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Summary

The distribution of ^{237}Np(V) between aqueous $NaHCO_3$ solutions and U(VI) hydroxide solids was investigated. Experiments were initiated by addition of U solids to Np solutions and by coprecipitation of U and Np. Analysis by U L_{III} extended X-ray absorption fine structure (EXAFS) spectroscopy and infrared absorption spectroscopy indicated the solid phase was synthetic schoepite. Equilibrium Np distribution coefficients were 5-44 mL/g in the pH range 6-8. The results are consistent with adsorption of Np by the solids and provide no evidence of Np incorporation in the bulk solid.

Introduction

An understanding of mechanisms controlling the release of radionuclides during corrosion of spent nuclear reactor fuel is essential for the long-term performance analysis of a spent fuel repository. In an oxidizing water, oxidative dissolution of the UO_2 waste form leads to precipitation of U(VI) alteration products such as uranyl oxide hydrates or uranyl silicates [1]. Adsorption or incorporation of impurities by the alteration phases may affect the release of certain radionuclides [2-5], but few experimental studies of these processes are available. Eu, Am and Cm coprecipitation with Na polyuranates in 5 m NaCl was consistent with spent fuel leaching results in the same medium [3]. Sr, Cs and Pu were identified in U(VI) alteration products of spent fuel [4].

UO_2^{2+} and NpO_2^{+} are linear molecular ions of similar size. If local charge-balancing processes (e.g., parallel uptake of alkali metal cations) occur, then Np(V) may form substitutional impurities in U(VI) phases [2]. The ratio of Np to U in dehydrated shoepite ($UO_3{\cdot}0.8H_2O$) crystallites formed on spent fuel was observed to be 6-12 times larger than the ratio of Np to U in the spent fuel [5]. However, Np may have been present as an adsorbate, a substitutional impurity, or a microprecipitate.

The objective of this work was to investigate Np(V) adsorption or incorporation by U(VI) oxide hydrates in equilibrium with aqueous solutions near pH 7. Synthetic schoepite phases containing ammonium and sodium were studied because they are readily formed as precipitates and equilibrium solids under these conditions. Experiments were conducted for Np:U molar ratios up to 5% and equilibration times of several months in order to look for evidence of Np substitution in the bulk solids.

Experimental Procedure

The ^{237}Np chloride stock solution was prepared by anion exchange followed by precipitation and dissolution of NpO_2OH. Optical absorption spectroscopy over the 400-1400 nm wavelength range indicated $\geq$ 98% of the Np was in the +5 oxidation state [6]. Alpha spectrometry and low energy (10-310 keV) gamma spectrometry revealed no radioactive impurities except for the ^{233}Pa daughter. Np concentrations were measured using the 29 keV gamma ray. The counting efficiency was determined with a NIST ^{237}Np standard. The U starting material was reagent grade $UO_2(NO_3)_2{\cdot}6H_2O$.

Sample Set I: The solid was prepared by addition of NH_4OH to a uranyl nitrate solution until a stable pH 5.5 was attained. The yellow precipitate was aged for 3 days in the mother liquor, rinsed with deionized water and dried at 30°C. Each sample was prepared by mixing a weighed quantity of about 30 mg solid and 25 mL aqueous $NaHCO_3/NpO_2Cl$ solution. The initial Np concentration was 1.54×10^{-5} or 1.51×10^{-4} M. Samples were equilibrated in closed polycarbonate tubes on an orbital shaker at 23°C for 93 days. Sample pH reached ± 0.1 unit of the equilibrium value in 10-20 days.

Sample Set II: Aqueous solutions of uranyl nitrate and NpO_2Cl were titrated with NaOH and $NaHCO_3$ to pH 6-8 to form yellow precipitates. After precipitation each sample contained about 34 mg solid and 38 mL liquid. In sample set II, ionic strength was adjusted to 18 mM with $NaClO_4$. The initial Np concentration was 1×10^{-5} or 1×10^{-4} M. The samples were equilibrated in closed polycarbonate tubes on an orbital shaker at 23°C for 116 days.

After equilibration the samples were centrifuged to separate the liquid and solid phases. A portion of each solid was dissolved in aqueous HCl solution, U was determined using the 414 nm optical absorption peak, and Np was determined using the 29 keV gamma ray. The amount of Np per g of solid was calculated from the Np:U molar ratio and a formula weight of 322 g/mole U. The quantity of Np in the liquid was calculated as the initial quantity minus the quantity in the solid. The distribution coefficient K_d was calculated as n_s/n_l, where n_s = moles of Np per g of solid and n_l = moles of Np per mL of liquid.

Uranium L_{III} X-ray absorption spectra of five solids from sample set I were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline IV-1 using a Si(220) double-crystal monochromator. The monochromator was detuned so that the incident flux was 50% of the maximum flux in order to reject higher-order harmonic content of the beam. About 10 mg of each solid was sealed in a polyethylene tube. The beam size was 3 mm horizontal by 0.5 mm vertical. Spectra were collected at room temperature in fluorescence mode using a Ge detector developed at Lawrence Berkeley National Laboratory [7]. Energy calibrations were made by simultaneous measurement of the transmission spectrum of a UO_2 reference using Ar-filled ionization chambers. The first inflection point of the absorption edge of the reference was defined as 17166.0 eV.

The raw X-ray absorption spectra were processed by standard methods [8] using the suite of programs EXAFSPAK developed by G. George of SSRL. The backscattering phases and amplitudes of the individual neighboring atoms were based on FEFF 7.2 [9]. Input files for FEFF 7.2 were prepared using the structural modeling code ATOMS 2.46b [10]. Modeled interactions were derived from FEFF 7.2 single or multiple scattering paths calculated for the model compound α-$UO_2(OH)_2$ [11] or the model molecular ion $UO_2(CO_3)_3^{4-}$ [12].

The solids were prepared for infrared analysis as pressed CsI pellets containing about 1 mg of sample and measured over the wavenumber range 400-4000 cm^{-1} at 4 cm^{-1} resolution using an FTIR spectrometer.

Results and Discussion

1. Liquid-Solid Equilibria

The equilibrium liquid compositions, solid phase Np:U molar ratios and distribution coefficients are listed in Tables 1 and 2. Similar results were obtained when equilibrium was approached from the two different kinetic paths, addition of U solids to Np solutions and coprecipitation of U and Np, which is evidence that a true equilibrium state was attained. In all cases the Np:U molar ratios are too small to demonstrate formation of a solid solution. The results are consistent with adsorption of Np by the solids. For example, a Np:U ratio of 10^{-3} is consistent with reasonable estimates of the average grain size (3 μm), density (4 g cm^{-3}) and sorbate surface density (4 nm^{-2}).

At a fixed pH, the observed distribution coefficients are nearly constant as the Np concentration in the liquid phase is changed by a factor of 10. The K_d values are in the range 5-44 mL/g over the pH range 6-8. Distribution coefficients in the same range are observed for Np(V) adsorption on silicate sedimentary materials [13]. In our results there is no clear trend in the pH dependence of Np adsorption on the solids. The observed variation in K_d values may be due to small differences in the specific surface area of the solids.

2. Solid Phases

The experimental k^3-weighted EXAFS spectra, the Fourier transformed spectra (FT), and the corresponding best theoretical fits are shown in Figures 1 and 2. Spectra of a previously analyzed synthetic schoepite sample are shown for reference purposes [13]. The structural parameters are summarized in Table 3. The primary FT peak is indicative of the uranyl ion with two axial oxygen atoms at 1.80-1.81 Å. There are 4-6 equatorial oxygen atoms split into two distinct shells at 2.24-2.27 Å and 2.43-2.51 Å. A U-U shell at 3.85-3.86 Å is observed in all samples. The EXAFS spectra and curve fits for all samples closely match previous results for schoepite-type precipitates equilibrated at pH 7 [13]. There was no evidence of uranyl-carbonate bonding in the EXAFS data.

Similar infrared absorption spectra were obtained for the initial solid of sample set I and the equilibrium solids of both sample sets. A representative spectrum is shown in Figure 3. The UO_2^{2+} asymmetric stretch is seen as a strong single band at 916-923 cm^{-1}. The observed frequency and absence of splitting are consistent with uranyl solids rather than uranates [13-15]. In pure $UO_3 \cdot 2H_2O$ the uranyl stretch occurs at 958 cm^{-1} [14]. The lower frequencies observed here indicate weaker uranyl bonding, likely due to the presence of ammonium or sodium in these solids. Estimated ammonium- or sodium-to-uranium ratios are about 1:3 based on the methods of preparation [16-17]. In sample set I, the strong band observed at 1400-1410 cm^{-1} corresponds to the NH_4^+ ν_4 mode [18]. In all samples, a lattice mode is observed at 461-465 cm^{-1}, the H_2O bend is observed at 1630-1635 cm^{-1} and broad OH stretching bands are observed at 2800-3600 cm^{-1}.

Conclusions

The distribution of Np(V) between aqueous $NaHCO_3$ solutions and synthetic schoepite solids was investigated. Equilibrium was approached from two different kinetic paths, addition of U solids to Np solutions and coprecipitation of U and Np. The results were consistent with adsorption of Np and provide no evidence of Np incorporation in the bulk solids.

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Table 1. Equilibrium data for sample set I. Initial condition: synthetic schoepite solid in aqueous Np(V) solution.

Sample	pH	$[CO_3^{2-}]_{Tot}$ (mM)	Ion.Str. (mM)	[Np] (M)	Solid phase Np:U ratio	K_d (mL/g)
138	6.3	0.89	1.71	1.53×10^{-5}	2.5×10^{-5}	5
140	7.1	0.61	1.01	1.49×10^{-5}	1.5×10^{-4}	32
137	7.2	0.93	1.51	1.48×10^{-5}	1.6×10^{-4}	33
139	7.4	0.69	1.01	1.47×10^{-5}	1.9×10^{-4}	40
136	7.9	0.97	1.01	1.48×10^{-5}	1.7×10^{-4}	37
133	6.5	0.89	1.82	1.47×10^{-4}	1.3×10^{-3}	27
135	7.1	0.62	1.14	1.45×10^{-4}	1.6×10^{-3}	33
132	7.2	0.93	1.63	1.44×10^{-4}	2.0×10^{-3}	44
131	7.4	0.97	1.14	1.46×10^{-4}	1.5×10^{-3}	32
134	7.4	0.70	1.14	1.45×10^{-4}	1.7×10^{-3}	36

Table 2. Equilibrium data for sample set II. Initial condition: coprecipitation of synthetic shoepite and Np(V).

Sample	pH	$[CO_3^{2-}]_{Tot}$ (mM)	[Np] (M)	Solid phase Np:U ratio	K_d (mL/g)
146	7.0	6.1	1.05×10^{-5}	3.3×10^{-5}	9.7
148	7.7	1.9	9.87×10^{-6}	3.2×10^{-5}	10
150	7.9	2.2	9.63×10^{-6}	2.9×10^{-5}	9.4
143A	7.2	2.1	9.90×10^{-5}	4.6×10^{-4}	14
145	7.6	1.7	1.06×10^{-4}	4.6×10^{-4}	13

Table 3. EXAFS structural results for the solids.

Sample	Shell	R (Å)[a]	N[a]	σ^2 (Å^2)[b]	ΔE_0 (eV)
131	U-O$_{ax}$	1.81	2.00	0.00132	-13.8
	U-O$_{eq1}$	2.24	4.00	0.01415	
	U-O$_{eq2}$	2.47	2.13	0.01415	
	U-U	3.86	2.19	0.00452	
132	U-O$_{ax}$	1.80	2.00	0.00119	-13.1
	U-O$_{eq1}$	2.26	2.71	0.00733	
	U-O$_{eq2}$	2.49	1.78	0.00733	
	U-U	3.86	1.81	0.00391	
133	U-O$_{ax}$	1.80	2.00	0.00170	-13.9
	U-O$_{eq1}$	2.26	4.01	0.01076	
	U-O$_{eq2}$	2.49	2.19	0.01076	
	U-U	3.85	2.23	0.00455	
134	U-O$_{ax}$	1.80	2.00	0.00151	-13.2
	U-O$_{eq1}$	2.27	2.73	0.00982	
	U-O$_{eq2}$	2.51	1.38	0.00982	
	U-U	3.86	2.57	0.00523	
135	U-O$_{ax}$	1.80	2.00	0.00051	-13.5
	U-O$_{eq1}$	2.24	2.18	0.00863	
	U-O$_{eq2}$	2.43	1.33	0.00863	
	U-U	3.85	0.88	0.00066	

[a] The 95% confidence limits for the bond lengths R and coordination numbers N for each shell are: U-O$_{ax}$, ±0.009 Å and ± %; U-O$_{eq1}$, ±0.057 Å and ±124%; U-O$_{eq2}$, ±0.14 Å and ±131%; U-U, ±0.019 Å and ±64%, respectively.

[b] σ is the EXAFS Debye-Waller term which accounts for the effects of thermal and static disorder through damping of the EXAFS oscillations by the factor $\exp(-2k^2\sigma^2)$.

Figure Captions

Figure 1. Data (- - -) and fits (——) for the raw k^3-weighted U L_{III} EXAFS spectra of samples: (a) 135, (b) 134, (c) 133, (d) 132, (e) 131, (f) synthetic schoepite.

Figure 2. Data (- - -) and fits (——) for the Fourier transformed U L_{III} EXAFS spectra of samples: (a) 135, (b) 134, (c) 133, (d) 132, (e) 131, (f) synthetic schoepite.

Figure 3. Infrared spectrum of solid from sample 136.

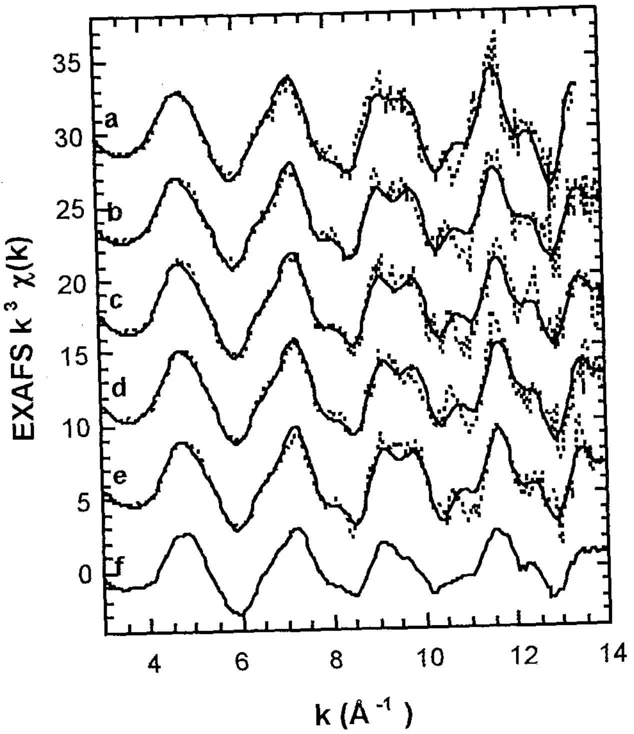


Figure 1.

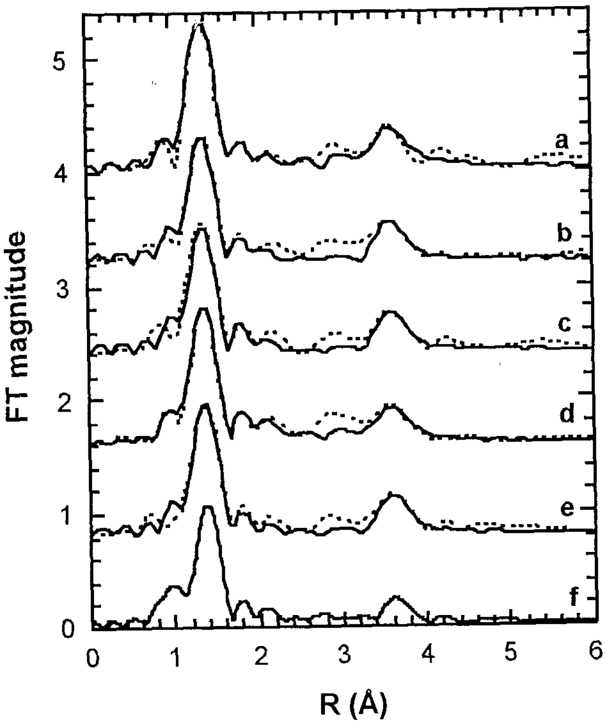
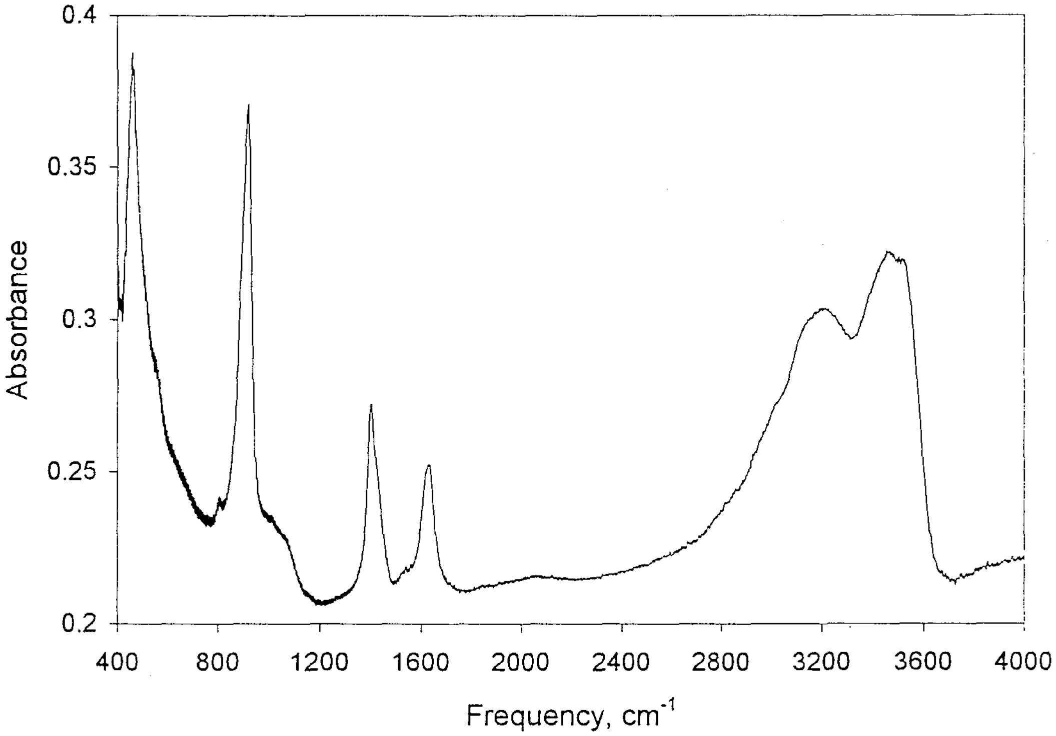


Figure 2.



0.4
0.35
0.3
0.25
0.2
Absorbance
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Frequency, cm-1

Figure 3.