Plutonium sorption and precipitation on goethite: A question of concentration

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Anthropogenic introduction of plutonium into the environment is an unfortunate legacy of the nuclear age. Although much Pu was distributed globally following atmospheric weapons testing, hotspots of contamination also exist at Pu production and underground testing sites such as Mayak, Russia and the Nevada National Security Site, USA. At these heavily contaminated sites, Pu mobility will be controlled by its interactions with mineral surfaces. Understanding Pu sorption and desorption reactions is key to predicting the fate of Pu.

Here we look at Pu(IV) and Pu(V) sorption to goethite, a common iron oxyhydroxide mineral, across a wide range of concentrations (10^{-15} – 10^{-5} M) at pH 8. For initial Pu concentrations of 10^{-15}-10^{-8} M, the sorption isotherm was linear, with equivalent Pu(IV) and Pu(V) K_d values obtained at 1-week and 2-week sampling time points. This indicated that Pu sorption is not concentration-dependent for these initial conditions and that Pu(V) is rapidly reduced to Pu(IV) on the goethite surface. At initial concentrations $>10^{-8}$ M, however, both Pu oxidation states exhibited deviations from linear sorption behavior with NanoSIMS and HRTEM analysis indicating that Pu precipitation was likely responsible for this. HRTEM analysis of samples with 10^{-6} M Pu(IV) and Pu(V), showed the formation of a bcc Pu_4O_7 structure on the goethite surface. This confirmed that reduction of Pu(V) had occurred on the mineral surface and that the epitaxial distortion previously observed for Pu(IV) sorption on goethite occurs for Pu(V) [1]. We also explore the implications of this concentration-dependent sorption behavior on the stability of Pu associated with goethite in a series of batch and flow cell desorption experiments performed at initial Pu(V) concentrations of 10^{-10} and 10^{-6} M.

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