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EXAFS SPECTROSCOPIC STUDIES OF URANIUM (VI) OXIDE PRECIPITATES

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ABSTRACT

We have investigated the structures of U(VI) oxides precipitated from room temperature aqueous solutions at low ionic strength as a function of pH. Using the uranium L_{III} - edge extended x-ray absorption fine structure (EXAFS) as a probe of the local structure around the uranium, a trend is observed whereby the axial oxygen bond lengths from the uranyl groups increase from 1.80 Å at pH=7 to 1.86 Å at pH=11. A concomitant decrease in the equatorial oxygen and nearest-neighbor uranium bond lengths also occurs with increasing pH. Expansion of the linear O=U=O group is seen directly at the L_{III} absorption edge where multiple scattering resonances systematically shift in energy. EXAFS curve-fitting analysis on these precipitates and a sample of synthetic schoepite indicate that the structure of the species formed at pH=7 is similar to the structure of schoepite. At pH=11, the precipitate structure is similar to that of a uranate.

INTRODUCTION

To accurately model radionuclide migration, it is important to identify the source terms and determine their speciation (i.e., thermodynamics, red-ox properties, molecular structure). This task becomes more difficult when the primary source term has the ability to transform into a secondary phase which effectively becomes the solubility-controlling solid. Spent nuclear reactor fuel is one such example where in an oxidizing environment, UO₂ transforms [1] into UO₂²⁺-containing solid phases, i.e., UO₂(OH)₂·H₂O (schoepite). For the uranyl ion, UO₂²⁺, the solubility equilibria and the corresponding controlling solids depend on the ionic strength and the type of medium, temperature, and pH.

Numerous structural determinations have been made on uranium(VI) oxides, hydroxides and alkali metal uranates [2, 3]. In contrast, the structure of the hydrated oxide, UO₂(OH)₂·H₂O, has been studied by x-ray diffraction (XRD), but atomic coordinates have yet to be determined [4]. The difficulty in obtaining a detailed structure by XRD for natural as well as synthetic schoepite polymorphs most likely arises from the tendency towards amorphous structures in these materials. In this work, we have sought to determine the structure of synthetic schoepite and other solids that are precipitated under environmental conditions as a function of pH using Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy.

EXPERIMENT

All solutions were prepared using CO₂-free, double-distilled and deionized water from a Millipore Corp. purification system. Stock solutions of ²³⁸U were made by dissolving an appropriate amount of uranyl nitrate in concentrated HCl (12 M) and were purified from daughter activities using an anion exchange column. The titrations and subsequent precipitation reactions were carried out in an argon (Ar)-filled, CO₂-free glove box. Schoepite was precipitated from a supersaturated solution of 0.1 mM uranyl ion in 0.1 M hydrochloric acid by addition of 1.0 M NaOH and was kept at pH=7. The XRD pattern obtained for the precipitated yellow solid matched that of metaschoepite which has been reported in the literature.

A second series of precipitation reactions was carried out as a function of pH using a uranium stock solution consisting of 0.1 M uranyl ion in 1.0 M hydrochloric acid. 0.6 ml

aliquots of this solution were added to three 100 ml portions of a 1.0 mM Na_2SO_4 solution. The pH of each mixture was adjusted with 1.0 M NaOH to the values of 7.2, 9.1, and 10.6. After 9 weeks of gentle stirring, the experiment was stopped and the pH values were remeasured at 7.2, 8.2, and 11.4. The precipitated solids (~10 mg each) were recovered by pressure membrane filtration and allowed to dry under atmosphere.

Approximately 5 mg of the precipitates (labeled as pH-7, pH-9, and pH-11) were mixed with boron nitride (BN) powder and placed in 1.5 x 20 mm slots cut out from 1.5 mm thick polyethylene frames. Uranium L_{III} -edge x-ray absorption spectra were collected on wiggler beamline 4-3 (unfocused) using a Si (220) double-crystal monochromator. All spectra were collected in the transmission geometry using argon-filled ionization chambers and a vertical slit of 0.5 mm. The EXAFS data reduction and non-linear least squares curve-fitting analysis were done using the suite of programs EXAFSPAK developed by G. George of SSRL. The theoretical EXAFS modeling code, FEFF6, of Rehr *et al.* [5] was used to calculate the backscattering phases and amplitudes of the individual neighboring atoms.

RESULTS

Figure 1 shows the raw k^3 -weighted EXAFS data for pH-11, pH-9, pH-7, and schoepite. The low- k region is dominated by a low frequency oscillation which arises from back-scattering of the oxygen atoms in the uranyl group, while at high- k , the spectra show a high frequency pattern emerging which can be attributed to the presence of more distant atoms having a large cross-section, (i.e. uranium). The pH-11 and pH-9 samples show a strong resemblance in their high k fine structure which is different than the fine structure observed for the pH-7 and schoepite solids. The difference is apparent at $k=15 \text{ \AA}^{-1}$ where the oscillations in the pH-11 and pH-9 samples are π (180 degrees) out of phase with the oscillations in the pH-7 and schoepite samples. The oscillations at high- k for schoepite are in phase with pH-7, although they are more pronounced and better resolved in schoepite due to thermal damping (schoepite studied at 20 K).

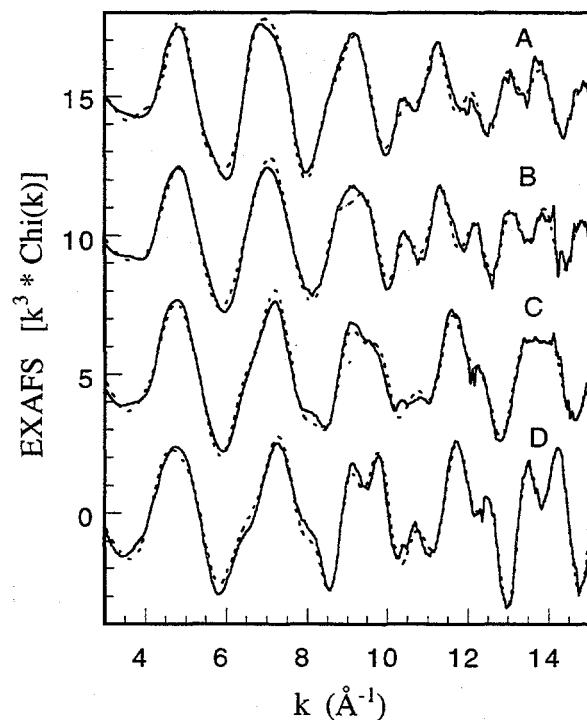


Figure 1. Raw U L_{III} -edge k^3 -weighted EXAFS data for (A) pH-11, (B) pH-9, (C) pH-7, and (D) schoepite samples: experimental (solid), theoretical fit (dashed).

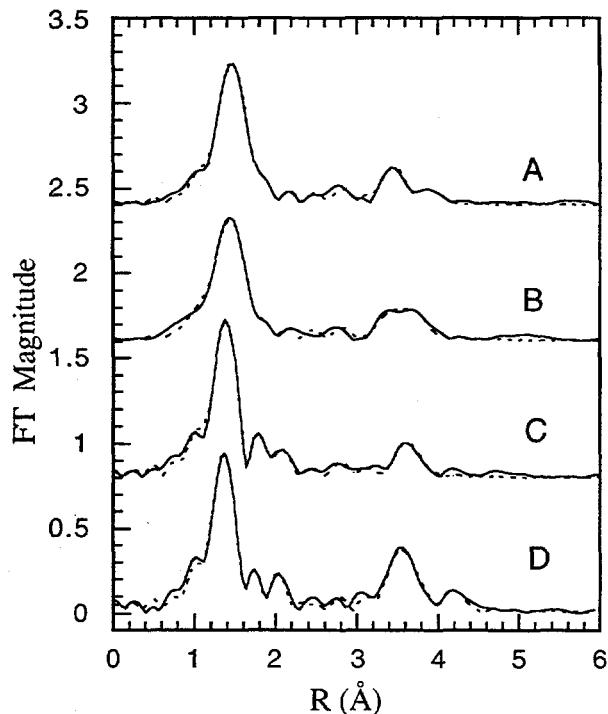


Figure 2. EXAFS Fourier transforms of U L_{III} EXAFS for (A) pH-11, (B) pH-9, (C) pH-7, and (D) schoepite samples: experimental (solid), theoretical fit (dashed).

The trends noted in the k-space data are also seen in the R-space plots of the Fourier transformed EXAFS spectra shown in Figure 2. The FTs illustrate that the EXAFS spectra are dominated by backscattering from the O atoms of the linear UO_2^{2+} group (peak at 1.30 Å). Backscattering from the O atoms lying in the equatorial plane of the UO_2^{2+} ion is observed in the pH-7 and schoepite data sets as shown by the pattern of FT peaks centered around 1.90 Å.

Moving from pH-7 to pH-11, a structural transformation is observed in the precipitates as the 1.30 Å peak broadens, shifts to higher R, and the pattern in the equatorial O region is lost. In addition, all of the spectra exhibit a feature(s) at ~ 3.6 Å, which is attributed to backscattering from more distant U neighbors. Low Z atoms are not normally detected at $R > 3$ Å, unless a multiple scattering enhancement of the amplitude is present. Examples of this have been observed when ligands like carbonate or nitrate adopt a symmetric bidentate geometry with the distal O atom being collinear with the absorbing atom and the C or N atoms. However, this type of configuration is not possible in our samples since nitrate and carbonate were not present in the preparations. The positions of the U peaks also shift to lower R with increasing pH.

Table 1. EXAFS Structural Results for U(VI) Oxide Precipitates

Sample	Bond	R(Å)	N	σ^2 (Å ²)	ΔE_0 (eV)
Schoepite	U-O _{ax}	1.80	1.7	0.0014	-10.6
	U-O _{eq1}	2.26	2.1	0.0077	-10.6
	U-O _{eq2}	2.47	1.9	0.0059	-10.6
	U-U	3.84	1.2	0.0023	-17.3
	U-U	4.53	1.4	0.0065	-17.3
pH-7	U-O _{ax}	1.80	1.8	0.0019	-12.6
	U-O _{eq1}	2.27	2.7	0.0074	-12.6
	U-O _{eq2}	2.49	1.5	0.0059	-12.6
	U-U	3.87	1.4	0.0052	-12.2
pH-9	U-O _{ax}	1.84	2.2	0.0049	-9.4
	U-O _{eq1}	2.25	3.5	0.0104	-9.4
	U-O _{eq2}	2.47	1.7	0.0131	-9.4
	U-U	3.71	1.6	0.0070	-15.7
	U-U	3.92	1.4	0.0051	-15.7
pH-11	U-O _{ax}	1.86	2.1	0.0035	-8.8
	U-O _{eq1}	2.24	2.4	0.0057	-8.8
	U-O _{eq2}	2.40	1.9	0.0110	-8.8
	U-U	3.71	1.2	0.0047	-15.5
	U-U	4.21	1.0	0.0068	-15.5

The results of curve-fitting analyses are shown in Figures 1 and 2, and the bond lengths and coordination numbers are summarized in Table 1. The sample pH-7 closely resembles schoepite with ~2 O at 1.80 Å, a split shell of ~4 equatorial O atoms at 2.26 Å and 2.48 Å, and ~1 U at 3.87 Å. Schoepite also shows ~1 U at 4.53 Å, the detection of which is likely due to a more homogeneous sample as well as the low temperature measurement. As the pH of the precipitation reactions increases from 7 to 9 and 11, the axial oxygen bond lengths increase to 1.84 Å and 1.86 Å, respectively while the equatorial bond lengths remain split and, on average, show a decrease.

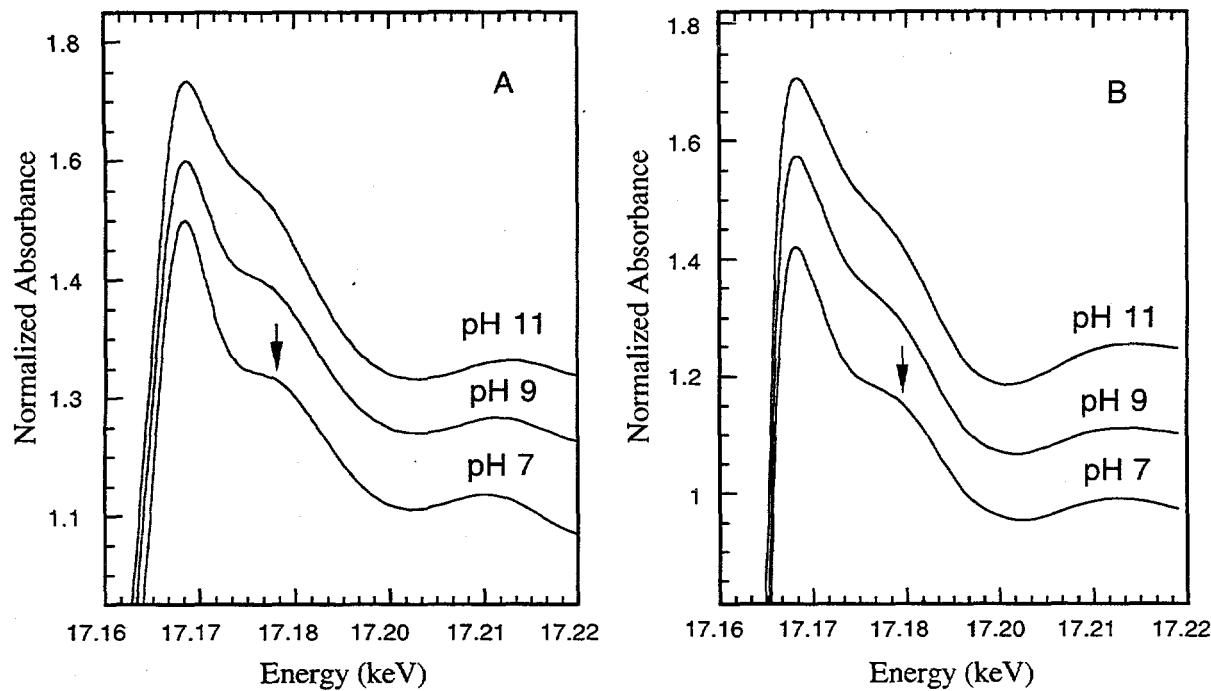


Figure 3. Normalized U L_{III}-edges measured from experiment (A) and calculated from theoretical models (B) for the precipitates pH-7, pH-9, and pH-11.

The normalized U L_{III}-edges for pH-7, pH-9, and pH-11 are shown in Figure 3a. The primary absorption peak at 17.17 keV is associated with an allowed 2p → 6d transition. The shoulder that appears at *ca.* 17.18 keV has been observed in the L_{III} XANES of numerous U(VI) oxides [6, 7], where it has been proposed to originate from MS resonances that are associated with the relatively short U-O bond interaction of the uranyl group. This assignment has been confirmed more recently by calculations using FEFF6 [8]. As the pH increases, the position of the MS resonance shifts to lower energy.

The U L_{III} XANES were modeled using FEFF6 and the structure from the model compound α -UO₂(OH)₂. The calculations were done using a 5 Å radius cluster with the uranium atom at the center. In order to simulate the shifts in the position of the MS resonance, the U-O_{axial} bond lengths were varied using the values obtained from the EXAFS curve-fits, 1.80 Å, 1.84 Å, and 1.86 Å. The results of the simulations are shown in Figure 3b. As is shown, the calculations are quite accurate at simulating both the MS resonance shape and its energy shift as a function of pH.

DISCUSSION

The U-O_{axial} bond lengths are 1.80, 1.84, and 1.86 Å in pH-7, -9, and -11 oxide samples, and the average U-O_{equatorial} bond lengths are 2.38, 2.36, 2.32 Å, respectively. These trends along with the contraction of the U-U bonds with increasing pH suggest the structural changes shown in Figure 4. In pH-7 the precipitated solid possesses U-O bond lengths indicative of the schoepite sample reported here. In pH-11, the uranyl group becomes elongated and the equatorial bonds contract while the sample has U-O bond lengths which are closer to those found in the structural determinations of Na₂UO₄, Na₂U₂O₇, and K₂U₇O₂₂. The pH-9 sample has a structure which is intermediate between the others.

The correspondence between the structures of pH-7 and schoepite may be explained by the nearly identical chemical conditions for each (i.e., low ionic strength and pH=7). Apparently, the presence of dilute sulfate has little effect on the structure of the precipitated solid. Although the synthesis of sodium uranates typically has been done at high temperature and in the solid state, it is possible to form the same structures from precipitation reactions using uranyl nitrate

solutions at high pH. Analogous to the pH-11 solid that was formed in the presence of dilute sulfate, precipitated polyuranates are orange in color. In addition, the formation of a polyuranate rather than a monouranate is favored in room temperature solutions at pH=11. Thus, it is likely that the pH-11 sample is a hydrated uranate (i.e., $\text{Na}_2\text{U}_3\text{O}_{10}\cdot\text{xH}_2\text{O}$).

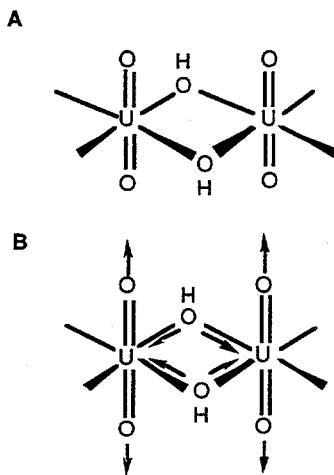


Figure 4. Proposed structural models for the pH-7 and schoepite samples (A) and pH-11 sample (B).

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