Ligand effects on uranyl sorption – key processes and models

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Abstract

The mobility of uranium(VI) is of concern in numerous natural and polluted environments. One of the main factors controlling uranyl mobility is the sorption of U^{VI} on mineral surfaces, which is strongly dependent on aqueous chemistry, particularly the pH. However, many environmental systems contain a variety of organic and inorganic components, which can have a major effect on sorption. For example, many groundwaters in the Alligator Rivers region of the Northern Territory contain significant amounts of ligands, including carbonate and phosphate. These ligands can increase or decrease uranyl uptake through several possible processes, including competition for binding sites, complexation of aqueous uranyl, formation of ternary uranyl-ligand surface complexes, and precipitation. We have developed surface complexation models of U^{VI} sorption on minerals including ferrihydrite, kaolinite, and more complex materials; utilising comprehensive U sorption databases and results from advanced spectroscopic techniques (e.g. EXAFS, TRLFS, and ATR-FTIR). These models require specific reactions to represent the effects of ligands. In systems containing sulfate, it was necessary to consider complexation between UO_2^{2+} and SO_4^{2-}, as well as competition for surface sites, to model the U sorption data. To simulate U sorption data in the presence of carbonate, ternary surface complexes of the form $(>SO_2)UO_2CO_3^{2-}$ were required (here >S represents a surface site). Similar ternary U-ligand-surface complexes appear to form in the presence of phosphate. The addition of citrate considerably reduced U sorption on both kaolinite and ferrihydrite and caused dissolution of the solid in the latter case. Complexation of citrate with both uranyl and ferric ions was taken into account in modelling this system. The model required the optimisation of the formation constant for a postulated mixed metal (U^{VI}/Fe^{III}/citrate) aqueous complex. The results emphasise the importance of considering interactions with ligands when modelling radionuclide sorption in environmental systems.