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Laboratory investigation of the role of desorption kinetics on americium transport associated with bentonite colloids

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ABSTRACT

Understanding the parameters that control colloid-mediated transport of radionuclides is important for the safe disposal of used nuclear fuel. We report an experimental and reactive transport modeling examination of americium transport in a groundwater–bentonite–fracture fill material system. A series of batch sorption and column transport experiments were conducted to determine the role of desorption kinetics from bentonite colloids in the transport of americium through fracture materials. We used fracture fill material from a shear zone in altered granodiorite collected from the Grimsel Test Site (GTS) in Switzerland and colloidal suspensions generated from FEBEX bentonite, a potential repository backfill material. The colloidal suspension (100 mg L^{-1}) was prepared in synthetic groundwater that matched the natural water chemistry at GTS and was spiked with 5.5×10^{-10} M ^{241}Am. Batch characterizations indicated that 97% of the americium in the stock suspension was adsorbed to the colloids. Breakthrough experiments conducted by injecting the americium colloidal suspension through three identical columns in series, each with mean residence times of 6 h, show that more than 95% of the bentonite colloids were transported through each of the columns, with modeled colloid filtration rates (k_f) of 0.01–0.02 h^{-1}. Am recoveries in each column were 55–60%, and Am desorption rate constants from the colloids, determined from 1-D transport modeling, were 0.96, 0.98, and 0.91 h^{-1} in the three columns, respectively. The consistency in Am recoveries and desorption rate constants in each column indicates that the Am was not associated with binding sites of widely-varying strengths on the colloids, as one binding site with fast kinetics represented the system accurately for all three sequential columns. Our data suggest that colloid-mediated transport of Am in a bentonite-fracture fill material system is unlikely to result in transport over long distance scales because of the ability of the fracture materials to rapidly strip Am from the bentonite colloids and the apparent lack of a strong binding site that would keep a fraction of the Am strongly-associated with the colloids.

1. Introduction

Safe disposal of radioactive waste is a concern for many countries around the world. Burial in deep geologic repositories is one strategy that has been investigated with the idea that waste packages would be isolated with natural and engineered barriers to prevent leakage until the radioactivity has largely decayed. Although laboratory experiments (Dittrich and Reimus, 2015; Huber et al., 2011; Schäfer et al., 2012) and field studies (Geckeis et al., 2004; Kersting et al., 1999; Kurosawa et al., 2006; Möri et al., 2003; Wang et al., 2014b, 2013a) have been conducted to evaluate radionuclide colloid-facilitated transport, uncertainty remains regarding the potential transport of strongly sorbing radionuclides associated with mobile colloidal particles (Baston et al., 1994; Dittrich and Reimus, 2014; Dittrich, 2012; Schäfer and Noseck, 2010; Wold, 2010). Reliable data concerning americium (Am) transport in association with bentonite colloids through geochemically altered granite materials is relatively sparse and is the focus of this paper.

Field experiments and environmental monitoring observations have shown that Am transport can be enhanced by the presence of colloids. Penrose et al. (1990) found Am released as part of a treated waste stream into a canyon at Los Alamos National Laboratory was detected over 3 km from the source and was associated very strongly with colloids in the 25–430 nm size range. However, some

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Abbreviations: GTS, Grimsel Test Site; FFM, Fracture fill material; SZW, Shear zone water; LANL, Los Alamos National Laboratory.

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uncertainty remains concerning the exact mechanism of Am and Pu transport documented for the Los Alamos site (Marty et al., 1997). Geckeis et al. (2004) conducted two *in situ* experiments at the Grimsel Test Site (GTS) in Switzerland by injecting radionuclides adsorbed to bentonite colloids in a fractured shear zone and found that most of the Am and Pu migrated without retardation in association with colloids. In their experiment, significant transport of both Am and Pu were attributed to slow desorption kinetics from mobile colloids. Up to 60% of the Am was removed from collected samples by centrifugation, suggesting either intrinsic Am colloids or Am sorbed to natural colloids played a role in transport. Vilks and Baik (2001) investigated Am transport through a natural fracture in a granite block and found that dissolved Am was completely adsorbed to fracture surfaces, but injecting dissolved Am and colloids together resulted in small but measurable transport.

Laboratory experiments with Am, granite, and bentonite colloids have demonstrated the need for more quantitative analysis to determine the role of desorption rates in Am transport. Kunze et al. (2008) found that FEBEX bentonite and Grimsel groundwater form stable colloids with an average diameter of 30 nm, and Liu and Neretnieks (2006) summarize the conditions that promote the generation and transport of bentonite colloids from engineered buffer systems. Murali and Mathur (2002) investigated Am adsorption to bentonite and granite as a function of contact time, pH, liquid—solid ratio, radionuclide concentration, and the presence of competing cations and found that Freundlich and Langmuir isotherms seem to accurately predict Am/bentonite sorption. Iijima et al. (2008) attributed differences in reported Am effective retardation factors for colloid-facilitated transport (R_d) to differences in solution composition and reaction site density. Iijima et al. (2010) investigated the effect of addition order on sorption rate coefficients and reversibility in batch experiments with Am, GTS granite, and bentonite colloids and found Am adsorption to bentonite to be reversible and independent of addition order. The sorption behavior was described well by a surface complexation and ion exchange model. Distribution coefficients for americium and bentonite clays reported in the literature for pH values ranging from 8 to 10 are summarized in Table 1. Flügge et al. (2010) and Huber et al. (2011) also investigated Am adsorption and desorption in the ternary system containing GTS groundwater, GTS fracture fill material (FFM) and bentonite colloids, and reported Am desorption rates of 1.4×10^{-9} M and 8.0×10^{-9} M of 0.009 h^{-1} and 0.0037 h^{-1} for initial Am concentrations of 1.4×10^{-9} M and 8.0×10^{-9} M, respectively. Linear free energy relationships (LFERs) have also been developed for Am sorption with montmorillonite and illite (Bradbury and Baeyens, 2005a, 2005b; 2006, 2009) and they suggest a distribution of binding sites based on complexation and ion exchange.

The objective of this study was to quantify Am colloid-facilitated transport through a geochemically altered granodiorite system to provide insights into upscaling in space and time, which are important in repository risk assessment calculations. Americium was adsorbed to bentonite clay colloids before injection through columns packed with fracture fill material to quantify the desorption rate constants that characterize Am release from bentonite colloids. We selected a fractured/weathered granodiorite at the Grimsel Test Site (GTS) in Switzerland as a model crystalline rock repository system because the system has been thoroughly studied (Dittrich and Reimus, 2013; Huber et al., 2011; Missana et al., 2004), and field experiments involving actinides have already been conducted at this site (Geckeis et al., 2004; Wang et al., 2014b, 2013a).

2. Materials and methods

A bentonite colloid suspension in synthetic Grimsel groundwater spiked with trace levels of ^{241}Am was successively injected through a series of three identically-prepared small columns that were packed with the GTS fracture fill material. A fraction of the effluent collected at the outlet of each column was used for analysis and the remainder was injected through a fresh column. This repeat injection procedure was conducted to determine if colloids that transported through one column were more likely to transport through a second and third column, and more importantly, to determine if Am that transported through one column in association with bentonite colloids was more likely to remain associated with the colloids and transport more efficiently through a second and third column. If either of these outcomes were observed, it would suggest a distribution of colloid filtration rate constants and/or a distribution of Am desorption rate constants from colloids, which would have important implications for the scale dependence of colloid-facilitated transport of Am. In effect, the repeat-injection experiments were designed to interrogate slow colloid filtration rates and slow desorption rates better than single-pass experiments and to effectively allow intermediate distance sampling. Slow rates have a much greater influence on large-scale performance assessment calculations of colloid-facilitated transport than faster rates (Wang et al., 2014a). However, faster rates can mask the presence of slower rates when there is a distribution of rates, particularly in a single-pass column experiment.

2.1. Groundwater

The groundwater used in all experiments was synthetic shear zone water (SZW) that matched the chemistry of the water found in the shear zone at the Grimsel Test Site (Huber et al., 2011; Missana et al., 2004). The SZW was prepared by adding analytical grade reagents to filtered, high-purity water (>18 MΩ cm resistivity) to achieve the elemental concentrations of constituents listed in Table 2. The ionic strength (0.66 mM) was calculated from the added reagents and pH 8.0 was measured for the solution equilibrated with the atmosphere in Los Alamos, NM (2231 m above sea level). The carbonate concentration listed in Table 2 is for the SZW as prepared, not after equilibration with the atmosphere. Although the actual SZW has a reducing redox potential, these experiments were conducted in contact with the atmosphere. Americium occurs as Am(III) under both oxidizing and reducing conditions and the infiltration of an oxidizing water at some future time in an otherwise reducing crystalline rock environment is possible under the influence of climate change or disruptive event scenarios.

Table 1
Americium distribution coefficients reported in the literature from pH 8 to pH 10.

Reference	System	pH	Distribution coefficient (m^3 kg$^-$1)
Geckeis et al. (2004)	FEBEX bentonite in Grimsel groundwater	9.6	$1.2–2.7 \times 10^3$
Degueldre et al. (2001)	Chlorite and illitised smectite	8.6	$1–3 \times 10^3$
Nagasaki et al. (1994)	Bentonite and intrinsic colloids	–	$>1 \times 10^1$
Iijima et al. (2008)	Bentonite	8	$4–90 \times 10^3$
Iijima et al. (2008)	Bentonite	10	$5–20 \times 10^4$
Iijima et al. (2010)	Bentonite	9.6	$7.6–8.7 \times 10^3$
Iijima et al. (2010)	Crushed Grimsel Test Site granite	9.6	$1–2 \times 10^1$