



Mobilization of actinides by dissolved organic compounds at the Nevada Test Site

Pihong Zhao^{a,b}, Mavrik Zavarin^{a,b}, Roald N. Leif^a, Brian A. Powell^c, Michael J. Singleton^a, Rachel E. Lindvall^a, Annie B. Kersting^{a,b,*}

^a Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94550, USA

^b Glenn T. Seaborg Institute, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94550, USA

^c Environmental Engineering and Earth Sciences, Clemson University, Anderson, SC 29625, USA

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ABSTRACT

The effect of dissolved organic matter (DOM) on Am(III), Pu(IV), Np(V), and U(VI) sorption was investigated with natural water (pH ~8) and zeolitized tuff samples collected from the Rainier Mesa tunnel system, Nevada Test Site, where the USA detonated underground nuclear tests prior to 1992. Perched vadose zone water at Rainier Mesa has high levels of DOM as a result of microbial degradation of mining debris (diesel, wood, etc.). The Am and Pu sorption K_d s were up to two orders of magnitude lower in water with high DOM (15–19 mg C/L) compared to the same water with DOM removed (<0.4 mg C/L) or in naturally low DOM (0.2 mg C/L) groundwater. In contrast, K_d s of Np and U were less affected by DOM at these solution conditions. Uranium sorption decreased as a result of high dissolved inorganic C (DIC) resulting from microbial degradation of DOM. Thermodynamic model predictions, based on actinide–humic acid stability constants available in the literature, are in general agreement with measured K_d data, correctly predicting the effects of DIC and DOM on actinide retardation. This agreement is encouraging to future modeling efforts and suggests that effects of DOM and DIC can be incorporated into reactive transport modeling predictions. The Am and Pu transport rates in Rainier Mesa tunnel waters will be substantially faster as a result of the elevated DOM levels. Low diffusion rates of actinide–DOM macromolecular complexes may focus Pu and Am transport into fractures and minimize retardation via matrix diffusion. The resulting transport behavior will affect actinide distribution patterns and associated risk estimates.

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1. Introduction

Over 800 underground nuclear tests were detonated from 1951 to 1992 at the Nevada Test Site (NTS) as part of the USA nuclear testing program (Fig. 1). As a result, approximately 4.8×10^{18} Bq (calculated to 1992, $\sim 1.3 \times 10^8$ curies) were deposited in the NTS subsurface (Smith et al., 2003). In the Rainier Mesa area of the NTS (Area 12), a total of 62 nuclear detonations were conducted (DOE, 2000), primarily in an extensive and complex system of tunnels drilled into zeolitized tuff of Rainier Mesa. Activities associated with underground nuclear testing and tunnel construction have altered the tunnel water geochemistry, resulting in much higher dissolved organic matter (DOM) content than local spring water. The source of the DOM is believed to be tunnel lagging, wood debris, drilling fluids, and their microbial decomposition products.

The concentration of Pu in these DOM-rich tunnel waters is higher than has been measured in most other contaminated groundwater samples at the NTS (Table 1). Interestingly, 87% and

65%, respectively, of Pu in U12n and U12t tunnel waters was found in the “aqueous” fraction (<20 nm). In contrast, Pu in NTS groundwaters with naturally low DOM is found to be associated with inorganic colloids (Kersting et al., 1999). The data suggest that Pu–DOM complexes will affect the mobility and transport behavior of Pu in NTS waters. Other actinides (e.g. Np, U, Am) may be affected as well.

In general, the affinity of DOM for mineral surfaces is high at low pH and decreases with increasing pH, behavior that is typical of anion sorption to mineral surfaces. For example, humic acid sorbs “completely” to hematite surfaces at pH <6 but this decreases substantially by pH 8 (Jain et al., 2007; Khasanova et al., 2007). The decrease is attributed to deprotonation of both the humic acid and hematite at high pH which results in electrostatic repulsion between the organic and inorganic phases. Similar behavior has been observed in the case of kaolinite, γ -Al₂O₃, silica, and other minerals with humic and fulvic acids (e.g. Niitsu et al., 1997; Righetto et al., 1991; Schulthess and Huang, 1991). The specific pH-dependent sorption behavior is controlled by the nature and deprotonation behavior of both the organic component and the mineral surface.

Actinide–DOM complexes have been shown to affect Am and Pu sorption to mineral surfaces. Pu sorption to alumina, and Am

* Corresponding author at: Glenn T. Seaborg Institute, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94550, USA.

E-mail address: kersting1@llnl.gov (A.B. Kersting).

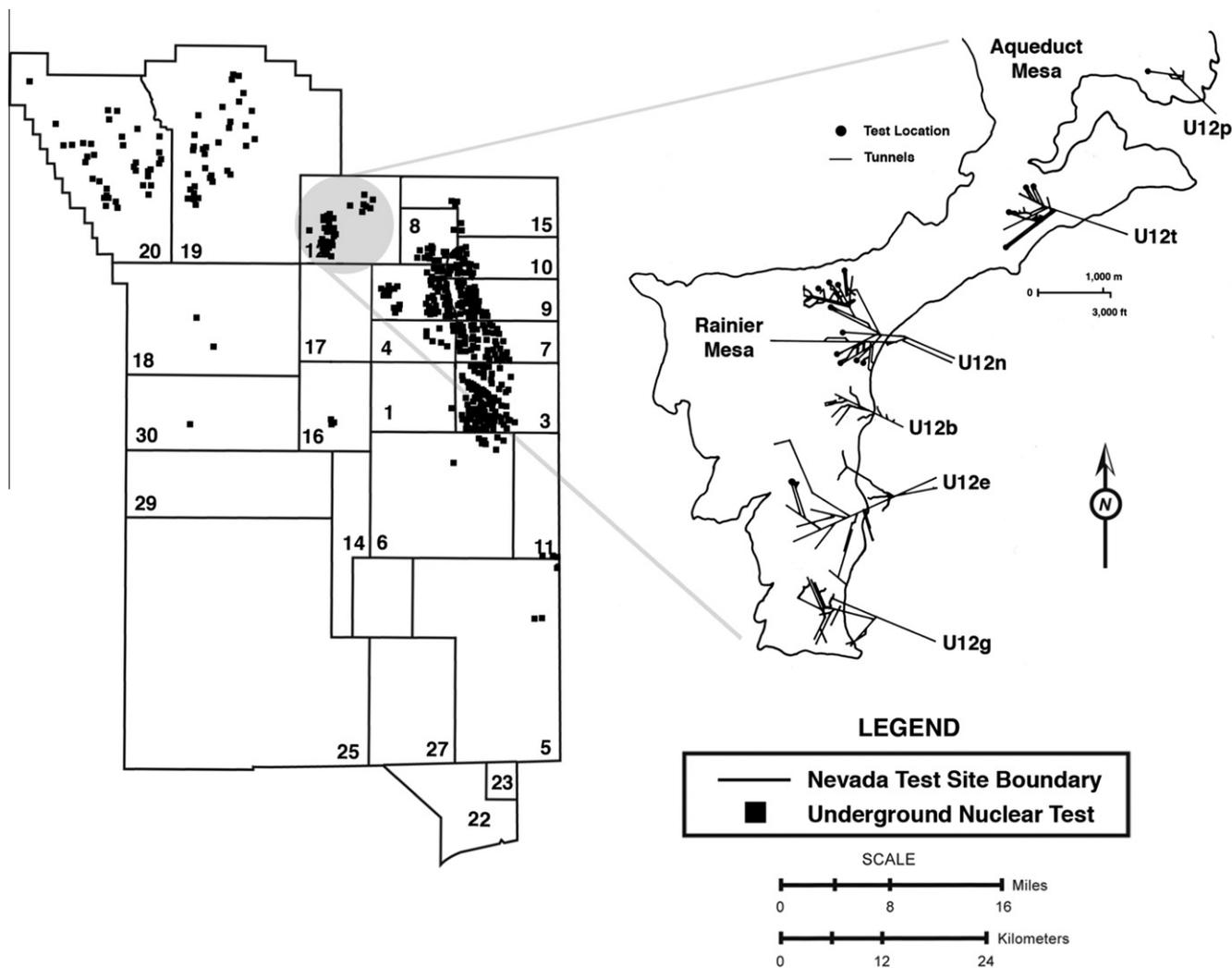


Fig. 1. The Nevada Test Site, located 100 km northwest of Las Vegas, NV is outlined on the left. Dots denote the location of individual underground nuclear tests. Rainier Mesa is shown by a circle. The tunnel system in Rainier Mesa is expanded on the right, showing the location of U12n and U12t.

sorption to silica and alumina is enhanced by humic acid at $\text{pH} < 7.5$ and reduced substantially at $\text{pH} > 8$ (Righetto et al., 1991). The sorption of Th(IV), a chemical analog of Pu(IV), to hematite is enhanced by humic acid at $\text{pH} < 4$ (Murphy et al., 1999) and reduced at $\text{pH} > 4$ (Reiller et al., 2002). Th(IV) sorption to silica was found to decrease by two orders of magnitude between 0 and 100 mg DOC/L at slightly acidic to alkaline pH (Reiller et al., 2003).

The pronounced effect of DOM on Am and Pu mobilization in neutral to alkaline waters has been observed under field conditions. Americium sorption to Lake Michigan sediments at pH 7.9 decreases at a 1:1 ratio in >1 mg C/L DOM waters (Nakayama and Nelson, 1988). A similar relationship is seen for Pu(III/IV) (Nelson et al., 1985). At Oak Ridge National Laboratory, McCarthy et al. (1998) found that mobile Am is associated with DOM, consistent with their modeling predictions, and that unretarded down-gradient transport through fractures and large pore spaces is a result of Am complexation with DOM.

The kinetics of actinide–DOM complex formation has been observed to affect Am transport. Column breakthrough experiments with Am and Boom Clay (Maes et al., 2006) at pH 8.5 indicate that most aqueous Am is retained by the solid matrix (i.e. effective competition between solid matrix and DOM) but a small fraction of the Am–DOM complexes disassociate very slowly, allowing for

essentially unretarded transport. The calculated kinetics correspond to a half-life for the complex of 97 days.

DOM impacts Np sorption primarily in anaerobic systems in which Np(V) may be reduced to Np(IV). For example, with the introduction of humic acid under aerobic conditions, Np(V) sorption to hematite is unaffected at $\text{pH} < 6$ and decreases only slightly at $\text{pH} > 8$ (Jain et al., 2007). With the introduction of as much as 40 mg/L humic acid, Np(V) sorption to kaolinite increases slightly at $\text{pH} < 8$ and decreases less than an order of magnitude at $\text{pH} > 8$ (Niitsu et al., 1997). Similar behavior was observed in the case of silica and $\gamma\text{-Al}_2\text{O}_3$ (Righetto et al., 1991). However, Np sorption to hematite increases substantially at low pH under anaerobic conditions (Jain et al., 2007; Khasanova et al., 2007). Schmeide and Bernhard (2009) found that Np(V) may be reduced by humic substances to Np(IV). Thus, increased sorption in low pH anaerobic conditions can be attributed to binary or ternary Np(IV) complexes on mineral surfaces.

DOM impacts U sorption primarily under acidic conditions. At pH 4.4, U(VI) sorption to hematite is enhanced by humic acid while at pH 6.4, it is inhibited (Ho and Miller, 1985). A comprehensive data and modeling effort by Lenhart and Honeyman (1999) found that 10 ppm humic acid increases U(VI) sorption to hematite at $\text{pH} < 6$ while the decrease at $\text{pH} > 8$ was slight. Importantly, formation of inorganic uranyl carbonate complexes at $\text{pH} > 8$ are

Table 1
Plutonium concentrations in NTS hot well groundwater samples.^a

Test	Well name	Distance from detonation point, m		Sampling date	DIC ^c , ppm C	DOC ^c , ppm C	Pu, total, pCi/L	Pu, total, Bq/L	%Pu aqueous
Bourbon	UE-7ns	137	H	2005	40	–	<0.04	<1.5E–3	–
Nash	UE-2ce	183	H	2008	84	–	<0.008	<3.0E–4	–
Bilby	U-3cn PS#2	210	V	2007	50	1.3	0.06	2.2E–3	–
Camembert	U19q PS1d	462	V	2003	98	0.5 ^b	<0.02	<7.4E–4	–
Cambric	RNM-2S	91	H	2007	30	0.3	<0.02	<7.4E–4	–
Cambric	RNM-1	6	V	2007	31	0.3	0.006	2.2E–4	–
Schooner	PM-2	270, 487	H, V	2005	441	–	0.006	2.2E–4	–
Dalhart	U4u PS2a	140	V	2008	38	1.2	0.44	1.6E–2	36 ^e
Benham	ER-20-5 #1	1300, 660	H, V	2004	38	–	0.42	1.6E–2	<1 ^d
Cheshire	U20n PS1 DDh	2	V	2005	19	<1 ^b	0.46	1.7E–2	<10 ^{e,f}
Almendro	U19v PS1ds	125–153	V	1999–2006	24–52	20	<0.004–9.5	<1.5E–4 to 3.5E–1	–
Chancellor	U19ad PS1A	48	V	2008	22	2.4	47	1.7	16 ^e
U12n tunnel	U12n extension drift gas sealed plug	450–1600	H	2006	57	16	1.2	4.4E–2	–
U12n tunnel	U12n main drift gas sealed plug	450–1600	H	2006	52	16	1.1	4.1E–2	85 ^e
U12t tunnel	U12t gas sealed door	450–1000	H	2006	55	7.0	0.009	3.3E–4	–
U12t tunnel	U12t gas sealed plug	450–1000	H	2006	89	21	54	2.0	65 ^e

^a Measured total inorganic carbon (DIC) and total organic carbon (DOC) in samples filtered through 0.45 µm pore size filter membranes.

^a Pu concentrations, DIC and DOC measured by LLNL as part of the Underground Test Area Environmental management project; otherwise as indicated. Data compiled and maintained by Stoller-Navarro (2007).

^b Data from Stoller-Navarro (2007) analyzed outside of LLNL.

^c <40 nm fraction.

^d <7 nm fraction. Based on 1997 sample reported in Kersting et al. (1999).

^e <20 nm.

^f 2003 sample.

predicted to affect U(VI) sorption to a greater extent than the formation of humic acid complexes. Asymmetrical flow field-flow fractionation of natural groundwaters in the pH range 7–8.1 and DOM concentrations of 4–136 mg C/L (Ranville et al., 2007) indicate that U(VI)–humic acid complexes account for ≤2% of the aqueous U. These results are in agreement with ternary system laboratory investigations suggesting that neither ternary complexes on mineral surfaces nor stabilization of U(VI) in the aqueous phase are likely to be significant at neutral to alkaline pH and in the presence of DIC. However, slow kinetics of disassociation between U(VI) and humics can provide a mechanism for fast migration of the small fraction of U–DOM complexes (e.g. Artinger et al., 2002).

Predictive modeling of the effect of DOM on radionuclide migration is essential for understanding actinide transport in the field. However, self-consistent sets of stability constants for actinide complexation with organic co-contaminants are lacking (Keith-Roach, 2008). The most recent effort to develop a stability constant database was performed by Hummel et al. (2005). However, this dataset did not include data for complex mixtures of organic acids such as DOM. Formation of actinide–DOM complexes has been most commonly quantified by conditional constants (log β) that are specific to the solution conditions (e.g. pH) and class of organic matter (e.g.

humic acid versus fulvic acid) present. In some cases, a “loading capacity” term has been used to address the effect of pH and ionic strength on conformation changes in the organic matter and accessibility of reactive sites for actinide complexation (e.g. Czerwinski et al., 1994). A more comprehensive approach was taken by Lenhart and coworkers (Lenhart and Honeyman, 1999; Murphy et al., 1999) in which a triple layer surface complexation model (for hematite) was coupled to a non-electrostatic discrete ligand approach (for humic acid–Th(IV) and –U(VI) complexation) to model a suite of binary and ternary sorption data. However, this level of detail has not been attempted for most actinides.

This study examines how anthropogenically altered groundwater at Rainier Mesa, NTS, may affect the sorption behavior of actinides and may impact transport. The sorptive properties of Am(III), Pu(IV), Np(V), and U(VI) which represent actinides with a range of oxidation states and affinities to both DOM and DIC were examined. Due to their long half-life, these actinides will increasingly make up a significant portion for the residual radioactivity left behind after an underground nuclear test (Smith et al., 2003). Batch sorption experiments were performed using crushed zeolitized tuff and groundwater from Rainier Mesa. The effect of DOM and DIC was evaluated by comparing actinide sorption in anthropogenical-

Table 2
Volcanic zeolitized tuff sample characteristics.

Hole	Depth interval, m	Geologic unit description ^a	Mineralogy	Surface area, m ² g ⁻¹
UE-12t #2	429.8–430.0	Tuff; ash-fall; pale greenish-yellow, pale to moderate red, & pale grayish-pink; zeolitized; silicified; fine to coarse grained; contains sparse to moderate, fine to coarse, lithic fragments & pumice	Quartz > feldspar > zeolites	5.1
UE-12t #4	390.8–390.9	Tuff; ash-fall, reworked ash-fall, peralkaline ash-fall, & tuffaceous sandstone; grayish-yellow, yellowish-gray, grayish-pink, moderate greenish-yellow; thin to thick bedded; zeolitized, several silicified zones, few argillized zones	Quartz > feldspar > zeolites	14.4
UE-12n #8	388.3–388.5	Tuff; alternately calc-alkaline reworked ash-fall, ash-fall, peralkaline ash-fall & reworked ash-fall, & tuffaceous sandstone; grayish-orange-pink, moderate red, & yellowish-gray; thin bedded; zeolitized; competent; contains several thin silicified beds	Feldspar > zeolites > quartz	19.2
UE-12n 15A	377.4–377.6	Tuff; calc-alkaline ash-fall, some peralkaline ash-fall, minor reworked ash-fall	Quartz > feldspar > zeolites	34.9

^a Magner (2006).

ly altered tunnel water to sorption in unaltered regional aquifer water and tunnel water with DOM removed. Finally, thermodynamic modeling was used to test whether complexation constants available in the literature can effectively predict the observed effects of DOM and DIC on actinide sorption.

2. Materials and methods

2.1. Volcanic tuff preparation and characterization

Four zeolitized tuff samples (UE-12t#2, UE-12t#4, UE-12n#8 and UE-12n#15A) were obtained from the NTS core library, Mercury, Nevada. All 4 samples are ash-fall tuffs. Samples were crushed to a particle size of <500 μm , then dry sieved to collect the 75–500 μm fraction (Hu et al., 2008; Roden and Scheibe, 2005). This fraction comprised greater than 70% of the original crushed rock. The mineralogy of the samples was qualitatively determined by X-ray diffraction and surface area measured using a Micrometrics Gemini 2370 BET surface area analyzer using N_2 (Table 2). Mineralogy was dominated by quartz, feldspars and zeolites (predominantly clinoptilolite and heulandite). This mineralogy is typical of zeolitized tuffs located at the Rainier Mesa tunnel level.

2.2. Water preparation and characterization

Water samples from two different flooded tunnel systems (U12t and U12n) were collected between October 30 and November 2, 2006. A third groundwater sample (ER-12-3) with naturally low DOM was pumped from a well located 2100 m SW of the entrance to U12n tunnel and completed in the regional carbonate aquifer on July 6, 2005. Sorption experiments were begun within 4 months and completed within 6 months of tunnel water collection. Samples were not preserved. Major ion and DOC/DIC analyses completed shortly after sampling and at the start of sorption experiments were compared and no significant changes were observed. Nevertheless, it is acknowledged that some groundwater alteration may have occurred in the 6 months between sampling, shipping and laboratory experimentation.

At the start of the experiments, all water samples were filtered through 20-nm pore size membrane filters to remove the majority of particulates, inorganic colloids and microorganisms. Based on pre- and post-filtration DOM analysis, >90% of DOM remained in the filtrate. Ion chromatography was used to determine major anions and inductively coupled plasma mass-spectrometry (ICP-MS) was used for major cations. A total organic C (TOC) analyzer was used for total organic and inorganic C analysis.

Table 3
Analyses of water from U12t tunnel, U12n tunnel, and well ER-12-3.

Water Sample	pH	Cl^- , mg/L	SO_4^{2-} , mg/L	Na, mg/L	K, mg/L	Mg, mg/L	Ca, mg/L	DIC ^a , mg/L	DOC ^b , mg/L
ER-12-3	8.29	6.1	29	32	2	10.1	14.9	23.1	0.2
U12t	8.85	21.7	107	236	6.7	<1	3.2	79	18.5
U12t low DOM (1st batch)	8.26	27.6	211	239	3	<1	<0.1	56.6	0.4
U12t low DOM (2nd batch)	8.85	23.4	142	220	5.6	0.1	0.4	68	0.2
U12n	8.76	14.6	32.5	143	4.2	<1	2.5	55.6	14.9
U12n low DOM (1st batch)	8.28	25.7	143	151	0.3	<1	<0.1	30.4	0.3
U12n low DOM (2nd batch)	8.75	13.8	40.7	135	5.8	0.4	1.6	52.8	0.3

^a Dissolved inorganic carbon.

^b Dissolved organic carbon; detection limit is ~ 0.2 mg/L.

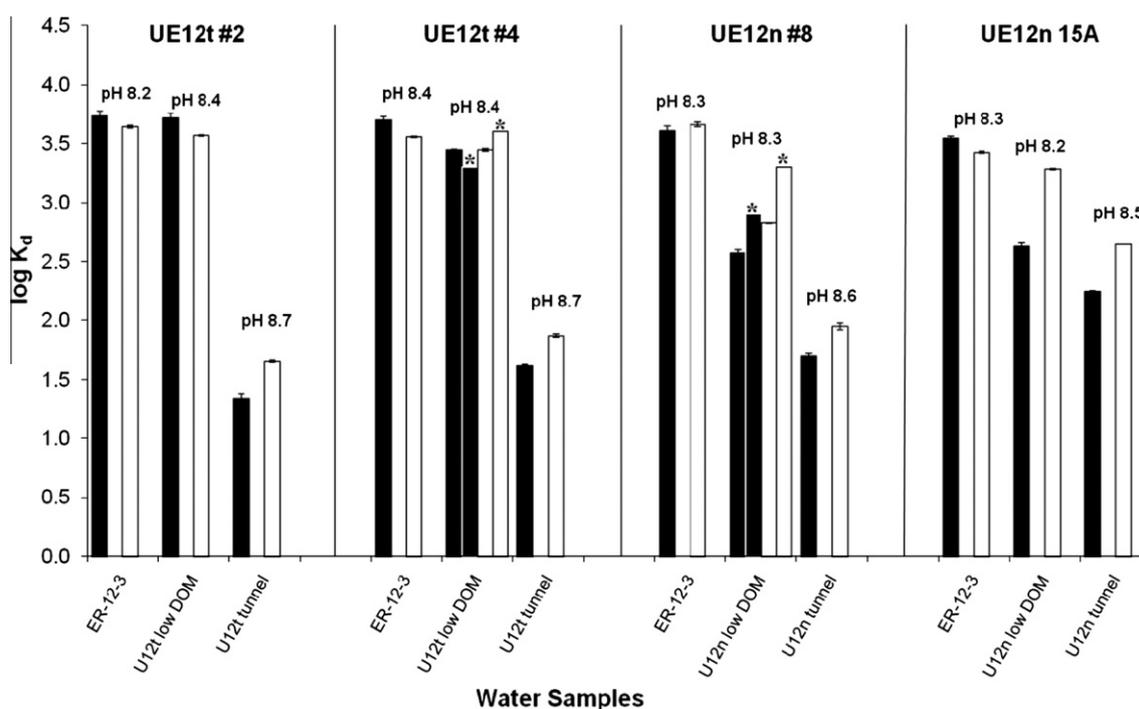


Fig. 2. Am(III) sorption in water samples from an environmental monitoring well (ER-12-3), U12t and U12n with high and low DOM concentrations. The Am K_d s collected after 2 days (■) and 33 days (□) for the four zeolitized tuff samples (UE-12t #2, UE-12t #4, UE-12n #8 and UE-12n#15A). *Sorption conducted using low sulfate/DOM batch 2 water for comparison.

To evaluate the role of DOM, tunnel water samples were treated with activated charcoal to remove DOM (Othman et al., 2000, 2001). The first batch of tunnel water treated with activated charcoal produced high SO_4^{2-} waters due to its leaching from the charcoal. The treatment also reduced the pH slightly (~ 0.5 pH) which, in turn, reduced DIC in solution (Table 3). These waters were, nevertheless, used for Am and Pu sorption experiments. In the second batch of treated tunnel water, SO_4^{2-} was leached from the activated charcoal by flushing the column with 1.5 L of 10^{-3} M NaHCO_3 before using it to treat tunnel waters; this pretreatment minimized changes in pH and DIC. The second batch of treated tunnel water was used for U and Np sorption experiments. A small number of Am and Pu sorption experiments carried out with the second batch of low- SO_4^{2-} waters indicated that the increased SO_4^{2-} did not affect the overall behavior of Am and Pu sorption (Figs. 2 and 3).

2.3. Radionuclide preparation, purification and oxidation state characterization

Alpha-emitting actinides ^{241}Am , ^{238}Pu , ^{233}U and ^{237}Np were used in batch sorption experiments. ^{241}Am in 3 M HNO_3 was purified using TEVA[®] and TRU resin columns (Eichrom[®]). The purified $^{241}\text{Am(III)}$ was eluted using 1 M HCl. ^{238}Pu in 4 M HNO_3 was reduced to Pu(IV) using NaNO_2 and purified using a TEVA[®] column and eluted using 1 M HCl. The oxidation state of the ^{238}Pu stock solution was characterized by both solvent extraction using 0.5 M bis-(ethylhexyl)-phosphoric acid (HDEHP) in xylene and 0.025 M 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (PMBP) in xylene (Bertrand and Choppin, 1982; Foti and Freiling, 1964; Neu et al., 1994; Nitsche et al., 1988) and Pu co-precipitation with lanthanum fluoride (Kobashi et al., 1988). The analysis errors for both methods were $<5\%$. The results indicated that the Pu stock solution consisted of 80% Pu(IV), 15% Pu(III) and 5% colloidal Pu. The experimental solutions were not protected from atmospheric $\text{O}_2(\text{g})$ and Pu(III) is unstable in oxic solutions above pH 4 (Cleveland, 1979). Therefore, it was assumed that Pu(III) oxidized to

Pu(IV) over the course of the experiment. Neptunium-237 was purified in concentrated HCl with KI using an AG1X8 (100–200 mesh) resin column. The Np was eluted from the column using 0.1 M HNO_3 . The Np solution was dried in HNO_3 on a hotplate before re-dissolving in 1 M HCl to make a Np(V) solution. The Np(V) oxidation state of the stock solution was confirmed by its UV/VIS spectrometry. Uranium-233 in 4 M HNO_3 was purified by UTEVA[®] column (Eichrom[®]) and eluted using 0.1 M HCl. The oxidation state of U in the final stock solution was U(VI). The activities of all four radioisotope stock solutions were determined using a liquid scintillation analyzer (Tri-Carb 2600XL, Packard Instruments). The purity of all four radioisotope stock solutions ($\sim 100\%$ pure by activity) was confirmed using alpha spectrometry.

2.4. Batch sorption experiments

All batch sorption experiments were carried out under oxic (atmospheric) conditions, at room temperature, in duplicate, and with associated blanks. Four solids (Table 2) and five solutions (Table 3) were used. The U12t waters were paired with UE-12t#2 and UE-12t#4 zeolitized tuff; the U12n waters were paired with UE-12n#8 and UE-12n#15A zeolitized tuff. The choice of solid and solution was based on the proximity of the rock and groundwater in the field. The ER-12-3 groundwater, with naturally low DOM, was used with all four zeolitized tuffs to compare sorption in anthropogenically altered fluids to sorption in unaltered groundwater. In the Pu and Am sorption experiments, 0.3 g of solid was equilibrated with 45 mL solution in 50 mL polypropylene tubes. In the Np and U sorption experiments, 3 g of solid was equilibrated with 45 mL solution. All water samples were allowed to equilibrate with the volcanic tuff for one week prior to the addition of a radionuclide spike. When adding acidic radionuclide spike, sufficient NaOH was added to neutralize the acid content of the spike solution. Initial Am(III), Pu(IV), Np(V), and U(VI) concentrations were 4.5×10^{-10} , 1.0×10^{-10} , 3.0×10^{-9} , and 2.6×10^{-8} mol/L, respectively.

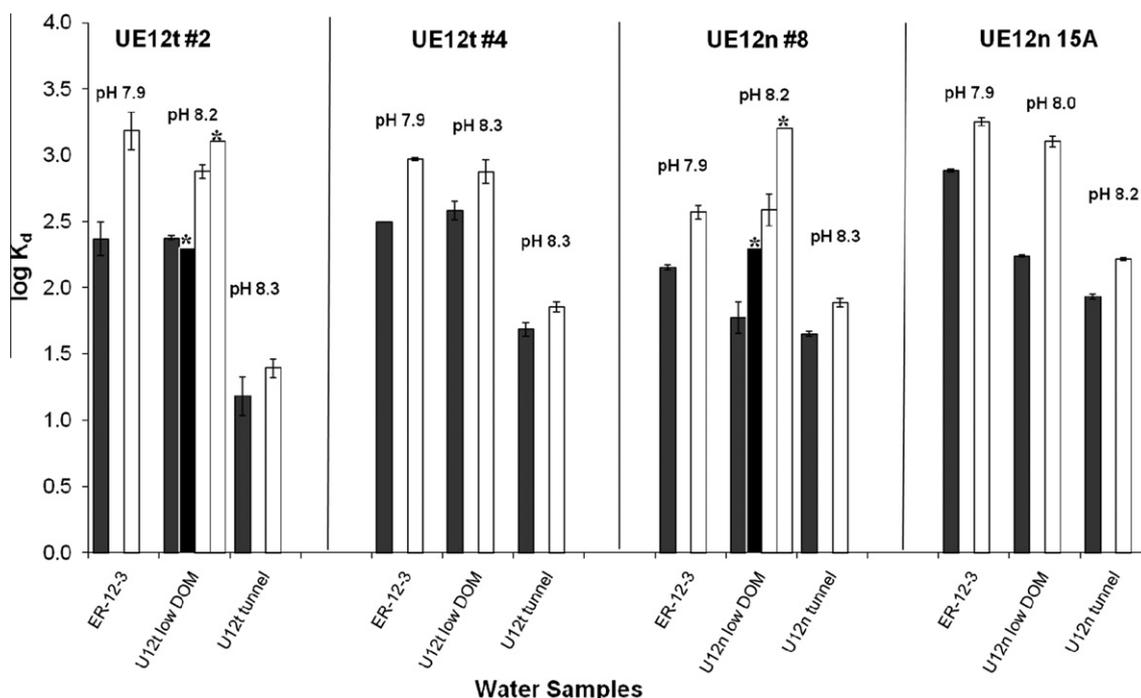


Fig. 3. Pu(IV) sorption in water samples from an environmental monitoring well (ER-12-3), U12t and U12n with high and low DOM concentrations. The Pu K_{ds} collected after 6 days (■) and 31 days (□) for the four zeolitized tuff samples (UE-12t #2, UE-12t #4, UE-12n #8 and UE-12n#15A). *Sorption conducted using low sulfate/DOM batch 2 water for comparison. Errors for all figures are 2 sigma.

During equilibration and sorption, samples were placed on a Glas-Col[®] rotator (~10 rpm). To sample the solutions, the 50 mL tubes were centrifuged at 4500 rpm for 10–15 min to separate most of the inorganic solid from the liquid phase (>250 nm particles based on sedimentation; Gee and Bauder, 1986). A 1.5 mL aliquot of the fluid was then removed from the top of the tube and placed into a microcentrifuge tube. This fluid was centrifuged at 10,000 rpm for 1 h to remove >30 nm colloids. The 30 nm cutoff retained the DOM compounds in solution while effectively removing inorganic particles associated with the introduced solid. A 1 mL aliquot was taken from the top of the centrifuged fluid for analysis of soluble radionuclide species. Dissolved ²⁴¹Am, ²³⁸Pu and ²³³U was measured by LSC. A Thermo[®] Scientific X series 2 ICP-MS was used for analysis of dissolved ²³⁷Np. Centrifugation was used instead of filtration to avoid actinide and DOM losses to filtration membranes.

Two samples (at approximately one and 30 days) were collected for each batch experiment. K_{ds} (mL/g) were calculated using:

$$K_d = \frac{A_i - A_f}{A_f} \times \frac{V}{m} \quad (1)$$

where A_i and A_f are initial and final aqueous radionuclide concentrations (mol/L), respectively; V is the volume of sorption fluid (mL) and m is the mass of tuff (g).

3. Results and discussion

The water samples collected from U12n and U12t tunnels are characterized by DIC and DOC concentrations substantially higher (and balanced by an increase in Na⁺) than ambient groundwater (e.g. ER-12-3) (Table 3). The altered water chemistry can be attributed to microbial degradation of mining debris (e.g. diesel, wood debris, etc.). The U12t water also has an elevated SO₄²⁻ concentration whose source is unknown. The DOC of ER-12-3 is two orders of magnitude lower than the tunnel water. Importantly, DOC concentrations in tunnel waters are high enough to expect a substantial reduction in Am and Pu sorption to aluminosilicate solids (Nakayama and Nelson, 1988; Reiller et al., 2003; Righetto et al., 1991) but a less significant effect for Np and U (Baston et al., 1994; Niitsu et al., 1997) under these mildly alkaline (pH 8.2–8.9) conditions.

3.1. DOM sorption

DOM sorption to volcanic tuff samples was tested in a separate set of experiments by equilibrating 3 g of tuff with 45 mL of tunnel water for one month. The fluid was separated from the solid and analyzed for DIC and DOC. The DOC concentration before and after equilibration with zeolitized tuff differed by less than 5%. This is consistent with humic and fulvic acid sorption to silica and montmorillonite (two dominant minerals in these tuffs) under similar conditions (Reiller et al., 2003; Righetto et al., 1991; Schulthess and Huang, 1991). Importantly, it indicates that the DOM will potentially stabilize aqueous concentrations of actinides in tunnel waters and, as a result, increase their mobility.

3.2. Am(III) sorption

For all four tuff samples, the Am K_d in water with high-DOM is significantly lower than in waters with low DOM (Fig. 2). For the two U12t volcanic tuff samples, Am K_{ds} measured in U12t water were between 30 and 250 times lower than in both the ER-12-3 water and U12t water that had 98% of its DOM removed. The effect of DOM is less pronounced in U12n samples. The K_{ds} in U12n water were 3 to 80 times lower than in both the ER-12-3 water and U12n

water that had 98% of the DOM removed. The difference may, in part, be the result of the 19% lower DOC concentration in U12n water and higher reactive surface areas of U12n tuff samples. The higher surface area tuff samples may provide more effective competition between DOM aqueous complexation and Am sorption. The nature of the DOM in U12n and U12t waters may also differ in such a way as to produce overall stronger or weaker associations with Am.

Previous studies have shown that DOM reduces sorption of Am to pure and mixed systems of aluminosilicate minerals in neutral to mildly alkaline conditions (Maes et al., 2006; McCarthy et al., 1998; Righetto et al., 1991). The examination of Am sorption is consistent with these earlier studies and indicates that water chemistry, notably DOM, will play a major role in controlling Am mobility in Rainier Mesa tunnel waters.

In samples where DOM was present, sorption was kinetically limited. Sorption increased significantly between 2 and 30 days in tunnel waters. This is consistent with Maes et al. (2006) who measured very slow Am desorption rates from soluble organic compounds ($t_{1/2} = 97$ days). The increasing Am K_d in tunnel waters over the 30 day timeframe is likely the result of slow disassociation of Am from soluble Am–DOM complexes and subsequent sorption to mineral surfaces. The slow disassociation provides a mechanism for unretarded Am transport in the short term but also suggests that Am–DOM aqueous complex formation is reversible.

3.3. Pu(IV) sorption

The effect of DOM on Pu sorption followed the behavior observed for Am (Fig. 3). For the two U12t volcanic tuff samples, Pu K_{ds} measured in U12t water were between 6 and 60 times lower than in both the ER-12-3 water and U12t water that had 98% of its DOM removed. The K_{ds} in U12n water were 1.3–13 times lower than in both the ER-12-3 water and U12n water that had 98% of the DOM removed.

Previous studies have shown that formation of Pu–DOM complexes will increase solubility and decrease sorption in neutral to alkaline waters. This behavior has been observed in single mineral systems (Sanchez, 1983), in lake sediments (Nelson et al., 1985), with synthetic (Boukhalfa et al., 2007; Ruggiero et al., 2002) and natural (Skipperud et al., 2000) organic matter. The examination of Pu sorption indicates that anthropogenically-derived DOM in Rainier Mesa tunnel waters will play a role in controlling Pu mobility as well.

In contrast to Am, the Pu K_d increase between 6 and 31 days was greater in the absence of DOM than in its presence. An underlying mechanism controlling Pu or Am sorption kinetics cannot be identified with these limited data. However, it is clear that the effect of DOM on actinide transport will be complicated by the kinetics of actinide–DOM complex formation and sorption.

3.4. Np(V) sorption

The presence of high concentrations of DOM reduced the Np K_d in tunnel waters only slightly (Fig. 4). The Np K_d in DOM-rich tunnel water was never more than three times lower than in ER-12-3 water or tunnel water that had its DOM removed. The results are indicative of weak Np(V)–DOM complexation in solution and a minor contribution of DOM to Np(V) mobilization. The results are consistent with the relatively negligible effects of DOM on Np(V) sorption to aluminosilicate minerals at neutral and alkaline pH previously reported in the literature (Niitsu et al., 1997; Righetto et al., 1991). Similar observations have been made for Np(V) interaction with hematite and goethite (Jain et al., 2007; Khasanova et al., 2007).

Humic acids enriched in reducing functional groups, such as hydroquinone, have been shown to effectively reduce Np(V) to

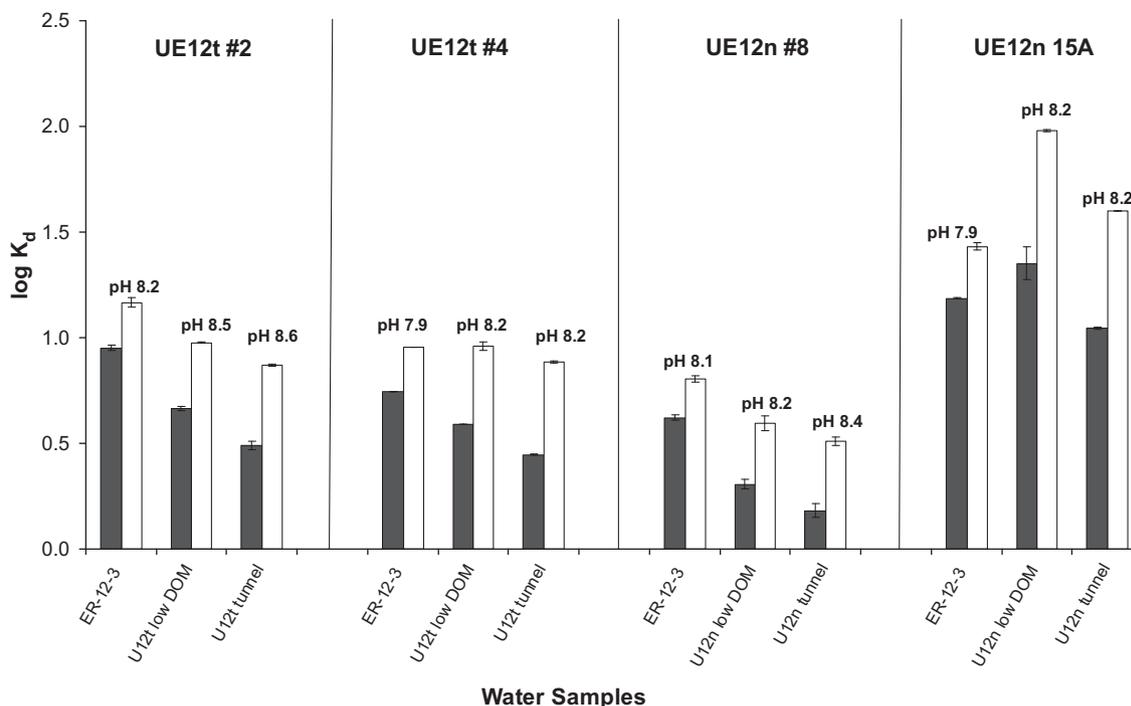


Fig. 4. Np(V) sorption in water samples from an environmental monitoring well (ER-12-3), U12t and U12n with high and low DOM concentrations. The Np K_d s collected after 1 day (■) and 31 days (□) for the four zeolitized tuff samples (UE-12t #2, UE-12t #4, UE-12n #8 and UE-12n#15A) are shown.

Np(IV) in the presence of goethite and result in dramatic decreases in Np sorption at pH > 6 (Khasanova et al., 2007). However, Shcherbina et al. (2007) observed no reduction of Np(V) by humic acid under oxic conditions. Thus, reduction of Np(V) to Np(IV) was not expected in the batch experiments. Nevertheless, if reducing conditions are established in Rainier Mesa tunnel waters, mobilization of the reduced Np(IV) species may occur.

Neptunium K_d s for UE-12n#15A tuff were substantially higher in comparison to the other three samples. The smaller surface area normalized K_d differences between tuff samples imply that sample surface area may play a role in the observed K_d s. However, this observation does not hold true for all four actinides examined here. Thus, mineralogical and other factors are likely to contribute to the observed K_d differences between tuff samples.

3.5. U(VI) sorption

Like Np, U sorption is relatively weak in all samples (Fig. 5). However, for U, the most substantial differences in K_d are found between the unaltered regional aquifer groundwater (ER-12-3) and the tunnel waters (with or without DOM removed). The presence or absence of DOM has only a small effect on U sorption. It is apparent that formation of uranyl carbonate complexes in solution is strongly favored and inorganic aqueous complexes effectively compete with DOM for U. The behavior is consistent with U–DOM complexation measurements for mildly alkaline groundwater with 4–132 mg/L DOC located in a clay-rich aquitard (Ranville et al., 2007). Uranium–DOM complexation in mildly alkaline groundwater is in stark contrast to observed strong U–DOM associations found in acidic groundwater (pH 4.5–6) from the Savannah River Site near Aiken, SC (Jackson et al., 2005). Anthropogenic increases in DIC rather than DOM play a major role in U mobilization under mildly alkaline Rainier Mesa tunnel water conditions.

3.6. Model predictions

To provide a quantitative comparison of the experimental results to modeling predictions, the effects of elevated tunnel water DIC and DOM were first quantified. The effect of elevated DIC and DOM on Am sorption in U12t water, for example, was estimated by

$$\Delta \log (K_{d-\text{Am-DIC}}) = \log \left(\frac{K_{d-\text{Am-U12t-low DOM}}}{K_{d-\text{Am-ER-12-3}}} \right) \quad (2)$$

and

$$\Delta \log (K_{d-\text{Am-DOM}}) = \log \left(\frac{K_{d-\text{Am-U12t-tunnel}}}{K_{d-\text{Am-U12t-low DOM}}} \right) \quad (3)$$

respectively. Average values for the two sampling times and two tuffs in U12t and U12n waters were calculated (Table 4). Under all conditions and for each radionuclide, the anthropogenic alteration of groundwater had either a negligible or negative effect on sorption. For Am and Pu, it is clear that DOM significantly reduces sorption. Furthermore, the effect in U12t water is more significant than U12n water. For Np, neither DIC nor DOM substantially reduce sorption. Lastly, DIC has a much greater effect on U sorption than DOM.

To model the effects of DIC and DOM, the aqueous speciation of each actinide was simulated (hydrolysis, carbonate complexation, sulfate complexation, and organic matter complexation) using the complexation constants available in the literature (Table 5) and solution chemistry of each batch experiment (Table 3). If sorption is linear and controlled by the concentration of free actinide ions and their hydrolysis products in solution (at constant pH), the effect of DIC and DOM on sorption can be predicted. In essence, if the concentration of the free actinide ion decreases by an order of magnitude as a result of DOM or DIC complexation, sorption will decrease by that same order. For example, the predicted DIC and DOM effects on Am sorption in U12t are estimated by:

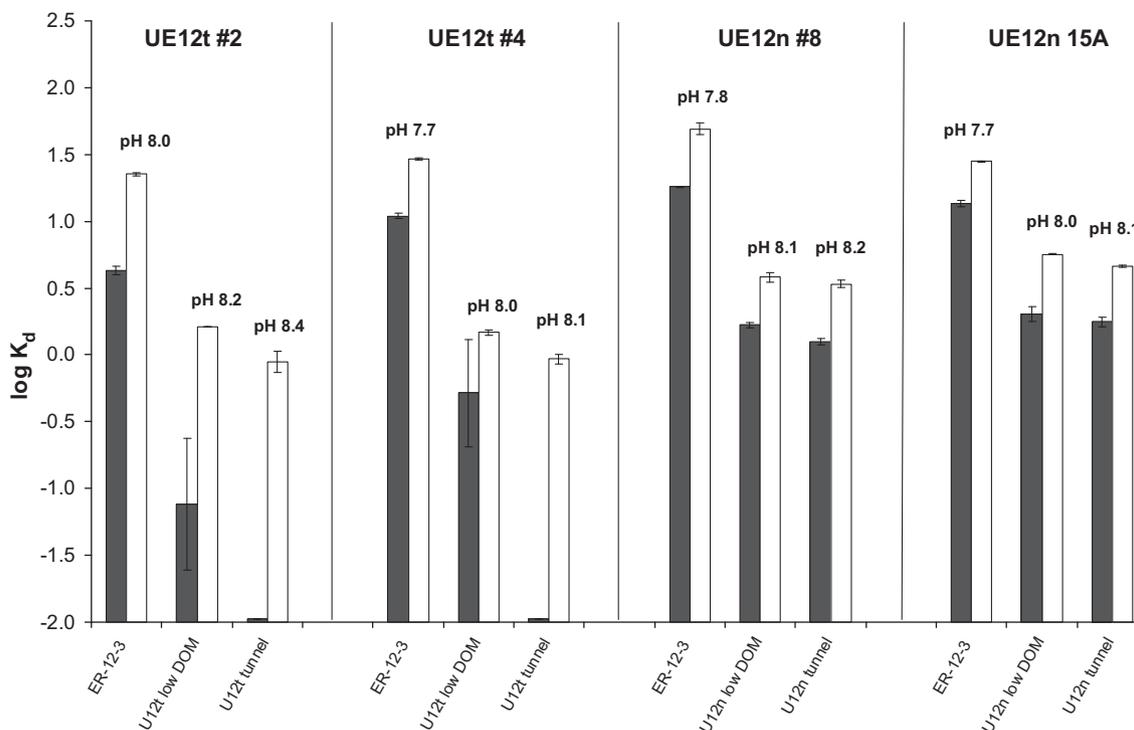


Fig. 5. U(VI) sorption in water samples from an environmental monitoring well (ER-12-3), U12t and U12n with high and low DOM concentrations. The $U K_d$ s collected after 1 day (■) and 31 days (□) for the four zeolitized tuff samples (UE-12 #2, UE-12t#4, UE-12n#8 and UE-12n#15A) are shown.

$$\Delta \log (K_{d-Am-DIC}) = \log \left(\frac{([Am^{3+}] + [AmOH^{2+}] + [Am(OH)_2^+] + [Am(OH)_3^0])_{U12t-low\ DOM}}{([Am^{3+}] + [AmOH^{2+}] + [Am(OH)_2^+] + [Am(OH)_3^0])_{ER-12-3}} \right) \quad (4)$$

and

$$\Delta \log (K_{d-Am-DOM}) = \log \left(\frac{([Am^{3+}] + [AmOH^{2+}] + [Am(OH)_2^+] + [Am(OH)_3^0])_{U12t-tunnel}}{([Am^{3+}] + [AmOH^{2+}] + [Am(OH)_2^+] + [Am(OH)_3^0])_{U12t-low\ DOM}} \right) \quad (5)$$

respectively.

Speciation calculation were based on the following DOM characteristics:

- C fraction in DOM = 50% by mass (McCarthy et al., 1998),
- proton exchange capacity of DOM = 8 meq/g (Lenhart and Honeyman, 1999), and
- loading capacity (LC) at pH 8 = 1.0 (McCarthy et al., 1998).

In addition, it was assumed that Rainier Mesa DOM characteristics are equivalent to humic acid and that ternary surface complexes do not form at pH 8, as suggested by NOM sorption experiments. Aqueous inorganic stability constants for Am(III),

Np(V), and U(VI) were taken from Guillaumont et al. (2003). Th(IV) stability constants were used in lieu of Pu(IV) because a self-consistent set of inorganic and humic acid stability constants was not available for Pu(IV). Th(IV) aqueous conditional inorganic stability constants were from Baes and Mesmer (1976) as reported in Reiller et al. (2003). Am(III)–humic acid stability constants were taken from Panak et al. (1996) and Czerwinski et al. (1996) as reported in McCarthy et al. (1998), and adjusted from LC = 0.68 to LC = 1.0. Np(V)–humic acid and U(VI)–humic acid stability constants were from Marquardt and Kim (1998b,a, respectively) adjusted from LC = 0.22 (pH 8 data) to LC = 1.0. The Th(IV)–humic acid stability constant was from Reiller et al. (2003). When necessary, conditional stability constants were corrected to $I = 0$ using

Debye–Huckel theory. While this correction is only approximate, comparison of simulated and reported conditional constants did not indicate substantial errors at low ionic strength that would affect the interpretation (Table 5). All modeling was performed using the Geochemist's Workbench® family of codes (Bethke, 2006).

Model predictions for Am agree with measured K_d effects, with a two order of magnitude decrease in sorption dominated by the

Table 4
Relative sorption reduction resulting from anthropogenic alteration of groundwater and comparison to model predictions.

	Am(III)	Pu(IV)	Np(V)	U(VI)
<i>U12t</i>				
$\Delta \log (K_{d-DIC})$	-0.1 (-0.6) ^b	-0.1 (0.0)	-0.2 (-0.8)	-1.4 (-1.7)
$\Delta \log (K_{d-DOM})$	-1.9 (-1.3)	-1.2 (-0.3)	-0.1 (-0.1)	- ^a (-0.2)
<i>U12n</i>				
$\Delta \log (K_{d-DIC})$	-0.7 (-0.2)	-0.3 (0.0)	0.0 (-0.6)	-0.9 (-1.2)
$\Delta \log (K_{d-DOM})$	-0.7 (-1.6)	-0.5 (-0.3)	-0.2 (0.0)	-0.1 (-0.1)

^a Non-detectable sorption.

^b Values in parentheses are predicted net decrease in actinide sorption, as defined by Eqs. (4) and (5).

Table 5
Am(III), Np(V), U(VI), and Th(IV) Complexation constants.

Reaction	log K , $I = 0$			Ref.	
$\text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+$	-10.3			1	
$\text{Am}^{3+} + \text{HCO}_3^- = \text{AmCO}_3^+ + \text{H}^+$	-2.3			1	
$\text{Am}^{3+} + 2\text{HCO}_3^- = \text{Am}(\text{CO}_3)_2^- + 2\text{H}^+$	-7.8			1	
$\text{Am}^{3+} + 3\text{HCO}_3^- = \text{Am}(\text{CO}_3)_3^{3-} + 3\text{H}^+$	-16.0			1	
$\text{Am}^{3+} + \text{H}_2\text{O} = \text{AmOH}^{2+} + \text{H}^+$	-7.2			1	
$\text{Am}^{3+} + 2\text{H}_2\text{O} = \text{Am}(\text{OH})_2^+ + 2\text{H}^+$	-15.1			1	
$\text{Am}^{3+} + 3\text{H}_2\text{O} = \text{Am}(\text{OH})_3(\text{aq}) + 3\text{H}^+$	-15.2			1	
$\text{Am}^{3+} + \text{SO}_4^{2-} = \text{AmSO}_4^+$	3.3			1	
$\text{Am}^{3+} + 2\text{SO}_4^{2-} = \text{Am}(\text{SO}_4)_2^-$	3.7			1	
$\text{NpO}_2^+ + \text{H}_2\text{O} = \text{NpO}_2\text{OH}(\text{aq}) + \text{H}^+$	-11.3			1	
$\text{NpO}_2^+ + \text{SO}_4^{2-} = \text{NpO}_2\text{SO}_4^-$	0.4			1	
$\text{NpO}_2^+ + \text{HCO}_3^- = \text{NpO}_2\text{CO}_3^- + \text{H}^+$	-5.4			1	
$\text{NpO}_2^+ + 2\text{HCO}_3^- = \text{NpO}_2(\text{CO}_3)_2^{3-} + 2\text{H}^+$	-14.1			1	
$\text{UO}_2^{2+} + \text{H}_2\text{O} = \text{UO}_2\text{OH}^+ + \text{H}^+$	-5.3			1	
$\text{UO}_2^{2+} + 2\text{H}_2\text{O} = \text{UO}_2(\text{OH})_2(\text{aq}) + 2\text{H}^+$	-12.2			1	
$\text{UO}_2^{2+} + 3\text{H}_2\text{O} = \text{UO}_2(\text{OH})_3^- + 3\text{H}^+$	-20.3			1	
$\text{UO}_2^{2+} + \text{SO}_4^{2-} = \text{UO}_2\text{SO}_4(\text{aq})$	3.2			1	
$\text{UO}_2^{2+} + 2\text{SO}_4^{2-} = \text{UO}_2(\text{SO}_4)_2^{2-}$	4.1			1	
$\text{UO}_2^{2+} + \text{HCO}_3^- = \text{UO}_2\text{CO}_3(\text{aq}) + \text{H}^+$	-0.4			1	
$\text{UO}_2^{2+} + 2\text{HCO}_3^- = \text{UO}_2(\text{CO}_3)_2^{2-} + 2\text{H}^+$	-4.0			1	
$\text{UO}_2^{2+} + 3\text{HCO}_3^- = \text{UO}_2(\text{CO}_3)_3^{4-} + 3\text{H}^+$	-9.1			1	
	Estimate	Reported log β , $I = 0.1$		Simulated log β , $I = 0.012$	
$\text{Th}^{4+} + \text{H}_2\text{O} = \text{ThOH}^{3+} + \text{H}^+$	-3.7	-3.9		-3.9	2
$\text{Th}^{4+} + 2\text{H}_2\text{O} = \text{Th}(\text{OH})_2^{2+} + 2\text{H}^+$	-7.4	-8.0		-7.8	2
$\text{Th}^{4+} + 3\text{H}_2\text{O} = \text{Th}(\text{OH})_3^+ + 3\text{H}^+$	-12.2	-13.0		-12.6	2
$\text{Th}^{4+} + 4\text{H}_2\text{O} = \text{Th}(\text{OH})_4(\text{aq}) + 4\text{H}^+$	-16.5	-17.4		-17.0	2
		Reported log β , $I = 0.02$, LC = 0.68	Calculated log β , $I = 0.02$, LC = 1	Simulated log β , $I = 0.012$	
$\text{Am}^{3+} + \text{HA}^- = \text{AmHA}^{2+}$	6.6	6.4	6.2	6.3	3
$\text{Am}^{3+} + \text{H}_2\text{O} + \text{HA}^- = \text{AmOHHA}^+ + \text{H}^+$	-0.2	13.3 ^a	13.2 ^a	13.3 ^a	3
$\text{Am}^{3+} + 2\text{H}_2\text{O} + \text{HA}^- = \text{Am}(\text{OH})_2\text{HA}(\text{aq}) + 2\text{H}^+$	-9.9	17.5 ^a	17.4 ^a	17.5 ^a	3
$\text{Am}^{3+} + \text{HCO}_3^- + \text{HA}^- = \text{AmCO}_3\text{HA}(\text{aq}) + \text{H}^+$	3.4	13.0 ^a	12.9 ^a	13.0 ^a	3
		Reported log β , $I = 0.1$, LC = 0.22	Calculated log β , $I = 0.1$, LC = 1	Simulated log β , $I = 0.012$	
$\text{NpO}_2^+ + \text{HA}^- = \text{NpO}_2\text{HA}(\text{aq})$	3.2	3.6	2.9	3.1	4
$\text{UO}_2^{2+} + \text{HA}^- = \text{UO}_2\text{HA}^+$	6.0	6.2	5.5	5.8	5
		Reported log β , $I = 0.1$, pH 8, LC = 1		Simulated log β , $I = 0.012$	
$\text{Th}^{4+} + \text{HA}^- = \text{ThHA}^{3+}$	21.9	21.6		21.7	2

Ref: 1 = Guillaumont et al. (2003), 2 = Reiller et al. (2003), 3 = McCarthy et al. (1998), 4 = Marquardt and Kim (1998b), 5 = Marquardt and Kim (1998a).

^a Complexation constants written using OH^- and CO_3^{2-} basis species.

effect of DOM (Table 4). The effect of DIC on Pu(IV) was not predicted due to the lack of Th(IV)–carbonate stability constants. However, Pu(IV) does form strong complexes with carbonate (Zavarin et al., 2005) and is likely to negatively affect K_{dS} . The effect of DOM on Pu(IV) sorption is underestimated. Results suggest that Pu(IV)–DOM complex stability may be higher than for Th(IV). The weak association of Np(V) with DOM is correctly predicted but the effect of DIC appears to be exaggerated. The difference may be the result of NpCO_3^- sorption to mineral surfaces, as has been identified with hematite (Arai et al., 2007). The substantial decrease in U(VI) sorption as a result of DIC was correctly predicted and the predicted importance of DIC over DOM is consistent with measured K_{dS} in these sorption experiments.

4. Concluding remarks

DOM concentrations as low as 15 mg C/L in groundwater will have a dramatic effect on the mobilization of Am and Pu on Rainier Mesa. The Am and Pu K_{dS} decreased by up to two orders of magnitude in high-DOM tunnel waters. The decrease was the result of aqueous actinide–DOM complexation and will result in faster acti-

nide transport rates. The low diffusivity of high molecular weight actinide–DOM complexes (e.g. McCarthy et al., 1998) in the fracture-dominated flow domain at Rainier Mesa will tend to increase transport rates as well. Slow disassociation rates of actinide–DOM complexes may further exacerbate actinide mobilization. In contrast to Am and Pu, sorption of Np and U was less affected by DOM, as only slightly lower K_d s were measured in high-DOM waters. Neptunium partitioning was only slightly affected by DIC while U(VI) sorption was affected substantially. The source of the DIC is believed to be microbial degradation of organic matter.

Model predictions are in general agreement with measured K_d data, correctly predicting the overall effects of DIC and DOM on actinide retardation. This agreement is encouraging to future modeling efforts and suggests that effects of DOM and DIC can be incorporated into reactive transport modeling predictions and risk estimates, albeit in a semi-quantitative manner. Dissimilarities between the predicted behavior of Th(IV), an analog to Pu(IV), and sorption data emphasizes the need to collect stability constant data for Pu interaction with DOM. It appears that the role of DOM in Pu mobilization may be underpredicted by Th(IV) stability constant data.

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References

- Arai, Y., Moran, P.B., Honeyman, B.D., Davis, J.A., 2007. In situ spectroscopic evidence for neptunium(V)–carbonate inner-sphere and outer-sphere ternary surface complexes on hematite surfaces. *Environ. Sci. Technol.* 41, 3940–3944.
- Artinger, R., Rabung, T., Kim, J.I., Sachs, S., Schmeide, K., Heise, K.H., Bernhard, G., Nitsche, H., 2002. Humic colloid-borne migration of uranium in sand columns. *J. Contam. Hydrol.* 58, 1–12.
- Baes, C.F., Mesmer, R.E., 1976. *The Hydrolysis of Cations*. Wiley Interscience Publication, New York.
- Baston, G.M.N., Berry, J.A., Bond, K.A., Boulton, K.A., Brownsword, M., Linklater, C.M., 1994. Effects of cellulose degradation products on uranium sorption in the geosphere. *J. Alloys Compd.* 213, 475–480.
- Bertrand, P.A., Choppin, G.R., 1982. Separation of actinides in different oxidation states by solvent extraction. *Radiochim. Acta* 31, 135–137.
- Bethke, C.M., 2006. *The Geochemist's Workbench: Release 6.0.4*. University of Illinois, Urbana-Champaign.
- Boukhalfa, H., Reilly, S.D., Neu, M.P., 2007. Complexation of Pu(IV) with the natural siderophore desferrioxamine B and the redox properties of Pu(IV)(siderophore) complexes. *Inorg. Chem.* 46, 1018–1026.
- Cleveland, J.M., 1979. *The Chemistry of Plutonium*. American Nuclear Society, La Grange Park, Illinois.
- Czerwinski, K.R., Buckau, G., Scherbaum, F., Kim, J.I., 1994. Complexation of the uranyl-ion with aquatic humic-acid. *Radiochim. Acta* 65, 111–119.
- Czerwinski, K.R., Kim, J.I., Rhee, D.S., Buckau, G., 1996. Complexation of trivalent actinide ions (Am^{3+} , Cm^{3+}) with humic acid: the effect of ionic strength. *Radiochim. Acta* 72, 179–187.
- Department of Energy (DOE), 2000. *United States Nuclear Tests: July 1945 through September 1992*. DOE/NV-209 Rev. 15. US Department of Energy, Nevada Operations Office.
- Foti, S.C., Freiling, E.C., 1964. The determination of the oxidation states of tracer uranium, neptunium, and plutonium in aqueous media. *Talanta* 11, 385–392.
- Gee, G.W., Bauder, J.W., 1986. Particle-size analysis. In: Klute, A. (Ed.), *Methods of Soil Analysis: Part I – Physical and Mineralogical Methods*. American Society of Agronomy, Inc., Madison, Wisconsin, pp. 383–411.
- Guillaumont, R., Fanghanel, T., Neck, V., Fuger, J., Palmer, D.A., Grenthe, I., Rand, M.H., 2003. Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium, and Technetium, *Chemical Thermodynamics*, vol. 5. Elsevier, Amsterdam.
- Ho, C.H., Miller, N.H., 1985. Effect of humic-acid on uranium uptake by hematite particles. *J. Colloid Interface Sci.* 106, 281–288.
- Hu, Q.H., Zavarin, M., Rose, T.P., 2008. Effect of reducing groundwater on the retardation of redox-sensitive radionuclides. *Geochem. Trans.* 9, 12.
- Hummel, W., Anderegg, G., Puigdomenech, I., Rao, L., Tochiyama, O., 2005. *Chemical Thermodynamics of Compounds and Complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with Selected Organic Ligands*, *Chemical Thermodynamics*, vol. 9. Elsevier, Amsterdam.
- Jackson, B.P., Ranville, J.F., Bertsch, P.M., Sowder, A.G., 2005. Characterization of colloidal and humic-bound Ni and U in the “dissolved” fraction of contaminated sediment extracts. *Environ. Sci. Technol.* 39, 2478–2485.
- Jain, A., Rawat, N., Kumar, S., Tomar, B.S., Manchanda, V.K., Ramanathan, S., 2007. Effect of humic acid on sorption of neptunium on hematite colloids. *Radiochim. Acta* 95, 501–506.
- Keith-Roach, M., 2008. The speciation, stability, solubility and biodegradation of organic co-contaminant radionuclide complexes: a review. *Environ. Sci. Technol.* 39, 1–11.
- Kersting, A.B., Eford, D.W., Finnegan, D.L., Rokop, D.J., Smith, D.K., Thompson, J.L., 1999. Migration of plutonium in ground water at the Nevada Test Site. *Nature* 397, 56–59.
- Khasanova, A.B., Kalmykov, S.N., Perminova, I.V., Clark, S.B., 2007. Neptunium redox behavior and sorption onto goethite and hematite in the presence of humic acids with different hydroquinone content. *J. Alloys Compd.* 444, 491–494.
- Kobashi, A., Choppin, G.R., Morse, J.W., 1988. A study of techniques for separating plutonium in different oxidation-states. *Radiochim. Acta* 43, 211–215.
- Lenhart, J.J., Honeyman, B.D., 1999. Uranium(VI) sorption to hematite in the presence of humic acid. *Geochim. Cosmochim. Acta* 63, 2891–2901.
- Maes, N., Wang, L., Hicks, T., Bennett, D., Warwick, P., Hall, T., Walker, G., Dierckx, A., 2006. The role of natural organic matter in the migration behaviour of americium in the Boom Clay – Part I: Migration experiments. *Phys. Chem. Earth* 31, 541–547.
- Magner, J.E., 2006. Characteristics of zeolitized tuff samples, pers. comm. to M. Zavarin. United States Geological Survey, Mercury, Nevada.
- Marquardt, C., Kim, J.I., 1998a. Complexation of Np(V) with fulvic acid. *Radiochim. Acta* 81, 143–148.
- Marquardt, C., Kim, J.I., 1998b. Complexation of Np(V) with humic acid: Intercomparison of results from different laboratories. *Radiochim. Acta* 80, 129–137.
- McCarthy, J.F., Czerwinski, K.R., Sanford, W.E., Jardine, P.M., Marsh, J.D., 1998. Mobilization of transuranic radionuclides from disposal trenches by natural organic matter. *J. Contam. Hydrol.* 30, 49–77.
- Murphy, R.J., Lenhart, J.J., Honeyman, B.D., 1999. The sorption of thorium (IV) and uranium (VI) to hematite in the presence of natural organic matter. *Colloids Surfaces A* 157, 47–62.
- Nakayama, S., Nelson, D.M., 1988. Comparison of distribution coefficients for americium and curium – effects of pH and naturally-occurring colloids. *J. Environ. Radioact.* 8, 173–181.
- Nelson, D.M., Penrose, W.R., Karttunen, J.O., Mehlhoff, P., 1985. Effects of dissolved organic-carbon on the adsorption properties of plutonium in natural-waters. *Environ. Sci. Technol.* 19, 127–131.
- Neu, M., Hoffman, D.C., Roberts, K.E., Nitsche, H., Silva, R.J., 1994. Comparison of chemical extractions and laser photoacoustic spectroscopy for the determination on plutonium species in near-neutral carbonate solutions. *Radiochim. Acta* (66/67), 251–258.
- Niitsu, Y., Sato, S., Ohashi, H., Sakamoto, Y., Nagao, S., Ohnuki, T., Muraoka, S., 1997. Effects of humic acid on the sorption of neptunium(V) on kaolinite. *J. Nucl. Mater.* 248, 328–332.
- Nitsche, H., Lee, S.C., Gatti, R.C., 1988. Determination of plutonium oxidation states at trace levels pertinent to nuclear waste disposal. *J. Radioanal. Nucl. Chem.* 124, 171–185.
- Othman, M.Z., Roddick, F.A., Hobday, M.D., 2000. Evaluation of Victorian low rank coal-based adsorbents for the removal of organic compounds from aqueous systems. *Water Res.* 34, 4351–4358.
- Othman, M.Z., Roddick, F.A., Snow, R., 2001. Removal of dissolved organic compounds in fixed-bed columns: evaluation of low-rank coal adsorbents. *Water Res.* 35, 2943–2949.
- Panik, P., Klenze, R., Kim, J.I., 1996. A study of ternary complexes of Cm(III) with humic acid and hydroxide or carbonate in neutral pH range by time-resolved laser fluorescence spectroscopy. *Radiochim. Acta* 74, 141–146.
- Ranville, J.F., Hendry, M.J., Reszat, T.N., Xie, Q.L., Honeyman, B.D., 2007. Quantifying uranium complexation by groundwater dissolved organic carbon using asymmetrical flow field-flow fractionation. *J. Contam. Hydrol.* 91, 233–246.
- Reiller, P., Moulin, V., Casanova, F., Dautel, C., 2002. Retention behaviour of humic substances onto mineral surfaces and consequences upon thorium (IV) mobility: case of iron oxides. *Appl. Geochem.* 17, 1551–1562.
- Reiller, P., Moulin, V., Casanova, F., Dautel, C., 2003. On the study of Th(IV)–humic acid interactions by competition sorption studies with silica and determination of global interaction constants. *Radiochim. Acta* 91, 513–524.
- Righetto, L., Bidoglio, G., Azimonti, G., Bellobono, I.R., 1991. Competitive actinide interactions in colloidal humic-acid mineral oxide systems. *Environ. Sci. Technol.* 25, 1913–1919.
- Roden, E.E., Scheibe, T.D., 2005. Conceptual and numerical model of uranium(VI) reductive immobilization in fractured subsurface sediments. *Chemosphere* 59, 617–628.
- Ruggiero, C.E., Matonic, J.H., Reilly, S.D., Neu, M.P., 2002. Dissolution of plutonium(IV) hydroxide by desferrioxamine siderophores and simple organic chelators. *Inorg. Chem.* 41, 3593–3595.
- Sanchez, A.L., 1983. *Chemical Speciation and Adsorption Behavior of Plutonium in Natural Waters*, PhD Thesis. University of Washington, Seattle, Washington.

- Schmeide, K., Bernhard, G., 2009. Redox stability of neptunium(V) and neptunium(IV) in the presence of humic substances of varying functionality. *Radiochim. Acta* 97, 603–611.
- Schulthess, C.P., Huang, C.P., 1991. Humic and fulvic-acid adsorption by silicon and aluminum-oxide surfaces on clay-minerals. *Soil Sci. Soc. Am. J.* 55, 34–42.
- Shcherbina, N.S., Kalmykov, S.N., Perminova, I.V., Konalenko, A.N., 2007. Reduction of actinides in higher oxidation states by hydroquinone-enriched derivatives. *J. Alloys Compd.* 444, 518.
- Skipperud, L., Oughton, D., Salbu, B., 2000. The impact of Pu speciation on distribution coefficients in Mayak soil. *Sci. Total Environ.* 257, 81–93.
- Smith, D.K., Finnegan, D.L., Bowen, S.M., 2003. An inventory of long-lived radionuclides residual from underground nuclear testing and the Nevada Test Site, 1951–1992. *J. Environ. Radioact.* 67, 35–51.
- Stoller-Navarro Joint Venture, 2007. *Geochem07.mdb and A User's Guide to the Comprehensive Water Quality Database for Groundwater in the Vicinity of the Nevada Test Site. S-N/99205-059-Rev.2*. Las Vegas, Nevada.
- Zavarin, M., Roberts, S.K., Hakem, N., Sawvel, A.M., Kersting, A.B., 2005. Eu(III), Sm(III), Np(V), Pu(V), and Pu(IV) sorption to calcite. *Radiochim. Acta* 93, 93–102.