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Speciation of uranium(VI) sorption complexes on montmorillonite.

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ABSTRACT: We have investigated the effect of changes in solution speciation on the nature of uranyl sorption complexes on montmorillonite at different surface coverages (342 to 13042 ppm). Aqueous U(VI) solutions between pH 3 to 7 were batch-equilibrated with montmorillonite for several days; specific pH values were selected such that the solutions consisted of dominantly monomeric, oligomeric, or a mix of monomeric and oligomeric aqueous uranyl species. Emission spectroscopy was used to investigate the nature of U(VI) sorbed to montmorillonite. Several surface cmoplexes have been identified. The distribution of these complexes changes markedly as a function of ssurface coverage at moderate uranyl loadings (8230 to 13042 ppm), but a single species dominates at lower coverages (342 to 476 ppm). A distinct set of sorption species form over a wide range of pH values at low to moderate coverages. Furthermore, there are only subtle differences in the nature of sorption complexes formed at different pH values but similar coverages despite markedly different uranyl speciation in solution. These results suggest that the speciation of the solution has minimal influence on the nature of the sorption complex under these experimental conditions.

1. INTRODUCTION

Environmental contaminant releases that contain uranium are among the most serious problems that must be confronted by restoration programs. To facilitate restoration, information concerning the speciation of uranium is needed. Under oxidizing conditions, dissolved uranium is predominantly in the U(VI) (uranyl) form and is quite mobile in the environment, however sorption onto soils may retard its movement. In this study, we have investigated the effect of changes in solution speciation on the nature of uranyl sorption complexes on montmorillonite, a common soil constituent.

2. EXPERIMENTAL

The reference clay SAz-1 from Cheto, Arizona, was obtained from the University of Missouri Source Clay Repository. This is a relatively pure, readily expandable, high cation exchange capacity (CEC ≈1.2 meq/g) montmorillonite with Ca^{2+} as the dominant interlayer cation (VanOlphen and Fripiat, 1979). Uranyl solutions were prepared from recrystallized $UO_2(NO_3)_2 \cdot 6H_2O$ using distilled, deionized water.

Sorption experiments were performed in polyethylene tubes. SAz-1 was mixed with an acidic solution for 36 to 48 hours in a series of individual tubes to fully hydrate the clay. UO_2^{2+} was added to the suspensions and pH adjusted to a range of values by adding varying amounts of $Ca(OH)_2$. Final solids concentration was 20g clay/ L solution and total uranium concentration was 0.04 or 1.1 mM. The suspension was then mixed end-over-end for ≈36 hours. Final pH of the supernatant was measured following centrifugation for

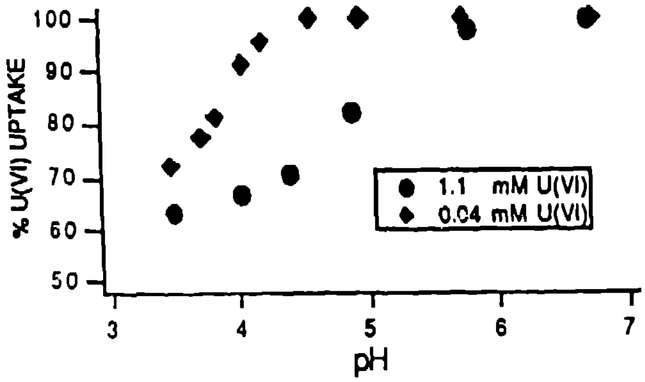

Figure 1. pH dependence of uranyl uptake onto SAz-1 from two different initial solution concentrations. At 100% uptake of 0.04 mM and 1.1 mM, the surface coverage is 472 and 13090 ppm, respectively. The solubility of "$UO_2(OH)_2$" was exceeded for the 1.1mM system above pH ≈ 5.

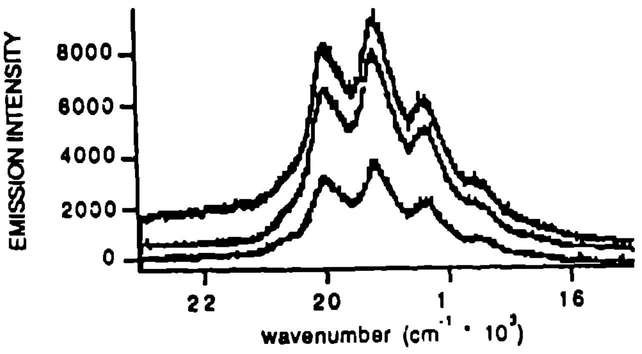

Figure 2. Luminesence spectra for low concentration samples using 364 nm excitation. The spectra (bottom to top) are for samples at pH = 3.47, 4.56, and 5.74.

≈ 10 to 20 minutes. Aliquots of the supernatant were removed for spectrophotometric determination of the uranium concentration using a modified Arsenazo-III method. The uranyl-loaded clays were allowed to air-dry prior to collection of luminescence data; the clay samples were then sealed in glass capillary tubes.

Luminescence spectra were obtained on a SPEX Industries Model 1403 scanning double monochromator equipped with 1800 gr/mm holographic gratings, an RCA C31034 photomultiplier tube, and Stanford Research Model SR400 photon counting electronics. The 364 or 351 nm line from a Spectra Physics Model 2045 continuous wave argon ion laser was used for excitation. Emitted light was collected using 180° backscattering geometry.

3. RESULTS

Results of the batch experiments are presented in Figure 1. As expected, the uranyl uptake curve (plotted as percent uptake versus pH) shifts to higher pH with higher total uranium concentration. The slope of the uptake curves are different for the different uranyl concentrations, which implies that different sorption processes may be involved under these conditions. Above pH ≈ 5 for the 1.1mM uranyl solution concentration samples, the solubility of "$UO_2(OH)_2$" was exceeded (based on thermodynamic calculations) and a lemon-yellow precipitate formed.

The luminescence spectra for aqueous U(VI) sorbed on SAz-1 are characterized by prominent vibronic structure in the emission band (Figures 2 to 6). The luminescence spectrum for UO_2^{2+} sorbed from 0.04mM U(VI) solution (resulting in coverages of 342 to 476 ppm) consists of a single dominant vibronic progression at all pH values (Figure 2). This similarity persists over the entire pH range studied despite the widely varying solution speciation; based on thermodynamic calculations (Tripathi, 1984), the fully aquated monomeric UO_2^{2+} solution species comprises ≥ 99 % of all uranyl species for a 0.04mM uranyl solution at pH ≈ 3.48, whereas oligomeric species consitute ≈ 88 % of the uranyl species at pH ≈ 5.74. Thus the luminescence data suggest that at low surface coverages (≤ 476 ppm), the nature of the sorption complex(es) is not affected by the solution speciation. Note, however, that excitation by 364 nm vs. 351 nm laser light yields slightly different luminescence

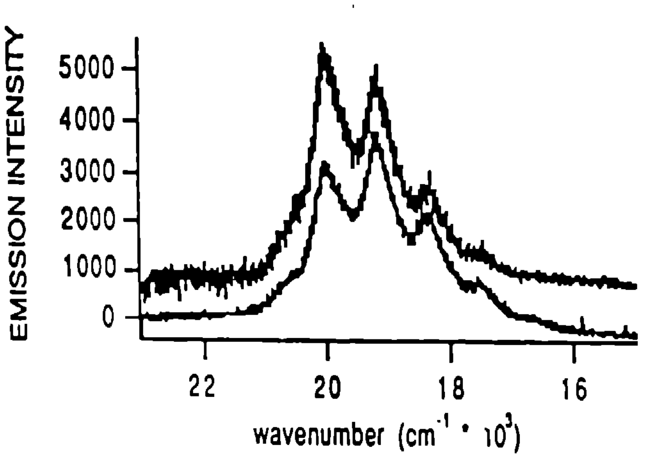

Figure 3. Comparison of the luminescence spectrum of uranyl sorbed to montmorillonite at 476 ppm using 364 (lower) and 351 (upper) nm excitation.

spectra for uranyl at these low coverages (Figure 3), indicating that there are at least two distinct uranyl sorption species on the clay at these coverages (342 to 476 ppm).

The spectra for uranyl sorbed from more concentrated solution (1.1 mM) show marked variation as a function of equilibrium pH and uranyl coverage (Figure 4). As the pH and surface coverage increases for these samples (from pH ≈ 3.48 to 5.78, corresponding to coverages of 8230 to 12804 ppm), the features in the luminescence spectra become broader and less distinct (Figure 4). The spectrum of the highest pH sample (pH ≈ 5.78) resembles that of freshly precipitated "$UO_2(OH)_2$", as expected: the overall amplitude is low despite the high uranyl concentration, and the spectrum is generally featureless. However, the broadening of the features in the spectra for uranyl sorbed at lower pH is not due to the presence of the precipitate; these bands can be deconvolved into two or more distinct spectra, one of which likely corresponds to the composite spectrum seen for uranium sorbed at low coverage (342 to 476 ppm), and others with different vibronic spacings. The presence of multiple species is supported by the excitation wavelength dependence of the luminescence spectra (Figure 5).

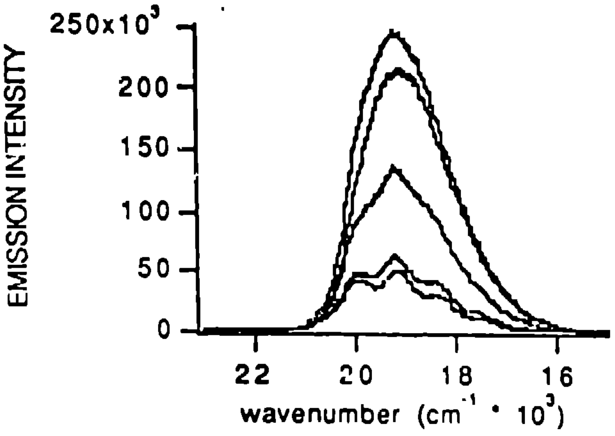

Figure 4. Luminesence data for uranium sorbed on clay from 1.1mM solutions using 364 nm excitation. The spectra (bottom to top) are for samples at pH = 3.48, 4.01, 4.39, 5.78, and 4.88. The overall emission intensity increases concomitant with increasing surface coverage, except for the highest coverage sample (pH = 5.78), which consists predominantly of a "$UO_2(OH)_2$" precipitate.

The formation of multiple sorption species at moderate coverages (≈ 8000 to 13000 ppm) could be the result of changes in pH or surface coverage, or both. The luminescence spectra for uranyl sorbed on clay at ≈ 11000 to 13000 ppm but at different pH values are slightly different (Figure 6), which suggests that equilibrium pH may influence the distribution of sorbed uranyl species. Variations in pH affect both the solution speciation and the nature of the sorption sites on clays. Thus the pH dependence could reflect changes either in the identity of the sorbing species or in the distribution and reactivity of surface sites. However, while the ratio of the different sorption complexes varies as a function of pH, the set of sorption complexes is the same over this range of pH; this is true for sorption from a solution with only monomeric species (pH = 3.48), and from solutions containing predominantly oligomeric species (pH > 4.4). Thus, apparently the uranyl solution speciation only minimally influences the speciation of the sorption complexes under these experimental conditions. The slight pH dependence seen in the luminescence

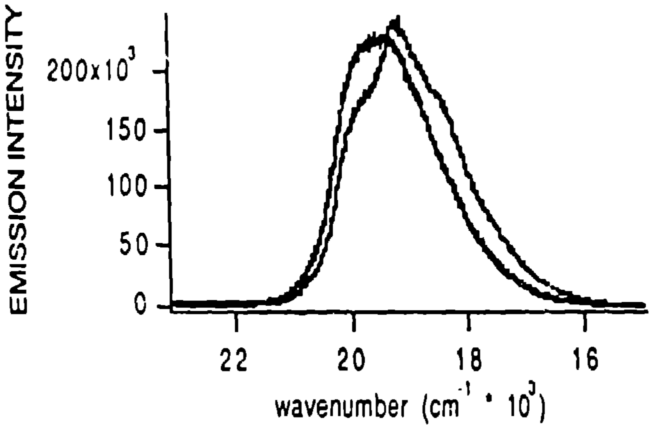

Figure 5. Comparison of the luminescence spectrum of uranyl sorbed to montmorillonite at 9227 ppm (pH = 4.39) from excitation wavelengths of 364 and 351 nm.

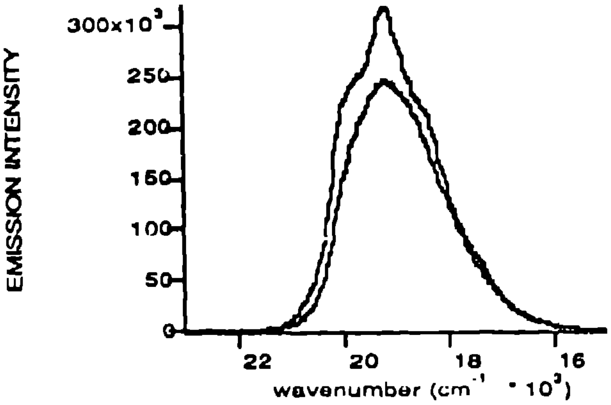

Figure 6. Comparison of the luminescence spectra for uranyl sorbed to montmorillonite at ∼ 11000 ppm (lower) and ∼ 13000 ppm (upper) but equilbrated at different pH values (pH ∼ 4.9 and 3.9, respectively). The pH ∼ 3.9 sample was prepared from a suspension with a higher [U]/clay ratio (103 umoles/g) than used in this study (55 umoles/g).

spectra of sorbed uranyl more probably reflects changes in the nature of the clay surface sites as a function of pH. This conclusion is supported by the lack of pH dependence of the uranyl sorption species formed at low surface coverages. In contrast to the weak dependence of the sorption complexes on pH, the spectra of sorbed uranyl varies markedly as a function of surface coverage. These results suggest that multiple uranyl sorption complexes form on montmorillonite as a function of surface coverage. The luminescence data are consistent with previous work which concluded that the presence of multiple sorption species reflect sorption of uranyl to distinct surface sites and not sorption of different solution species (Morris et al., 1992).

4. CONCLUSIONS

There is a marked change in the distribution of surface complexes as a function of surface coverage at moderate uranyl loadings (8230 to 10787 ppm); these differences are not due to formation of a uranyl precipitate but reflect sorption of uranyl to distinct surface sites on montmorillonite. In contrast to the large effect of surface coverage, the distribution of uranyl sorption complexes varies only slightly as a function solution pH. There is also little difference in the uranyl sorption complexes formed from solutions at different pH's with markedly different uranyl speciation at low surface coverages (342 to 476 ppm). These results suggest that the speciation of the solution has minimal influence on the nature of the sorption complex.

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