

STRUCTURE OF URANIUM(VI) SURFACE COMPLEXES ON KAOLINITE

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The sorption of U(VI) onto the reference kaolinite KGa-1b has been investigated both by batch experiments and EXAFS measurements. Sorption samples were prepared in 0.1 mol/L NaClO₄ at total U concentrations ranging from 1 μmol/L to 20 μmol/L, 4 g/L kaolinite, pH 3.0 to 10.5, presence and absence of ambient CO₂, and 60-h equilibration. The sorption curves for 1 μM U(VI) obtained in presence and absence of CO₂ show that the adsorption edge occurs at pH 5.5. The uptake of U(VI) by kaolinite strongly increased above pH 4.0 and reached its sorption maximum (100 %) in the pH range from 6.0 to 8.0. Above pH 8.0, the amount of U(VI) sorbed onto kaolinite decreased due to the formation of the U(VI) carbonato species in aqueous solution, to 0 % at pH 10.5. In the closed system without CO₂ the sorption of U(VI) was 100 % in the pH range 6.0 to 10.5. At 10 μM total U(VI), the sorption edge is shifted slightly higher to pH 6.0. The uranium uptake also decreased above pH 8.0 in the presence of CO₂ and remains at 100 % in the CO₂-free system. Similar results were found by Sekine, Redden and coworkers [1,2].

The aim of our study was to combine batch experiments with EXAFS spectroscopy to study the speciation of U(VI) at the kaolinite surface in more detail. The samples for the EXAFS measurements were prepared as shown in Table 1. The highest uranium loading of the EXAFS samples was 1200 ppm and the lowest loading was less than 100 ppm, i.e., significantly less than in the previous EXAFS study of Thompson et al. [3]. The uranium L₃-edge EXAFS spectra were recorded in fluorescence mode at room temperature at the Rossendorf Beamline (ROBL) at the European Synchrotron Radiation Facility (ESRF). The software packages EXAFSPAK and FEFF 8.20 were used for the analysis of the EXAFS data using atomic cluster based on the crystal structure of soddyite [4].

The raw data of the U L₃-edge k³-weighted EXAFS spectra of the samples with their corresponding FTs are shown in Fig. 1. The metrical parameters derived from the least-square fits are summarized in Table 1. The U-O_{ax}, U-O_{eq}, and U-Al/Si distances measured by EXAFS suggest that U(VI) forms inner-sphere, monomeric surface complexes with kaolinite in the pH range 5.0 - 8.5. In the presence of atmospheric CO₂, the average U-O_{eq} distance increased from 2.32 to 2.38 Å when the pH was increased from 5.0 to 8.5. This points to the formation of ternary U(VI)-carbonato com-

plexes on kaolinite. A weak and broad feature in the Fourier transform of all samples at approximately 2.3 Å (see Fig. 1) could be fit best with one Si atom at an average U-Si distance of 2.74 ± 0.02 Å. This very short U-Si distance can be rationalized by a corner-sharing model of U(VI) with the [SiO₄] tetrahedrons of kaolinite. However, this possibility needs to be investigated further, for example, by measuring the EXAFS spectra of suitable reference samples.

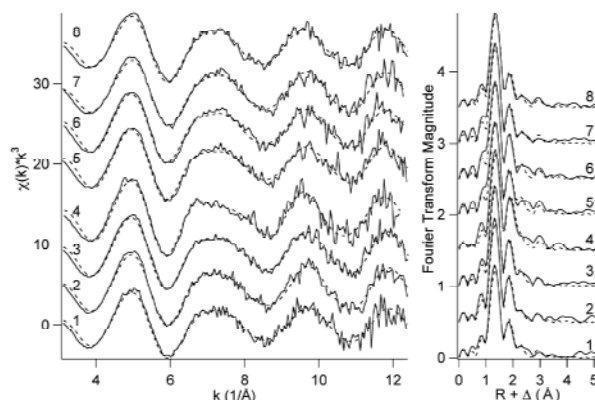


Figure 1: Uranium L₃-edge k³-weighted EXAFS spectra (left) and their corresponding FTs (right) for U(VI) adsorbed on kaolinite.

Table 1: EXAFS fit results.

Sample	Conditions	2xO _{ax}	5xO _{eq}	1xSi
	[U(VI)](μM)/pH	R(Å)	R(Å)	R(Å)
1	10/5.0, air	1.78	2.32	2.71
2	10/6.0, air	1.78	2.33	2.69
3	10/7.0, air	1.78	2.35	2.72
4	10/8.5, air	1.80	2.38	2.71
5	5/7.0, air	1.79	2.35	2.74
6	10/7.0, air	1.79	2.35	2.74
7	20/7.0, air	1.79	2.35	2.88
8	10/8.5, no CO ₂	1.79	2.32	2.71

* ΔR = ± 0.02 Å

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