



Interaction of U(VI) with birnessite: a solution chemistry and EXAFS study.

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Radionuclide migration in natural aqueous environment is an ongoing concern in environmental research. Because layer Mn oxides are widespread, have a large surface area and a high density of binding sites, they control the fate of many important metals, including radionuclides. This work investigates the mechanism and kinetic of the uranyl interaction with birnessite, the predominant layer-type MnO_2 mineral at the Earth's surface. The sorption of U(VI) on synthetic birnessite was studied macroscopically with experiments performed under various conditions of pH (ranging from 4 to 6), dissolved U(VI) concentrations ($[\text{U}^{VI}] = 3.10^{-7}$ to 7.10^{-4} M), and ionic strength (0.01M to 0.1M, in NaClO_4 or Na_2CO_3 media). Under these conditions, the speciation of U(VI) in solution was contrasted, being dominated either by hydrolyzed species, uranyl-carbonato complexes, or polynuclear species. Sorption kinetic depended on the concentration of dissolved U(VI). The amount of sorbed U(VI) per specific surface area largely exceeded the coverages previously reported on related environmental minerals, such as montmorillonite and ferrihydrite, under similar experimental conditions, thus confirming the strong affinity of U(VI) for the birnessite surface. Sorption isotherms exhibited a complex form, and was indicative of, at least, two types of sorption sites.

EXAFS data revealed the presence of two equatorial O shells at ca. 2.31 Å and 2.42-2.51 Å (in addition to the two axial oxygens at about 1.80 Å), and a Mn shell (except in the Na_2CO_3 media) at 3.4 Å in the pH 4 sorption samples. The average number of Mn atoms decreased and the distance of the second equatorial O shell increased to 2.51 Å with increasing aqueous U(VI) concentration. At pH 6, the equatorial oxygens remained split into two distinct shells, but no nearest Mn was detected. No C shell

was detected for any samples, even in the Na_2CO_3 media, nor U-U pair, despite the prevailing presence of polynuclear dissolved species in some of the samples.

From the combination of solution chemistry and EXAFS results, a structural model for the sorption of U(VI) at low pH is proposed, in which the oxygens from the equatorial plane of uranium form two types of surface complexes with edge sites from the birnessite layers. At low aqueous U concentration, adsorption occurred via a bidentate complexation. When the U(VI) concentration increased, the saturation of the previous sites led to the formation of a second type of surface complex, involving monodentate binding to the mineral surface.