

Plutonium Sorption to Mineral Surfaces at Attomolar to Micromolar Concentrations

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A focus of the LLNL SFA has been the study of Plutonium (Pu) sorption and desorption in simple binary systems at concentrations ranging from those commonly observed in the field ($<10^{-12}$ M) to higher concentrations that are routinely used in laboratory experiments (10^{-6} to 10^{10} M). This experimental effort has addressed concerns that sorption behavior determined at concentrations used in laboratory measurements might not be representative of sorption processes occurring under actual subsurface conditions.

We have investigated the sorption behavior of Pu(V) and Pu(IV) over a minimum of 8 orders of magnitude in Pu concentration (10^{-8} – 10^{-15} M) onto Fe-oxyhydroxide (goethite), clay mineral (montmorillonite) and clay rock (bentonite) at pH 8. In addition, we investigated Np(V) sorption to goethite over an initial concentration range of 10^{-5} – 10^{-18} M. Pu(V) sorption was found to be broadly linear over a range of initial concentrations from 10^{-6} – 10^{-16} M for montmorillonite and 10^{-6} – 10^{-15} M for goethite. Similarly, Pu(IV) sorption to goethite also appeared linear over an initial concentration range of 10^{-5} – 10^{-15} M. In contrast to the Pu isotherms, Np(V) sorption to goethite exhibited a non-linearity that implies the presence of high-affinity sorption sites. However, the nature of these high-affinity sites has yet to be determined.

The sorption of Pu(IV) and Pu(V) to goethite reached equivalent sorption equilibria within 15 days. In contrast, the sorption of Pu(IV) to montmorillonite was greater than Pu(V) after 30 days. After 1 year, the Pu(V) isotherm matched the Pu(IV) data, indicating that equilibrium was achieved but only after 3 months. We attribute the slow sorption to continued reduction of Pu(V) to Pu(IV) on the mineral surface and stress the need to account for such slow processes when predicting field-scale transport.

Importantly, our experimental data accumulated in the past three years as part of this SFA indicate that the affinity of Pu for mineral surfaces will not increase significantly at ultralow Pu concentrations compared to higher concentrations routinely used in the laboratory (10^{-9} – 10^{-11} M). However, above 10^{-9} M, Pu(IV) can precipitate as an intrinsic oxide. The results have broad implications to our conceptual understanding of processes controlling colloid facilitated Pu transport and, more broadly, to contaminant reactive transport. Pu sorption processes and associated kinetics identified at moderately high concentrations ($<10^{-9}$ M) appear to be scalable to ultra-low femtomolar environmental concentrations, justifying the use of existing experimental data in transport models.