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U.S. Nuclear Regulatory Commission  
ATTN: Mrs. Deborah A. DeMarco  
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Subject: Programmatic Review of Poster

Dear Mrs. DeMarco:

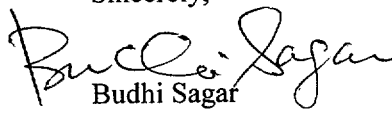
The enclosed poster is being submitted for programmatic review. This poster will be submitted for presentation at the Surface Chemical Processes in Natural Environments Conference, to be held October 1-6, 2000, in Ascona, Switzerland. The title of this poster is:

“Local Structure of Uranium(VI) Sorbed on Clinoptilolite and Montmorillonite”  
by Richard J. Reeder, Melissa Nugent, and Roberto Pabalan.

This poster is a product of the CNWRA and does not necessarily reflect the view(s) or regulatory position of the NRC.

Please advise me of the results of your programmatic review. Your cooperation in this matter is appreciated.

Sincerely,

  
Budhi Sagar  
Technical Director

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Enclosure

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## INTRODUCTION

Sorption is an important mechanism for attenuating the migration of radionuclides from nuclear waste repositories, such as the proposed geologic repository at Yucca Mountain (YM), Nevada, to the accessible environment. In this study, x-ray absorption fine structure (XAFS) spectroscopy was used to elucidate the structure and oxidation state of uranium species sorbed onto the clay mineral montmorillonite and the zeolite mineral clinoptilolite, which are important minerals at YM. Both minerals contain two types of sorption sites: (i) permanently charged cation-exchange sites and (ii) variably charged surface hydroxyl groups. The former is due to isomorphous substitution in the structure, e.g., of Al(III) for Si(IV) within the tetrahedral layer of montmorillonite or within the zeolite framework, causing a permanent negative charge that is compensated by cations interacting with the interlayer or intracrystalline exchange sites. The latter is due to partially coordinated Al and Si exposed at the clay crystallite edges or zeolite surfaces, which hydrolyze to form aluminol (AlOH) and silanol (SiOH) groups. These hydroxylated sites exhibit acid/base behavior and coordinative properties similar to those of oxide (e.g., SiO<sub>2</sub>) surfaces.

Uranium(VI) sorption onto mineral surfaces is a strong function of pH. As shown in Figure 1a, at atmospheric PCO<sub>2</sub>(g), uranyl sorption on montmorillonite, clinoptilolite, and quartz is highest at near-neutral pHs where aqueous uranyl species are mainly in the form of hydroxy-complexes (Figure 1b). Uranyl sorption is low at alkaline pHs where uranyl-carbonate species are predominant. For minerals with no permanently charged cation-exchange sites such as quartz (Figure 1b), uranyl sorption is also low at acidic pHs where aqueous uranyl exists primarily as the mononuclear, ionic species UO<sub>2</sub><sup>2+</sup>. However, uranyl sorption onto negatively-charged cation-exchange sites of montmorillonite and clinoptilolite from solutions of low pH and low ionic strength has been shown to be important [refs. 1, 2].

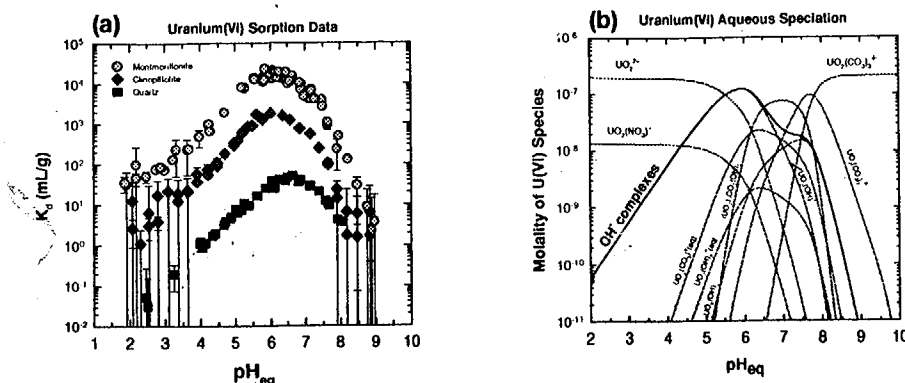
## EXPERIMENTAL

### Sample preparation

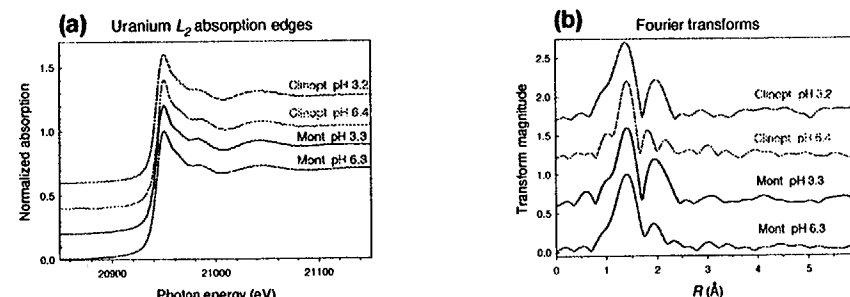
The Ca-montmorillonite (SAZ-1; source locality: Cheto, AZ) and Na-clinoptilolite (source locality: Death Valley Junction, CA) used in the study were pretreated to remove carbonates and iron oxides, and dried prior to the experiments. The measured surface areas of montmorillonite and clinoptilolite are 109 and 10 m<sup>2</sup>/g, respectively, and the reported cation exchange capacities [refs. 3, 4] are 1.2 and 2.04 meq/g, respectively. Samples for XAFS analysis were prepared by reacting 1 gram of mineral powder with 450 mL of uranyl nitrate solution (11 or 22 mg/L <sup>238</sup>U). Samples were prepared at pH ~3 and ~6 so the effect of pH on the sorption mechanism could be evaluated. The reaction bottles were placed on a gyratory shaker, and air was bubbled through the solutions to maintain atmospheric PCO<sub>2</sub>. Periodic adjustments of pH were made with HNO<sub>3</sub> or NaOH to maintain a pH of ~3 or ~6. After about two weeks, the mixtures were centrifuged and the moist pastes were loaded onto XAFS sample holders. The uranium concentrations before addition of solid and after sorption equilibrium was achieved were analyzed by ICP to determine the uranyl uptake.

### X-ray absorption fine structure spectroscopy

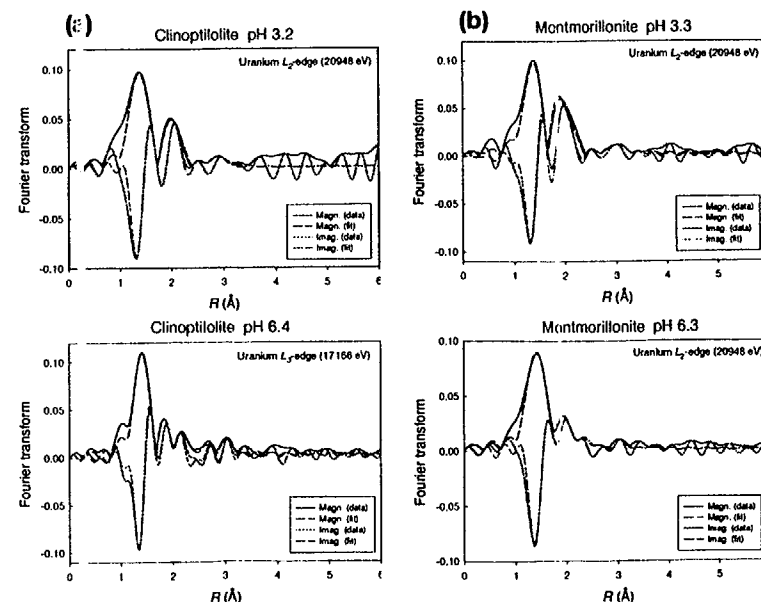
XAFS spectra were collected on the moist paste samples at beamline X11A of the National Synchrotron Light Source at Brookhaven National Laboratory. Multiple scans were taken over the uranium L<sub>2</sub> (20948 eV) and L<sub>3</sub> edges (17166 eV) using a pair of Si(111) monochromator crystals, with one crystal detuned by ~30% for harmonic rejection. Absorption spectra were obtained at room temperature using fluorescence detection with a 13-element solid-state Ge detector. Data analysis included subtraction of pre-edge background, normalization, and conversion to k-space, followed by μ<sub>0</sub> fitting using a cubic spline. The χ(k) function was Fourier transformed using k<sup>3</sup> weighting (typical k-range: 2.9–12.8 Å<sup>-1</sup>). All fitting was done in R-space using WinXAS [ref. 5], and theoretical backscattering amplitudes and phase shifts were calculated using FEFF7 [ref. 6]. Reference spectra from previous studies [ref. 7] were used to assess the fit quality with the theoretical amplitudes and phases. Several starting models were used for the FEFF7 calculations, including soddyite [(UO<sub>2</sub>)<sub>2</sub>(SiO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] and sklodowskite [MgO(UO<sub>2</sub>)<sub>2</sub>(SiO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>7</sub>]. A single threshold energy value (ΔE<sub>0</sub>) was allowed to vary during fitting. Errors in the fit parameters, estimated from fits of well-characterized model compounds, are ± 20 % for coordination number (CN) and ± 0.02 Å for first and second shell distances (R). Debye-Waller type factors (σ<sup>2</sup>) have approximate errors of ± 0.002–0.003 Å<sup>2</sup>.



**Figure 1.** Comparison of (a) uranyl sorption on Na-montmorillonite, Na-clinoptilolite, and quartz and (b) uranyl aqueous speciation ( $\Sigma U_i = 2.1 \times 10^{-7}$  M;  $PCO_2 = 10^{-3.5}$  atm; 0.1 M NaNO<sub>3</sub> matrix) [figures from ref. 8]. Potential ion exchange of UO<sub>2</sub><sup>2+</sup> with Na<sup>+</sup> in montmorillonite and clinoptilolite at pH < 4 is suppressed by the 0.1 M NaNO<sub>3</sub> background electrolyte.



**Figure 2.** (a) Near-edge regions of uranium L<sub>2</sub> absorption spectra and (b) Fourier transform magnitudes (k<sup>3</sup>-weighting; uncorrected for phase shifts) for uranyl sorbed on clinoptilolite and montmorillonite at different pH values



**Figure 3.** R-space fits showing the real and imaginary parts for uranyl sorbed onto (a) clinoptilolite and (b) montmorillonite at different pHs

**Table 1.** Best-fit XAFS parameters for uranyl sorbed on clinoptilolite and montmorillonite

Clinoptilolite pH 3.2					Clinoptilolite pH 6.4				
Shell	CN	R (Å)	σ <sup>2</sup> (Å <sup>2</sup> )	χ <sup>2</sup> (Å <sup>2</sup> )	Shell	CN	R (Å)	σ <sup>2</sup> (Å <sup>2</sup> )	χ <sup>2</sup> (Å <sup>2</sup> )
U-O <sub>eq</sub>	2	1.78	0.041		U-O <sub>eq</sub>	2	1.78	0.041	
U-O <sub>ax</sub>	4	2.41	0.002		U-O <sub>ax</sub>	4	2.48	0.003	
U-O <sub>ax</sub>	4	2.48	0.004		U-O <sub>ax</sub>	4	2.48	0.005	
U-Si	2	3.54	0.004		U-Si	2	3.57	0.004	
ΔE <sub>0</sub>	4.1				ΔE <sub>0</sub>	4.1			

Montmorillonite pH 3.3					Montmorillonite pH 6.3				
Shell	CN	R (Å)	σ <sup>2</sup> (Å <sup>2</sup> )	χ <sup>2</sup> (Å <sup>2</sup> )	Shell	CN	R (Å)	σ <sup>2</sup> (Å <sup>2</sup> )	χ <sup>2</sup> (Å <sup>2</sup> )
U-O <sub>eq</sub>	2	1.77	0.001		U-O <sub>eq</sub>	2	1.78	0.002	
U-O <sub>ax</sub>	4	2.41	0.007		U-O <sub>ax</sub>	4	2.48	0.016	
U-O <sub>ax</sub>	4	2.48	0.004		U-O <sub>ax</sub>	4	2.44	0.015	
U-Si	2	3.54	0.004		U-Si	2	3.58	0.002	
ΔE <sub>0</sub>	4.5				ΔE <sub>0</sub>	4.4			

<sup>1</sup> Coordination numbers from ref. 7 at 2.25 Å.  
<sup>2</sup> Errors on distances are ± 0.02 Å.  
<sup>3</sup> Errors on Debye-Waller type factor parameters are ± 0.001 Å<sup>2</sup>.  
<sup>4</sup> Fixed at 1.7 for axial and 2.4 for equatorial distances.  
<sup>5</sup> Peak shifted slightly to account for UO<sub>2</sub>·xH<sub>2</sub>O.  
<sup>6</sup> Initial energy threshold varied during fitting.

## RESULTS

The near-edge regions of the uranium L<sub>2</sub>-edge absorption spectra are shown in Figure 2a. For all samples, the edge positions, relative to U(IV) and U(VI) reference standards, and the presence of a characteristic shoulder above the absorption maximum confirm the uranium remains in the 6+ oxidation state. No obvious difference in the near-edge structure is observed among the samples. Fourier transform (FT) magnitudes are shown in Figure 2b. All FT magnitudes show a principal peak at 1.4 Å, corresponding to two axial oxygens at ~1.8 Å in the uranyl moiety. Peaks at ~2 Å in the FT correspond to equatorial oxygen shells. For the clinoptilolite and montmorillonite reacted at pH ~3, the FT magnitudes show a single peak well separated from the axial oxygen component. In contrast, both minerals at pH ~6 show separate and weaker peaks, suggesting split equatorial oxygen coordination. No significant peaks are apparent at higher R, indicating no significant backscattering from silicon, aluminum, or other uranium atoms and unlikely formation of a uranyl-containing second phase. A weak peak at ~3 Å in the FT reflects a multiple-scattering path within the UO<sub>2</sub> moiety. For all fits, a multiple-scattering contribution at ~3.58 Å was fitted with the four-legged O<sub>ax1</sub>-U-O<sub>ax2</sub>-U path.

Best fit results are reported in Table 1. All fits show two axial oxygens in the range 1.77–1.79 Å. The uranyl sorbed onto montmorillonite at pH 3.3 shows a single equatorial shell of 5–6 oxygens at 2.41 Å. At pH 6.3, the montmorillonite is best fitted with two equatorial shells (each with ~3 O atoms) at 2.28 and 2.44 Å. Generally similar fit results were found for the uranyl sorbed on clinoptilolite. The sample of clinoptilolite reacted at pH 6.4 shows two equatorial oxygen shells at 2.28 and 2.45 Å. For the clinoptilolite sample reacted at pH 3.2, the single peak in the FT suggested a single equatorial oxygen shell, and fitting yielded ~5 O atoms at 2.45 Å. However, the fit quality was not as good as for the montmorillonite at pH 3.3. The fit was improved by an additional, weak equatorial oxygen component, giving best fit results of ~1 oxygen at 2.21 Å and ~4 oxygens at 2.42 Å. The significance of the weak contribution at 2.21 Å needs additional clarification. Attempts to fit U-Al and U-Si paths generally resulted in very small CN values that were significantly less than the estimated errors. The lack of uranium backscattering also suggests that sorbed uranyl species are mononuclear.

## CONCLUSIONS

The results demonstrate a difference in the equatorial coordination of the uranyl sorbate as a function of pH for both montmorillonite and clinoptilolite. Split equatorial shells are evident for both samples at pH ~6, whereas primarily a single shell exists at pH ~3. The results for montmorillonite are consistent with the EXAFS data reported by Sylwester et al. [ref. 9].

The difference in U-O distances in the equatorial oxygen shell for the samples at pH ~6 must reflect a difference in the bonding of these oxygens with the sorption sites of the minerals. Hence, the split equatorial shells probably indicate discrete equatorial oxygens form chemical bonds at surface functional groups, as would be expected for an inner-sphere-type surface complex. In contrast, the single equatorial shell for samples at pH ~3 suggests a more uniform bonding environment for the oxygens as would be expected for an outer-sphere-type complex. Such an environment is consistent with ion exchange at cation-exchange sites of the sorbents. However, the experiments do not provide direct evidence the uranyl ion is located in the interlayer exchange sites of montmorillonite or in the intracrystalline channels of clinoptilolite. The alternate XAFS fit indicating equatorial splitting for clinoptilolite reacted at pH ~3 is consistent with distortion of the equatorial shell due to steric limitations imposed by the zeolite structure. Further investigations are needed to refine the sorption mechanisms.

## REFERENCES

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## ACKNOWLEDGMENTS

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