



Microbial mobilization of plutonium and other actinides from contaminated soil

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ABSTRACT

We examined the dissolution of Pu, U, and Am in contaminated soil from the Nevada Test Site (NTS) due to indigenous microbial activity. Scanning transmission x-ray microscopy (STXM) analysis of the soil showed that Pu was present in its polymeric form and associated with Fe- and Mn- oxides and aluminosilicates. Uranium analysis by x-ray diffraction (μ -XRD) revealed discrete U-containing mineral phases, viz., schoepite, sharpite, and liebigite; synchrotron x-ray fluorescence (μ -XRF) mapping showed its association with Fe- and Ca-phases; and μ -x-ray absorption near edge structure (μ -XANES) confirmed U(IV) and U(VI) oxidation states. Addition of citric acid or glucose to the soil and incubated under aerobic or anaerobic conditions enhanced indigenous microbial activity and the dissolution of Pu. Detectable amount of Am and no U was observed in solution. In the citric acid-amended sample, Pu concentration increased with time and decreased to below detection levels when the citric acid was completely consumed. In contrast, with glucose amendment, Pu remained in solution. Pu speciation studies suggest that it exists in mixed oxidation states (III/IV) in a polymeric form as colloids. Although Pu(IV) is the most prevalent and generally considered to be more stable chemical form in the environment, our findings suggest that under the appropriate conditions, microbial activity could affect its solubility and long-term stability in contaminated environments.

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1. Introduction

The presence of low levels of plutonium (Pu) in contaminated soils and at remediated sites is a major concern because of its potential for dissolution and mobilization in the environment. Primary worries center on plutonium's toxicity, and the relatively long half-lives of its isotopes ($87.7\text{--}8.0 \times 10^8$ y). Nuclear weapons testing at the Nevada Test Site (NTS) during the 1950s and early 1960s have resulted in the contamination of large area of soil with plutonium and other radionuclides at levels in excess of 40 pCi per gram. The bulk of the activity typically resides within the top few centimeters of the soil; the primary radionuclides of concern are plutonium, uranium, and americium, with lesser amounts of cesium, strontium, and europium (Walker and Liebendorfer, 1998). Studies of the soils at the NTS's Area 11 demonstrated that more than 75% of the total radionuclides are dispersed as particles in the 40-micron soil fractions (Papelis et al., 1996), and/or are partially attached to clay particles. The plutonium particles are relatively

immobile and expected to remain so until disturbed.

Although Pu is considered stable in soil, its transport, albeit at very low concentrations, was observed at several Department of Energy's sites, and at the Mayak Production Association, Urals, Russia (Kersting, 2013). Thus, Pu was present in colloidal form at Los Alamos National Laboratory's (LANL) waste site (Penrose et al., 1990); similarly, at Maxey Flats, a former low-level radioactive waste site, Pu occurred as colloids, as well as soluble tetravalent species complexed with organic ligands (Cleveland, and Rees, 1981). At Mayak, it was bound to iron-oxide colloids (Noviko et al., 2006). The predominant form of Pu in the soil at Rocky Flats, CO, was $\text{PuO}_2(\text{s})$ (Clark et al., 2006), while, in surface waters, it existed as colloids associated with organic macromolecules (Santschi et al., 2002; Xu et al., 2008). At three other disposal sites, Pu formed similar associations: at the Hanford site, Pu (III/IV) was associated with colloids in the groundwater at the 100 K-Area (Dai et al., 2005); at the Savannah River Site, it was detected in combination with colloids in groundwater samples near the disposal basins in F-Area (Buesseler et al., 2009); and, at the NTS Pu was complexed with mineral colloids (Kersting et al., 1999). Studies at NTS show that the U and the fission products Sr and Cs also are associated with colloids (Utsunomiya et al., 2009).

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Microorganisms were detected in low-level radioactive- and TRU- wastes, in Pu-contaminated soils, and in waste-repository sites under consideration for nuclear-waste disposal (Au and Leavitt, 1982; Barnhart et al., 1980; Johnson et al., 1974; Francis, 1990, 2001, 2007). Microbiological studies at the NTS showed the presence of bacteria and fungi in Area 13 soils (Au and Leavitt, 1982), and bacteria in the subsurface environments at the Rainier Mesa, in oxygenated volcanic tuff, and in groundwater (Amy et al., 1992; Haldeman, and Amy, 1993; Horn et al., 2004). Microbes may affect the solubility and mobility of Pu (Francis, 2001; Neu et al., 2002, 2005; Boukhalfa et al., 2007; Francis et al., 2007, 2008; Renshaw et al., 2009).

Several studies have shown that bacteria and fungi play a major role in the dissolution of PuO₂, amorphous forms of Pu(IV)OH, and other chemical forms. Some bacteria and fungi grown in the presence of Pu produced extracellular Pu complexes that increased the concentration of Pu in soil-column eluates compared to controls. Elution through soil effectively removed positively charged Pu complexes (Wildung et al., 1987). The increased mobility of Pu in the soil resulted from the formation of neutral and negatively charged Pu complexes. In the presence of known microbial metabolites and the synthetic ligands DTPA, EDTA, and EDDHA, Pu(VI) was reduced to Pu(IV) before complexation, suggesting that the latter valence state would be the dominant one associated with organic complexes in soils (Wildung, and Garland, 1980). Studies show that biologically produced ligands mediate Pu transport, such as cutin-derived soil degradation products containing siderophore-like moieties (Xu et al., 2008).

Although a wide variety of microorganisms were detected at the Pu contaminated sites, very little is known of the effects of microbial activity on the stability and mobility of the actinides in soils and wastes. An increase in moisture content and the availability of metabolizable organic carbon in contaminated soils in arid and semi-arid regions could increase microbial activity. In this study, we investigated the potential effects of indigenous microbial activity on the dissolution of actinides in NTS soil amended with citrate or glucose as carbon sources and incubated under aerobic and anaerobic conditions. Citrate is a naturally-occurring organic compound capable forming stable complexes with actinides and metals. Citrate is readily metabolized soil microorganisms. Glucose an intermediate of cellulose degradation product is metabolized by microorganisms; and under anaerobic and water logged conditions results in the accumulation of low molecular weight organic metabolic products such as acids and alcohols.

2. Materials and methods

2.1. Soil sample

About 100 g of plutonium-contaminated soil (HP-11) was obtained from Area 11 of the Double Track test shot area at the NTS. Soils at the NTS region are classified as medium-to fine-grained sands (Turner et al., 2003). The predominant vegetation in the area is the shrub species of basin big sagebrush and black sagebrush (Nevada Test Site Annual Site Environmental Report-2002, DOE/NV/11718-842, 2003). One gram of the soil was transferred to each of three platinum crucibles, was digested with concentrated nitric acid and analyzed for the metals Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sr, and Zn by inductively coupled plasma-optical emission spectrometer (ICP-OES).

2.2. Actinide analysis

The total activity in “as received” soil was 50 nCi/g. One gram of the soil was digested in a mixture of hydrochloric/nitric acid. The U-

233/234, U-235/236, U-238, Am-241, Pu-238, Pu-239/240 and Pu-241 were separated by anion-exchange column chromatography, followed by liquid scintillation counting (LSC) (EML Procedures Manual, HASL-300, 28th Edition, Volumes I and II. 1970).

2.3. Mineralogical analysis

The major mineralogical constituents of the soil are clay, quartz, magnetite, titanomagnetite, and limestone (Hoeffner et al., 2005). The fine fraction consisted of clay, quartz, and feldspar.

The minerals present in the soil were determined by x-ray diffraction (XRD) using beam line X7A at the National Synchrotron Light Source (NSLS). The soil was placed on an Al sample holder, and sealed with Kapton tape. The beamline's energy was 0.69850 Å, and a 2θ scan was obtained from 5 to 68° with a scan rate of 0.02° per second.

The mineralogical association of actinides in the soil was determined using a modified sequential selective-extraction method (Tessier et al., 1985). Briefly, the soil was extracted with (i) 1 M MgCl₂ and 0.05 M citric acid (pH 7) for 1 h (exchangeable fraction), (ii) an acetate buffer prepared by adjusting a 1 M NH₄-acetate solution to pH 5 with acetic acid, adding 0.05 M citric acid, and then agitating the mix for 5 h (association with carbonate), and, (iii) 25% acetic acid with NH₂OH·HCl for 6 h (association with Fe-, Mn-oxides). Citric acid was added to the extractant to prevent/minimize actinide precipitation from solution; it had a minimal effect on the extraction of actinides at this pH. The samples were then filtered through a 0.45 μm filter before analysis.

2.4. Elemental mapping and actinide association

Approximately 0.5 g soil was placed in an Al sample holder, and sealed with Kapton tape and analyzed by x-ray absorption near edge spectroscopy (μ-XANES), and μ-x-ray diffraction (μ-XRD) at the NSLS's X26A beam line to determine the oxidation state and the mineralogical association of the actinides in the soil. Synchrotron μ-x-ray fluorescence (SXRF) analysis was performed to map the elemental distribution and for determining the association of actinides with the selected elements Ca, Cr, Cu, Fe, Mn, Sr, U, and Zn. The Pu-containing particles in the soil was analyzed Synchrotron scanning transmission x-ray microscopy (STXM) at beam line MES 11.0.2 at the Advanced Light Source (ALS).

2.5. Extraction of actinides

To compare the leachability of actinides, the alpha- and beta-emitting isotopes were extracted from the soil by water, citric acid, and nitric acid, as follows. Duplicate one gram samples of soil were transferred to 20 ml serum bottles and ten milliliters of the following solutions added: (i) deionized water, (ii) 0.1 M citric acid, or, (iii) 1 M nitric acid. The soil samples were agitated on a rotary shaker for three hours. An aliquot was removed for analysis of α and β activities in the unsettled suspension, in the settled supernatant and filtered supernatant. The sample was allowed to settle for 1 h and the supernatant was filtered through a 0.45 μm filter (Millipore, MA). The α and β activities determined by liquid scintillation counting (LSC) using a Wallac Guardian 1414 digital spectrum analyzer.

2.6. Effect of adding citric acid or glucose on microbial activity and the dissolution of actinides from the soil

To 150 ml Erlenmeyer flasks 40 ml of one of the following solutions (wt. %) were added: (i) deionized water (unamended), (ii) deionized water containing glucose (0.5%) and NH₄NO₃ (0.015%), or,

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