
The Influence of Uranyl Hydrolysis and Multiple Site-Binding Reactions on Adsorption of U(VI) to Montmorillonite

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Abstract: Adsorption of uranyl to SWy-1 montmorillonite was evaluated experimentally and results were modeled to identify likely surface complexation reactions responsible for removal of uranyl from solution. Uranyl was contacted with SWy-1 montmorillonite in a NaClO₄ electrolyte solution at three ionic strengths (I = 0.001, 0.01, 0.1), at pH 4 to 8.5, in a N_{2(g)} atmosphere. At low ionic strength, adsorption decreased from 95% at pH 4 to 75% at pH 6.8. At higher ionic strength, adsorption increased with pH from initial values less than 75%; adsorption edges for all ionic strengths coalesced above a pH of 7. A site-binding model was applied that treated SWy-1 as an aggregate of fixed-charge sites and edge sites analogous to gibbsite and silica. The concentration of fixed-charge sites was estimated as the cation exchange capacity, and non-preference exchange was assumed in calculating the contribution of fixed-charge sites to total uranyl adsorption. The concentration of edge sites was estimated by image analysis of transmission electron photomicrographs. Adsorption constants for uranyl binding to gibbsite and silica were determined by fitting to experimental data, and these adsorption constants were then used to simulate SWy-1 adsorption results. The best simulations were obtained with an ionization model in which AlOH₂⁺ was the dominant aluminol surface species throughout the experimental range in pH. The pH-dependent aqueous speciation of uranyl was an important factor determining the magnitude of uranyl adsorption. At low ionic strength and low pH, adsorption by fixed-charge sites was predominant. The decrease in adsorption with increasing pH was caused by the formation of monovalent aqueous uranyl species, which were weakly bound to fixed-charge sites. At higher ionic strengths, competition with Na⁺ decreased the adsorption of UO₂²⁺ to fixed-charge sites. At higher pH, the most significant adsorption reactions were the binding of UO₂²⁺ to AlOH and of (UO₂)₃(OH)₅⁺ to SiOH edge sites. Near-saturation of AlOH sites by UO₂²⁺ allowed significant contributions of SiOH sites to uranyl adsorption.

Key Words: Montmorillonite • Uranyl

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