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Desorption of plutonium from montmorillonite: An experimental and modeling study

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Abstract

Desorption of plutonium (Pu) will likely control the extent to which it is transported by mineral colloids. We evaluated the adsorption/desorption behavior of Pu on SWy-1 montmorillonite colloids at pH 4, pH 6, and pH 8 using batch adsorption and flow cell desorption experiments. After 21 days adsorption, Pu(IV) affinity for montmorillonite displayed a pH dependency, with K_d values highest at pH 4 and lowest at pH 8. The pH 8 experiment was further allowed to equilibrate for 6 months and showed an increase in K_d, indicating that true sorption equilibrium was not achieved within the first 21 days. For the desorption experiments, aliquots of the sorption suspensions were placed in a flow cell, and Pu-free solutions were then pumped through the cell for a period of 12 days. Changes in influent solution flow rate were used to investigate the kinetics of Pu desorption and demonstrated that it was rate-limited over the experimental timescales. At the end of the 12-day flow cell experiments, the extent of desorption was again pH dependent, with pH 8 > pH 6 > pH 4. Further, at pH 8, less Pu was desorbed after an adsorption contact time of 6 months than after a contact time of 21 days, consistent with an aging of Pu on the clay surface. A conceptual model for Pu adsorption/desorption that incorporated known surface-mediated Pu redox reactions was used to fit the experimental data. The resulting rate constants indicated processes occurring on timescales of months and even years which may, in part, explain observations of clay colloid-facilitated Pu transport on decadal timescales. Importantly, however, our results also imply that migration of Pu adsorbed to montmorillonite colloids at long (50–100 year) timescales under oxic conditions may not be possible without considering additional phenomena, such as co-precipitation.

Keywords: Plutonium; Sorption; Desorption; Montmorillonite

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1. INTRODUCTION

Plutonium mobility in the environment is a topic of key concern because of its radiological toxicity and extremely low EPA drinking water limit (equivalent to 10^{-12} mol L^{-1} for ^{239}Pu) (EPA, 1996). Given its presence in the environment, from the production and testing of nuclear weapons, nuclear accidents and authorized discharges of radionuclides, it is important to understand how Pu mobility is controlled in order to develop reliable predictive transport models (Nelson and Lovett, 1978; Morris et al., 2000; Montero and Sanchez, 2001; Smith et al., 2003). These transport models are necessary for risk assessments of both existing contaminated environments and future nuclear waste repositories.

Adsorption reactions are likely to play a key role in determining Pu transport in subsurface environments (Powell et al., 2005, 2011a; Zavarin et al., 2005, 2012; Sabodina et al., 2006; Hixon et al., 2010; Romanchuk et al., 2011; Lujaniene et al., 2012). On the one hand, evidence of strong sorption to bulk mineral phases suggests that Pu transport will be limited (Sanchez et al., 1985; Kaplan et al., 2004, 2007). On the other hand, strong

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adsorption to mobile, inorganic or organic colloids has led to Pu migration on the kilometer scale at some currently contaminated locations (e.g. Nevada National Security Site, USA, Rocky Flats, USA, and Mayak, Russia) (Kersting et al., 1999; Santschi et al., 2002; Novikov et al., 2006). Further, field-scale colloid transport experiments at the Grimsel Test Site, designed to simulate nuclear waste repository scenarios, demonstrate that Pu sorbed to bentonite colloids can migrate in fractured granite (Möri et al., 2003).

Pu adsorption behavior is linked to its oxidation state. Although Pu can exist in the (III), (IV), (V) and (VI) oxidation states under environmental conditions, Pu(IV) and Pu (V) are believed to predominate under oxic conditions at circumneutral pH (Nitsche and Edelstein, 1985; Orlandini et al., 1986; Choppin, 1991; Kaplan et al., 2007). While both oxidation states may sorb to mineral surfaces, Pu(IV) tends to sorb more strongly than Pu(V) (Sanchez et al., 1985; Begg et al., 2013). It has also been demonstrated that the oxidation state of Pu can be altered on the surface of certain minerals (Powell et al., 2004, 2005; Felmy et al., 2011; Kirsch et al., 2011). For example, Pu(V) reduction to Pu(IV) has been observed, or inferred, to occur on Mn(II) and Fe(III) minerals as well as silica and montmorillonite (Keeney-Kennicutt and Morse, 1985; Sanchez et al., 1985; Powell et al., 2005, 2006, 2011a; Zavarin et al., 2012; Begg et al., 2013; Hixon et al., 2013). Depending on the minerals present, the rates of surface mediated reduction can vary by orders of magnitude (Begg et al., 2013). One consequence of surface mediated reduction is that given sufficient timescales, the extent of Pu(V) adsorption is very similar to that of Pu(IV), despite observations of initial differences in adsorption behavior for some minerals (Sanchez et al., 1985; Zavarin et al., 2012; Begg et al., 2013; Hixon et al., 2013; Zhao et al., 2016). This surface-mediated Pu(V) reduction is consistent with a previous definition of aging: “surface chemical process(es) that follow(s) the initial sorption reaction and cause(s) changes in contaminant surface speciation over time” (Tinnacher et al., 2011). One consequence of this redox aging is that adsorbed Pu (V), which is reduced to Pu(IV) on the surface, will likely be more resistant to desorption than the original Pu(V) (Smith et al., 2009; Wendling et al., 2009).

Desorption of Pu from mineral surfaces has not been as systematically studied as adsorption. Nonetheless, desorption will play a key role in determining the stability of Pu on both immobile and mobile mineral surfaces. Moreover, rates of desorption are particularly important as these will control the spatial and temporal extent of Pu migration, especially in colloid-facilitated transport scenarios (Saiers and Hornberger, 1996; Cvetkovic et al., 2004). Pu desorption is typically investigated via batch experiments that have shown that the majority of adsorbed Pu remains associated with the mineral surface, consistent with the high sorption affinity of Pu(IV) for mineral surfaces. For example, Pu(IV) and Pu(V) batch desorption experiments with goethite and hematite have indicated that less than 1% of the solid associated Pu will be desorbed (Lu et al., 1998). Similarly, experiments with sediments from the Esk Estuary, near Sellafield, UK showed that only about 5% of surface-associated Pu(IV) could be desorbed (Hamilton-Taylor et al., 1987). However, greater extents of Pu desorption have been reported for montmorillonite and silica, where up to 20% of Pu was desorbed after a period of 293 days at pH 8.3 (Lu et al., 2003). While these results may be dependent in part on the experimental conditions, they do indicate that Pu desorption may be limited and mineral dependent. Further, they do not necessarily provide the quantitative measure of desorption rates needed for transport models.

As in the case of adsorption, desorption of Pu from minerals exhibits a pH dependency, with increasing desorption observed to occur with decreasing pH for both natural sediments and pure phase silica and alumina (Kaplan et al., 2006b; Kumar et al., 2012). Moreover, oxidation state also appears to be an important controlling factor for Pu desorption. Although both desorption of Pu(IV) and Pu(V) from sediments may occur, the oxidation of Pu(IV) to Pu (V) on the mineral surface appears to be an important mechanism in the desorption of Pu(IV) (McCubbin and Leonard, 1996; McCubbin et al., 2002). For example, experiments with sediments from Aiken, SC have shown that although adsorbed Pu was present as Pu(IV), desorbed Pu in solution was predominantly Pu(V) (Kaplan et al., 2006b). The mobilization of Pu(IV) associated with Irish Sea sediments following exposure to natural sunlight was found to be predominantly Pu(V) thought to be formed via photooxidation of Pu(IV) (McCubbin and Leonard, 1996). The importance of Pu oxidation in its remobilization from mineral surfaces is similar to the behavior of other redox active radionuclides, such as Tc and U, where oxidation of reduced, solid-associated species results in their remobilization (Burke et al., 2006; McBeth et al., 2007; Moon et al., 2007; Newsome et al., 2014).

In this study, we quantify rates of Pu desorption from montmorillonite colloids using a combination of batch and flow cell experimental techniques and numerical modeling. Experiments were performed at pH 4, 6, and 8 and included batch adsorption periods, a dynamic flow-cell period and, in selected cases, a static desorption period. Changes in flow rate during the flow cell experiment were made to examine the kinetics of desorption. The experimental results were fitted with a model evolved from one developed by Tinnacher et al. (2011). Our results provide broad estimates for the scale of possible colloid-facilitated transport times for Pu in currently contaminated environments while also emphasizing some of the key geochemical conditions to be considered in predictions for nuclear waste disposal scenarios.

2. MATERIALS AND METHODS

2.1. Plutonium stock preparation

A ^{238}Pu stock (99.77% ^{238}Pu, 0.16% ^{241}Pu, and 0.04% ^{239}Pu by activity) was purified using an anion exchange resin (BioRad AG 1 × 8, 100–200 mesh). Prior to loading on the resin, Pu was reacted with $NaNO_2$ to convert Pu to Pu(IV). The Pu was loaded onto the column in 8 M HNO_3 and the column was washed with three column volumes of 8 M HNO_3. The Pu was stripped from the column using 0.1 M HCl which selects for the Pu(IV) oxidation