Effects of monomeric silicate anion on uranyl adsorption and surface speciation at the hematite-water interface

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Widespread uranium(U)-contaminated plumes have been identified at U.S. Department of Energy sites due to uranium mining operations and nuclear weapon and energy production. Accurate assessment of environmental risks and development of optimal *in-situ* remediation strategies for vadose zones and aquifers requires fundamental knowledge of uranium reactivity and surface speciation under field simulated reaction conditions (e.g., in the presence of common groundwater ions such as bicarbonate and silicate).

As a continuation of previous studies by Bargar and co-workers (Bargar et al, 1999; 2000), we investigated the effects of monomeric silicate anion (Si) on U(VI) adsorption and surface speciation on hematite (Fe_2O_3) surfaces (suspension density = 0.3 g L^{-1}, $[U(VI)]_T$= 10 μM, I=0.1 M $NaClO_4$, $PCO_2=10^{-3.5}$ atm, and $[Si]_T$ = 5-200 μM). Silicate anions are of interest in U(VI) aqueous geochemistry because dissolved Si is known to complex with U(VI)(aq) near neutral pH (e.g., Langmuir, 1978).

As known from previous work, U(VI) adsorption is pH dependent, maximizing at near neutral pH in air-equilibrated systems. Addition of $[Si]_T$ up to 200 μM had a negligible effect on macroscopic U(VI) adsorption. However, the U L_{III} edge in XAS analyses of these samples show that the uranyl cation is coordinated with both Si and Fe atoms at 2.78 and 3.47 (±0.02-0.04) Å, respectively, suggesting the presence of mono-silicate-U(VI) ternary species with U(VI) bidentate binuclear coordination on iron octahedral structures at pH 5 and 7. These research findings add new insight to the mineral-water interfacial chemistry of U-anion (e.g., carbonate and phosphate) ternary species in predicting U(VI) transport processeses in vadose zones and aquifers.

References

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Adsorption of neodymium onto goethite in the presence of fulvic acid at 25 °C

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Adsorption onto goethite may inhibit the migration of REE/actinides, not only in geologic repositories of nuclear waste, but also in soils and other environments that have been accidentally contaminated with nuclear materials. Trivalent lanthanides such as neodymium (Nd), are reasonable analogues of trivalent actinides such as Am^{3+}, Cu^{3+}, Pu^{3+}. Natural organic matter such as humic and fulvic acids may be present in soils and sediments contaminated with nuclear material. This organic matter may either enhance or inhibit adsorption of lanthanides and actinides. Therefore, studies of the effect of humic substances on the adsorption of lanthanides onto goethite and other mineral substrates are required. In this investigation, the adsorption of neodymium to well-characterized goethite was studied as a function of pH and fulvic acid concentration.

Potentiometric titrations were carried out under the following conditions: 0.1m ionic strength, 25 °C and 1 atm. The pH was varied from 2 to 12 via forward titration with a NaOH solution. The pH was then lowered back to 2 via a reverse titration using an HCl solution. At each step, samples were taken for Nd analyses by ICP-AES, after filtration through a 0.2 μm membrane. Binary experiments were carried out involving the adsorption of neodymium onto goethite with total concentrations of 5 ppm neodymium. The degree of adsorption of Nd was essentially zero below pH 4.5, and then rose steeply to near 100% at pH 8 and greater, so a plot of dissolved Nd concentration vs. pH showed a classic cation adsorption edge at approximately pH 6. During the reverse titration, roughly 20% of the adsorbed Nd remained adsorbed over the time-scale (tens of minutes) of the experiments as the pH was lowered to values below 4.5.

Initial experiments in the ternary system were conducted involving the adsorption of neodymium to goethite in the presence of Suwannee River fulvic acid. Initial studies show that FA enhances the adsorption of neodymium onto goethite. There was approximately 20% adsorption at all pH values less than 4.5, and the adsorption edge was shifted to lower pH by 0.5 to 1.0 units. This observation can most likely be explained by the formation of a ternary complex between the goethite surface, Nd and fulvic acid.