Plutonium Incorporation into Iron Oxide Minerals

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For the long-term performance assessment of nuclear waste repositories, knowledge about the interactions of actinide ions with minerals is imperative. Plutonium is a highly toxic, long lived radionuclide characterized by complex chemical and physical properties and much attention has been paid to understanding its behavior in order to guarantee safe handling and long term storage. The mobility of plutonium (Pu) in the subsurface is affected by Pu-mineral interactions such as adsorption-desorption and structural incorporation. Previous studies have demonstrated a high affinity of Pu for Fe-oxide minerals that are ubiquitous in the environment and are characterized by high redox reactivity and surface area. In addition to forming in soil and sediments, iron (oxy)hydroxides form as corrosion products of steel and are present in intermediate level radioactive waste. The hydrous ferric oxide, ferrihydrite, is a common, poorly crystalline, metastable early product of both biotic and abiotic precipitation of iron, and is a precursor to other more crystalline iron oxides such as hematite (Fe_2O_3) and goethite (FeOOH).

The aim of this work is to evaluate how Fe-oxide minerals structurally incorporate plutonium during crystallization. By studying Pu(IV) adsorption and coprecipitation with various synthetic iron oxides, we are determining the mechanism of Pu incorporation and identifying the atomic scale bonding environment of Pu in the various mineral structures. Initially, the adsorption of Pu(IV) onto ferrihydrite was studied. These data indicate that the affinity of Pu(IV) for ferrihydrite is very high and adsorption equilibrium is reached within 24 hours at pH above 7. The fate of Pu(IV) during subsequent ferrihydrite alteration to goethite and hematite was subsequently monitored. Upon transformation of Pu(IV)–ferrihydrite, goethite showed a higher extent of Pu-incorporation than hematite. The extent of Pu incorporation in ferrihydrite, goethite and hematite has important implications for the long-term performance of nuclear waste repositories, particularly from the standpoint of irreversible association of Pu with mineral phases.