI) experiments show that the particles consisted of U, Na, K, and Ca (Figure 5).

HR-TEM image from a 1 week sample collected from the 4.2 μM U(VI) experiment shows crystalline nanoparticles of 2−5 nm within a ∼10 nm aggregate (Figure 4a). This confirms that U(VI) colloids also formed in the 4.2 μM U(VI) experiment and were of a similar size and aggregation state to those formed in the 42 μM U(VI) experiment. Furthermore, TEM characterization shows that the crystallinity (lattice fringes spaced at 3.0−3.3 Å, emphasized by circles in Figure 4a) and composition (U, Na, K, and Ca, Figure 5) of the nanoparticles were also similar to those from the 42 μM U(VI) experiment.

High-resolution TEM (HR-TEM) images of the particles throughout the 252 μM experiments show small crystalline platelets with lattice fringes spaced at 5.9−6.2 Å (arrows, Figure 5).
4e,h,j) and 3.0–3.3 Å. These particles formed part of larger aggregated structures (Figure 4f,l,k). At 10 min, these platelets were 2−10 nm in size and the 5.9−6.2 Å lattice fringes were aligned in some adjacent particles, indicating that the particle size may be increasing via oriented attachment. After 1 month, the crystalline domains with 5.9−6.2 Å lattice fringes grew to about 25 nm in diameter with a width of ∼4 nm (arrows, Figure 4j). These observations confirm that initially nanocrystalline particles formed from solution and grew through oriented attachment.45

The SAED patterns from the 42 and 252 μM U(VI) experiments (Figure 4c,g) and EDX spectra (Figure 5) from the aggregates from the 4.2, 42, and 252 μM U(VI) experiments were all similar (Figure 4a,b,d,e,h,j). This implies the same phase formed in all three systems even though their morphologies (Figure 4) and filtration behavior (Figure 1) differed. The positions of the dominant diffraction rings in the SAED images (Figure 4c,g) correspond to d-spacings of ∼3.2, ∼2.7, 1.9, and 1.6 Å, which indicates that the particles were the alkali/alkaline-earth metal uranate phase clarkeite (Figure 3 in the SI).46,47 This explains the 5.9−6.2 Å lattice fringes which correspond to the d-spacing of the (003) diffraction peak, which can be related to the distance between adjacent U layers in the uranate structure. The lack of the 5.9−6.2 Å lattice fringes in the particles from the 4.2 and 42 μM U(VI) experiments is likely caused by the limited size of the nanoparticles or limited order between adjacent U layers. Finally, TEM analyses suggest that in all experiments, initially nanoparticles formed (1−5 nm) from solution which then aggregated. In the 252 μM experiment the freshly formed nanoparticles crystallized presumably via oriented attachment to form larger platelets.

The U LIII-edge XANES spectra from the 252 μM U(VI) experiment precipitate and a solution aliquot from the 42 μM U(VI) experiments are plotted in Figure 6a. Also plotted are the XANES from uranate17,48 and uranyl standard (Figure 6a) compounds. Both spectra from the experimental samples show relatively broad white lines at ∼17.178 keV (dashed line B, Figure 6a) similar to the uranate standard, while the uranyl standard has a sharper white line at ∼17.176 keV (dashed line A, Figure 6a). In addition, the positions of the resonance features in both experimental XANES spectra match those of the uranate standard.

Figure 6. (a) Normalized XANES spectra from the precipitate from the 252 μM U(VI) experiment and the 42 μM U(VI) solution samples and a uranate (CaUO4)17,48 and an in-house uranyl (UO3) standard. The vertical dashed line represents the position of the multiple scattering of the axial U=O bonds from uranyl. (b) Stick and ball representation of the clarkeite structure used to model the EXAFS spectrum, the dashed outline shape denotes the unit cell of clarkeite. (c) Fourier transform of the EXAFS collected from the precipitate of the 252 μM U(VI) experiment. (d) EXAFS from the precipitate of the 252 μM U(VI) experiment.
the uranate standard (dashed lines C–F, Figure 6a).49 This indicates that, in the 42 μM U(VI) experiment, uranium is predominantly present as colloidal uranate nanoparticles, rather than as dissolved uranyl or a solid uranyl compound.

The extended X-ray adsorption fine structure (EXAFS) spectrum and corresponding Fourier transform for the 252 μM U(VI) precipitate are shown in Figure 6c,d. Four consecutive fits were performed on the EXAFS spectrum. The first fit was calculated using only U–O and U–U bonds from clarkeite.47,51 As observed in the TEM-EDX analyses, the composition of the precipitated phase included Na, Ca, and K (Figure S). Thus, three subsequent fits were refined by including Na, K, or Ca.47

The U–O$_\text{axial}$ bond length of 1.87 Å corresponds to the U–O$_\text{axial}$ bond lengths in uranate phases (1.86–1.97 Å)\textsuperscript{17,51,52} and is longer than the U–O$_\text{axial}$ bond lengths in uranyl phases (1.70–1.82 Å).\textsuperscript{1,3} Furthermore, the U–O$_\text{eq}$ of 2.22 Å is comparable to U–O$_\text{eq}$ distances calculated for several layered metal uranate phases at 2.15–2.30 Å\textsuperscript{17,51,52} while U–O$_\text{eq}$ distances in uranyl phases are 2.27–2.49 Å.\textsuperscript{51,53} Combined with the SAED (Figure 4g) and the XANES (Figure 6a), this confirms the formation of an alkali/alkaline-earth uranate phase in the 252 μM U(VI) experiments (and, by extension, in the 4.2 and 42 μM U(VI) experiments). Furthermore, adding Na, K, or Ca to the EXAFS model significantly improved the overall fit (Table 3) with the result resembling the structure of clarkeite ((Na,K, Ca)$_2$UO$_2$(OH)$_2$·(H$_2$O)$_{0.5}$). Table 4 and Figure 6b–d).47,51 However, it is impossible to determine whether the clarkeite-type structure is not truly hexagonal, and variable hydration of clarkeite could cause multiple uranium crystallographic positions and changes in the cation occupation. Furthermore, the U–Na distance is ~5% shorter than previously determined,47,51 which could be caused by distortions induced by variable hydration or the incorporation of foreign elements such as Ca and K in the interlayer (Figure S).51 Interestingly, the EXAFS fits were also improved by the addition of K and Ca (Table 3), indicating that these may be replacing some of the Na in the interlayer of clarkeite, which has been observed previously in natural samples.\textsuperscript{47} Thus, the identification of a clarkeite-type phase containing a mixture of Na, K, and Ca is confirmed, which is consistent with the formation of similar phases in other high-pH systems.\textsuperscript{4,53}

**Nanoparticle Solubility.** As discussed previously uranium in the 4.2 and 42 μM U(VI) experiments (Figure 6a) was present as colloidal clarkeite nanoparticles. Additionally, the PHREEQC calculations show that if the solutions were in equilibrium with clarkeite, 100.0 and 99.8% of the U(VI) would be in the solid phase in the 42 and 4.2 μM U(VI) experiments, respectively. However, because reducing the size of nanoparticle tends to increase their solubility,\textsuperscript{59} a smaller proportion of U(VI) could be in the solid phase. The solubility of a phase tends to increase with decreasing nanoparticle size as described (increasing specific surface area, A (m$^2$/mol)) via eq 2,\textsuperscript{57,59}

$$\log[K_{sp,nano}] = \log[K_{sp}] + \frac{2\sigma}{3RT}$$

where $K_{sp}$ and $K_{sp,nano}$ are the ion activity products at equilibrium with a bulk and nanoparticulate phase, respectively ($K_{sp} = 10^{9.4}$).\textsuperscript{12} T is the absolute temperature (239 K), R is the universal gas constant (8.3145 J/K), and σ is the surface free energy (J/m$^2$). However, the surface free energy of clarkeite is

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### Table 3. Summary of the EXAFS Parameters Fitted for a Uranium Phase without Na, for Clarkeite (NaUO$_2$(OH)$_2$·(H$_2$O)$_{0.5}$) and for Clarkeite Where Sodium Was Substituted for Potassium and Calcium (K-Clarkeite and Ca-Clarkeite, Respectively)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reduced $\chi^2$</th>
<th>$R$-Factor</th>
<th>Confidence (%)</th>
<th>$E_0$ (eV)</th>
<th>$\sigma^{ab}$ (Å)</th>
<th>$\sigma^{ab}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U–O$_w$</td>
<td>80.93</td>
<td>0.0140</td>
<td>0.0140</td>
<td>1.37(82)</td>
<td>2.04(66)</td>
<td>1.28(85)</td>
</tr>
<tr>
<td>U–O$_{eq}$</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>U–O$_{eq}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>U–Na</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>U–K</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>U–Ca</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

*Confidence level whether the fit was significantly improved by adding the Na, K, or Ca shell compared to the uranium phase without Na; calculated using the F-test for EXAFS.\textsuperscript{49} $N$ is the coordination number, $R$ is the distance between uranium and the scatterer, and $\sigma$ is the Debye–Waller factor. \textsuperscript{49}Constrained parameter.

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### Table 4. Clarkeite Uranium Coordination Environment Obtained from Literature, Modeled from an XRD Pattern and an EXAFS Spectrum

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$N$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD\textsuperscript{51}</td>
<td>U–O$_{eq}$</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>U–O$_{eq}$</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>U–Na</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>U–U</td>
<td>6</td>
</tr>
<tr>
<td>EXAFS\textsuperscript{51}</td>
<td>U–O$_{eq}$</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>U–O$_{eq}$</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>U–O$_{eq}$</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>U–Na</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>U–U</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>U–U</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>U–U</td>
<td>2</td>
</tr>
</tbody>
</table>

\textsuperscript{51}XRD and EXAFS: Distance (Å) and coordination number.

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unknown; therefore, we have estimated $\sigma_{\text{clarkeite}}$ using the Gibbs–Thomson equation (eq 3).^{60}

$$r^* = \frac{2\Omega}{k_B T \ln \left( \frac{\text{IAP}}{\sigma_r} \right)} \quad \text{(3)}$$

where $r^*$ is the critical nucleus radius (m), $k_B$ is the Boltzmann constant (1.38 x 10^{-23} J/K), IAP is the ion activity product of the solution with respect to clarkeite prior to nucleation (calculated for the 42 $\mu$M U(VI) experiment as 10^{15.35}), and $\Omega$ is the crystal volume per unit formula as described by the IAP (a third of the unit cell of clarkeite, 0.0797 nm3).^{12,47} It is noteworthy that the nanoparticles nucleate as an amorphous phase. However, no thermodynamic information is available on amorphous uranate phases. Thus, we assumed that the thermodynamic properties of the amorphous phase are close to clarkeite. As discussed earlier, the SAXS and TEM analyses indicate that the U(VI) nucleated as $\sim 0.75\text{ nm}$; therefore this value was used as an upper limit for the critical nucleus size. The clarkeite unit cell size was used as the lower limit of the critical nucleus size ($r^* \approx 0.4\text{ nm}$). Using these values resulted in a $\sigma$ for clarkeite of 0.085–0.16 $\mu$m, which is low compared to the $\sigma$ of metaschepoite (0.94 $\mu$m) and uraninite (0.47 $\mu$m).^{37,61} The rate of crystal growth and ripening (e.g., Ostwald ripening) are proportional to $\sigma$;^{58,59} therefore, such a low $\sigma$ could explain the lack of significant ripening of the primary particles following nucleation. Combined with the inhibition of aggregation caused by a highly negative surface charge, this explains the long-term stability (>32 months) of the colloidal U(VI) nanoparticles.

The $\sigma$ of 0.085–0.16 $\mu$m can now be used in eq 2 to estimate the solubility of clarkeite nanoparticles with a diameter of 1.5 nm ($A \approx 1.9 \times 10^8$ m^2/mol). The resulting $K_{sp,nano}$ (10^{9.8}–10^{10.2}) was included in the PHREEQC calculations on U(VI) equilibrium concentrations in the experimental solutions (95 mM Na, 95 mM K, and 0.14 mM Ca) with 42 and 4.2 $\mu$M U(VI) experiments. This predicted equilibrium concentrations of $\leq 0.07\mu$m U(VI), and as described previously, the equilibrium concentration changed minimally (~0.074 $\mu$m U(VI)) when equilibrium with calcite was added to the PHREEQC calculations. These values would mean that 99.8 and 98.3% of the U(VI) would be in the solid phase in the 42 and 4.2 $\mu$M U(VI) experiments, respectively. This supports our interpretation that U(VI) is predominantly colloidal in all experiments rather than dissolved uranyl.


