Stabilization of a mixed-valence U(V)-U(VI) phase in systems with reduced SWy-2 and NAu-1 clays

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Depleted uranium (^{238}U) is a legacy contaminant from Cold War activities, as well as an ever-increasing product from nuclear power generation. Predicting the consequences of accidental dispersal and designing storage facilities for the spent fuel requires a molecular-level understanding of the interfacial and redox chemistry of U in the presence of minerals, bacteria, and dissolved ligands. Our current knowledge is apparently incomplete—we have shown previously that when aqueous U^{VI} ions encounter biological or abiotic reductants the resulting U^{IV} species are often different from the predicted U^{IV} product, uraninite (UO_2).

In this work we examined the interaction of U^{VI} with reduced Fe-containing clay minerals of environmental relevance (SWy-2, NAu-1, NAu-2). Using synchrotron x-ray spectroscopy (U L_{III}-edge XANES and EXAFS) we find that these clay minerals are able to transfer electrons to aqueous U^{VI} under the studied conditions (2-100 g/L clay loading, 250 μM U^{VI}, 2 mM bicarbonate, pH 7.2 MOPS). Despite the stoichimetric excess of Fe^{II} in the system, U^{VI} is reduced to U^{IV} only at high solids loadings, whereas a mixed-valence U^{V}-U^{VI} oxide is stabilized at lower loadings. By varying the amounts of reductant in the system we find that the transformation of U^{VI} to the U^{V} or the U^{IV} state is controlled by the reducing capacity. In the most reducing systems the distrubution of U^{IV} between uraninite and adsorbed U^{IV} species depends on surface site availability[1]. The results suggest that Fe-containing clays have a significant role in controlling both the valence state and the molecular coordination of reduced uranium. These reaction pathways are currently not considered in transport models, which may affect the accurate prediction of U migration in reduced subsurface and wetland sediments.

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