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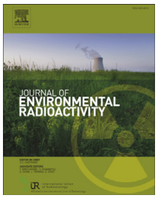

Plutonium sorption and desorption behavior on bentonite

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ABSTRACT

Understanding plutonium (Pu) sorption to, and desorption from, mineral phases is key to understanding its subsurface transport. In this work we study Pu(IV) sorption to industrial grade FEBEX bentonite over the concentration range 10^{-7}–10^{-16} M to determine if sorption at typical environmental concentrations ($\leq 10^{-12}$ M) is the same as sorption at Pu concentrations used in most laboratory experiments (10^{-7}–10^{-11} M). Pu(IV) sorption was broadly linear over the 10^{-7}–10^{-16} M concentration range during the 120 d experimental period; however, it took up to 100 d to reach sorption equilibrium. At concentrations $\geq 10^{-8}$ M, sorption was likely affected by additional Pu(IV) precipitation/polymerization reactions. The extent of sorption was similar to that previously reported for Pu(IV) sorption to SWy-1 Na-montmorillonite over a narrower range of Pu concentrations (10^{-11}–10^{-7} M). Sorption experiments with FEBEX bentonite and Pu(V) were also performed across a concentration range of 10^{-11}–10^{-7} M and over a 10 month period which allowed us to estimate the slow apparent rates of Pu(V) reduction on a smectite-rich clay. Finally, a flow cell experiment with Pu(IV) loaded on FEBEX bentonite demonstrated continued desorption of Pu over a 12 day flow period. Comparison with a desorption experiment performed with SWy-1 montmorillonite showed a strong similarity and suggested the importance of montorillonite phases in controlling Pu sorption/desorption reactions on FEBEX bentonite.

1. Introduction

Permanent interment in a deep geological repository is seen as the most viable option for radioactive waste disposal in many countries with a civilian nuclear fuel program (IAEA, 1995). Conceptually, the repository scenario comprises a geological barrier (host rock) combined with engineering barriers that aim to contain the radionuclides until they have decayed below harmful levels. The waste itself will likely be contained in steel canisters surrounded by a layer of compacted clay. The efficacy of this disposal option is related to its capacity to confine radioactivity and isolate it from the biosphere (Dozol et al., 1993).

Due to its swelling properties, plasticity, ion exchange and sorption behavior, and sealing capability, bentonite is considered a good candidate for backfill material (Guven, 1990). Traditionally, the term bentonite refers to aluminum phyllosilicate clays derived from the devitrification and chemical alteration of glassy volcanic ash or tuff (Ross and Shannon, 1926). However, the term has been used to describe smectite-rich materials, regardless of origin (Grim, 1968). The smectite mineral group includes a number of 2:1 layer silicates, the most common of which is montmorillonite. Montmorillonites constitute a large proportion of bentonite mineralogy (65–90 wt %) with the result that the two names are often used synonymously, although the former is a clay mineral and the latter a clay rock (Grauer, 1986). Montmorillonite can display significant morphological and chemical differences depending on its provenance (Guven, 1988).

ENRESA, the body responsible for the management of Spanish radioactive waste, has proposed FEBEX bentonite from Cortijo de Archidona in Almeria, Spain for use in its repositories. As a result, the physiochemical properties of this clay rock have been well studied, particularly in an extensive experimental program performed at the National Cooperative for the Disposal of Radioactive Waste's (Nagra) Grimsel Test Site in Switzerland. The FEBEX bentonite has a high montmorillonitic smectite content (93 ± 2%) with minor quartz (2 ± 1%), plagioclase (3 ± 1%), cristobalite (2 ± 1%), potassium feldspar, calcite and tridymite as accessory minerals (Missana et al., 2004). The less than 2 μm fraction (after Ca homoionization)

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of this bentonite is composed of >99% smectite with the structural formula: $(Si_{7.78}Al_{0.22})(Al_{2.78}Fe^{3+}{}_{0.33}Fe^{2+}{}_{0.02}Ti_{0.02}Mg_{0.81})O_{20}(OH)_4(Ca_{0.50}Na_{0.08}K_{0.11})$ (Fernandez et al., 2004).

Due to their long half-lives and toxicity, the isotopes ^{239}Pu (2.41 × 10^4 y) and ^{240}Pu (6.56 × 10^3 y) are expected to contribute significantly to the total hazardous inventory in a waste repository scenario (Schwenk-Ferrero, 2013). Despite several decades of study, our understanding of how Pu migrates in subsurface environments is far from complete due to the wide array of factors which can significantly influence its mobility. These include Pu redox processes (Choppin, 1991; Sanchez et al., 1985), colloid-facilitated transport processes (Kersting et al., 1999; Novikov et al., 2006), solubility effects (Efurd et al., 1998; Neck et al., 2007), sorption/desorption rates and affinities for natural mineral surfaces (Powell et al., 2004; Zavarin et al., 2012), and interactions with natural organic matter (including bacteria) (Icopini et al., 2009; Zhao et al., 2011). Pu exhibits a complex redox chemistry in natural waters with four oxidation states (VI, V, IV, III) potentially stable and with each oxidation state displaying a unique solubility (Neck et al., 2007) and mineral sorption affinity (Begg et al., 2013; Keeney-Kennicutt and Morse, 1985; Sanchez et al., 1985; Silva and Nitsche, 1995). Pu(IV) and Pu(V) are the more common species under mildly oxic environmental conditions and also represent the oxidation states with the lowest (Pu(V)) and highest (Pu(IV)) affinities for mineral surfaces (Choppin, 2007; Kaplan et al., 2007; Silva and Nitsche, 1995).

Mineral-colloid facilitated transport is thought to be a significant contributor to Pu migration in the subsurface (Kersting et al., 1999; Novikov et al., 2006). One of the concerns with the use of bentonite as a backfill material in a repository is that it can form colloids, which may enhance the migration of radionuclide species that are sorbed to them (Geckeis et al., 2004). As a result, attention has been focused on the interaction between Pu and bentonite colloids (Huber et al., 2011; Missana et al., 2008). Previous work on FEBEX bentonite has shown that colloids with a hydrodynamic size of 250 ± 50 nm have an XRD pattern consistent with an aluminum-rich dioctahedral smectite with no significant impurities (Missana et al., 2004).

The sorption of Pu species to Khakassiya bentonite and SWy-1 montmorillonite has been found to exhibit pH and ionic strength dependency, indicating that both ion-exchange and surface complexation processes are occurring (Sabodina et al., 2006; Zavarin et al., 2012). However, surface complexation processes will dominate at neutral to alkaline pHs. Smectite minerals have been shown to have a high sorption affinity for Pu. For example, Pu(V) partitioning to Yucca Mountain tuffs found a ubiquitous and preferential association of Pu with smectite minerals (Vaniman et al., 1995). Further, Pu(IV) K_d values from 10,000 to 40,000 L kg^{-1} (log K_d 4.0–4.6) have been reported for smectite-rich sediments from Lithuania in the pH range 5–12 (Lujaniene et al., 2007). Missana et al. (2008) studied the sorption of Pu(IV) to FEBEX bentonite colloids (>99% smectite) at pH 9.5 and reported log K_d values of 5.37 ± 0.18. Pu(IV) sorption to FEBEX bentonite colloids under anaerobic conditions at pH 9.6 resulted in log R_d values (a term equivalent to K_d but without the assumption of equilibrium) of 5 and 5.9 after one and three weeks of sorption time, respectively (NAGRA, 2006). The increase in R_d values with time was attributed to the presence of a small amount (~5%) of Pu(VI) in the spike solution which was slowly reduced to Pu(IV) on the mineral surface (NAGRA, 2006).

In a recent study, we examined the long term sorption behavior of Pu(IV) and Pu(V) on SWy-1 Na-montmorillonite under aerobic conditions. After 30 d equilibration, calculated log K_d values for Pu(IV) and Pu(V) were 4.25 ± 0.15 and 3.57 ± 0.18, respectively (Begg et al., 2013). However, following one year of equilibration, calculated log K_d values in the Pu(V) experiments had increased to 4.32 ± 0.15, similar to those calculated for Pu(IV) after 30 d. The convergence of K_d values for Pu(IV) and Pu(V) was attributed to the slow reduction of Pu(V) on the montmorillonite surface causing increased uptake of Pu(V). This finding highlights the need to ensure that experimental studies used to inform predictive transport models accurately encapsulate long term environmental behaviors.

Several recent studies have indicated that actinide concentration can affect their sorption to mineral surfaces (Hixon and Powell, 2014; Missana et al., 2008; Snow et al., 2013). In the case of Pu(IV), its low solubility at circumneutral pH means that sorption may demonstrate an apparent concentration dependence as solubility limits are reached. For example, the study of Pu(IV) sorption to bentonite colloids showed that sorption was linear for initial Pu concentrations of 1 × 10^{-8}–1 × 10^{-7} M but at higher concentrations precipitation of Pu was evidenced by a sharp increase in the isotherm slope (Missana et al., 2008). Concentration dependent sorption behavior may also be observed at low actinide concentrations: work with goethite and Np(V) found that K_d values differed by an order of magnitude at solution concentrations below 10^{-11} M compared to higher concentrations (Snow et al., 2013). This behavior was attributed to the existence of different adsorption sites on the mineral having different adsorption affinities for Np. These examples of concentration dependent behavior of actinides indicate that there may be a difference between the sorption behavior of Pu at the concentrations found in contaminated subsurface waters (10^{-12}–10^{-20} M) (Dai et al., 2005; Kersting et al., 1999; Novikov et al., 2006; Penrose et al., 1990) and concentrations typically used in laboratory experiments (10^{-7}–10^{-11} M Pu). Although a primary assumption of reactive transport models, the validity of extrapolating Pu-mineral sorption behavior from relatively high concentration laboratory experiments to the low concentrations found in many field settings has not been widely tested.

Pu desorption reactions have been far less well studied than sorption reactions. This is problematic because application of thermodynamic equilibrium parameters in field transport models which incorrectly represent desorption processes are likely to be flawed (Artinger et al., 2002). One of the pertinent issues for Pu, especially given the evidence that its mobility may be enhanced by mineral-colloid facilitated transport, is whether there is equality in sorption and desorption behavior (Kersting et al., 1999). Differences in behavior may be caused by aging processes, hysteresis effects, and irreversible sorption, amongst others (Tinnacher et al., 2011). A study of Pu(IV) sorption to Callovo-Oxfordian argillite found that after seven days' desorption, Pu K_d values were of the same order of magnitude as they were following a seventy four day adsorption period, indicating sorption reversibility (Latrille et al., 2006). Similarly, Lu et al. (2003) investigated Pu interaction with montmorillonite and found that with a 20 day adsorption period and a 32 day desorption period, similar K_d values were obtained for both adsorption and desorption steps.

The aim of the current work is two-fold: to provide information on Pu sorption/desorption to/from industrial grade FEBEX bentonite, a potential repository backfill material, and to determine if the linearity observed for Pu(V) sorption to a pure Na-montmorillonite (Begg et al., 2013) extends to Pu(IV) sorption to a multi-component clay rock material. We investigate the sorption behavior of Pu(IV) to FEBEX bentonite across a wide range of initial concentrations (10^{-7}–10^{-16} M) over a 120 d period. In addition, we perform long term (10 month) sorption experiments with Pu(V) to compare with the slow apparent rates of reduction previously observed for Pu(V) on montmorillonite (Begg et al., 2013). The results of these experiments demonstrate the apparent control that the montmorillonite component in bentonite exerts on the