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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 mineral surfaces is imperative. In the United States, nuclear weapons production and testing has led to approximately 10^{14} Bq of ^{239}Pu subsurface contamination at the Hanford site and more than 10^{15} Bq of plutonium contamination at the Nevada National Security Site (previously Nevada Test Site). 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 of 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). It has been shown that goethite and hematite are able to accommodate various impurities into their structure including Si, Ti, Mn, Ni and U(VI). The aim of this work is to evaluate how Fe-oxide minerals structurally incorporate plutonium during crystallization. By studying various synthetic iron oxides co-precipitated with Pu(IV) we are aiming at determining the mechanism of plutonium incorporation and define the atomic scale bonding environment of Pu in the various mineral structure. Ferrihydrite, goethite and hematite have been synthesized from solution with varying amount of plutonium (100s-1000s of ppm). The extent of Pu incorporation into ferrihydrite and subsequent alteration to goethite and hematite was monitored by liquid scintillation counting. Mineral powders were characterized by P-XRD, SEM, and HR-TEM. Preliminary data indicate that sorption equilibrium of Pu(IV) onto ferrihydrite is reached within one week. 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.