

The stabilization of U(V) on the surface of reduced nontronite depends on clay to uranium ratio

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The role of Fe-containing clay minerals in absorbing various contaminants and in controlling the redox state of soils and sediments is now well established. Uranium (U) is a contaminant that emerged both from U enrichment activities during the Cold War, as well as from electricity generation at nuclear power stations. Upon accidental release, dissolved U^{VI} will interact with the minerals and bacteria in the subsurface, where it can be adsorbed or can be reduced to less-mobile U^{IV} species. However, the current knowledge is apparently incomplete—we have shown in previous studies that when aqueous U^{VI} ions encounter biological or mineral reductants the resulting U^{IV} species are often different from the thermodynamically-predicted precipitation of uraninite (UO₂) [e.g., 1].

Here, we observe the stabilization of a U^V/U^{VI} species when U^{VI} is reacted with the Fe-containing clay mineral nontronite (NAu-1) under specific conditions (2 g/L CBD-reduced NAu-1, 250 μM U^{VI}, 2 mM bicarbonate, pH 7.2). The determination is based on U L_{III}-edge XANES and EXAFS measurements and spectral comparisons to a well-characterized U^V/U^{VI} mineral [2]. Only adsorbed U^{VI} species were observed in control reactors with oxidized NAu-1, suggesting that interfacial electron transfer from Fe^{II} in the reduced clay was responsible for U^{VI} reduction. Increasing the reduced NAu-1 loading from 2 g/L to 20, 40, and 100 g/L NAu-1 resulted in complete reduction to U^{IV} in the form of nano-particulate uraninite. Adsorbed U^{IV} was only detected at the highest surface loading of 100 g/L, indicating that unlike Fe or Ti oxides, the surface sites of NAu-1 are not very effective at binding mononuclear U^{IV}. We attribute the stabilization of the observed U^V/U^{VI} phase at low solids:U ratios to the blocking of binding/electron transfer sites on the clay surface or to appropriate redox potential buffering by the clay mineral.

[1] D. E. Latta, B. Mishra, R.E. Cook, K. M. Kemner, M. I. Boyanov "Stable U(IV) complexes form at high-affinity mineral surface sites", *Environ.Sci.Tech.*, 48 (3), 1683–1691 (2014)

[2] Belai, N., Frisch, M., Ilton, E.S., Ravel, B., Cahill, C.L., 2008. "Pentavalent Uranium Oxide via Reduction of [UO₂]²⁺ Under Hydrothermal Reaction Conditions". *Inorganic Chemistry*, 47(21): 10135-10140