Experimental Evidence for Ternary Colloid-facilitated Transport of Th(IV) with Hematite (α -Fe₂O₃) Colloids and Suwannee River Fulvic Acid

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ABSTRACT

Previous field experiments have suggested colloid-facilitated transport via inorganic and organic colloids as the primary mechanism of enhanced actinide transport in the subsurface at former nuclear weapons facilities. In this work, research was guided by the hypothesis that humic substances can enhance tetravalent actinide (An(IV)) migration by coating and mobilizing natural colloids in environmental systems and increasing An(IV) sorption to colloids. This mechanism is expected to occur under relatively acidic conditions where organic matter can sorb and coat colloid surfaces and facilitate formation of ternary colloid-ligand-actinide complexes. The objective of this work was to examine Th transport through packed columns in the presence of hematite colloids and/or Suwannee River fulvic acid (SRFA). In the presence of SRFA, with or without hematite colloids, significant transport (>60% recovery within the effluent) of thorium occurred through quartz columns. It is notable that the SRFA contributed to increased transport of both Th and hematite colloids, while insignificant transport occurred in the absence of fulvic acid. Further, in the presence of a natural sandy sediment (as opposed to pure quartz), transport is negligible in the presence of SRFA due to interactions with natural, clay-sized sediment coatings. Moreover, this data shows that the transport of Th through quartz columns is enhanced in ternary Th-colloid-SRFA and binary Th-SRFA systems as compared to a system containing only Th.

KEYWORDS

Tetravalent actinide, colloids, hematite, fulvic acid, thorium

ABBREVIATIONS

SRFA – Suwannee River fulvic acid

1.0 INTRODUCTION

Colloid-facilitated transport of the actinide elements is an important topic of research with respect to risk assessment modeling for future deep geologic disposal of nuclear waste and to cleanup and containment efforts. Because of the actinides' nearly irreversible association with minerals, rock and sediment phases; mobile colloid-facilitated transport represents one of few vectors for significant transport. Further, environmental systems commonly have both organic and inorganic colloids present as previous researchers have concluded that colloids are ubiquitous in groundwater systems (Degueldre et al., 1996; McCarthy and Degueldre, 1993). Moreover, organic carbon is also ever-present and have been previously measured in a range of 0.1 – 200 mg/L in natural systems (Buddemeier and Hunt, 1988; Degueldre et al., 1996; Kersting, 2013; McCarthy and Degueldre, 1993; Moulin and Ouzounian, 1992; Roberts et al., 2004; Vilks et al., 1988).

Research first suggested colloids, made up of mobile inorganic minerals or organic matter, as a mechanism for actinide transport in the 1980's and early 1990's. Early researchers suggested that the movement of the actinides in groundwater systems may be due to attachment to mobile colloids (Wahlgren and Orlandini, 1982; Nyhan et al., 1985). For example, Nyhan *et al.* observed that plutonium (Pu) and americium (Am) was mobilized from aqueous defense waste disposal trenches in Bandelier tuff in Los Alamos, NM with up to 5.1% of the Pu migrating outside of the beds. They included colloidal transport as one of several possible mobilization mechanisms but did not investigate further.

In response to suggestions that enhanced transport of the actinides may be due to association with mobile colloids, field assessments were conducted at several different sites. Nelson *et al.*

(1985) first determined that Pu was strongly associated with colloidal organic carbon in natural water samples from a pond near Argonne and Lake Michigan. His work was a response to conjecture by Wahlgren and Orlandini that binding of Pu with colloidal organic carbon may represent a controlling mechanism in sorption of Pu to sediments (Wahlgren and Orlandini, 1982; Nelson et al., 1985). Moreover, Short *et al.* (1988) identified uranium (U) and thorium (Th) leached from a natural ore in the Alligator River in Australia in association with iron and silica colloids with up to 11% of U and 47% of Th associated with colloids. The authors concluded that colloidal transport could be significant for Th(IV) but not U(VI), i.e. transport is more significant for the reduced oxidation states of the actinides.

Further research has shown that the majority of the mobile, aqueous fraction of the actinides is associated with the colloidal or particulate size fraction based on filtration. Field measurements have observed the following fractions of the actinides in reduced (III and IV) oxidation states in association with the colloidal or particulate size fraction: 79% to greater than 99% of Pu (Penrose et al., 1990; Kersting et al., 1999; Novikov et al., 2006; Kersting, 2012, 2013), up to 60% of Am (Penrose et al., 1990; Santschi et al., 2002) and up to 47% of Th (Short et al., 1988). These studies have further suggested the association of the trivalent and tetravalent actinides with zeolites and clays (Kersting, 2012, 2013; Kersting et al., 1999), iron oxides and hydroxides (Short et al., 1988; Novikov et al., 2006), or organic colloids (Nelson et al., 1985; Santschi et al., 2002). Moreover, additional field studies have suggested hybrid organic/inorganic colloids (ternary complexes) forming with both trace contaminants and inorganic and organic colloids (Davis, 1982; Bouby et al., 2002; Novikov et al., 2006).

In addition to field measurements demonstrating the association of actinides with naturally occurring colloids in environmental systems, researchers have shown that kilometer scale

transport of Pu has occurred in the presence of colloids. Transport of up to 3.8 km was observed based on isotope ratios and migration distances from the release or disposal locations at Mortandad Canyon near Los Alamos National Laboratory, the Nevada National Security Site and the Mayak Production Association in Russia (Penrose et al., 1990; Kersting et al., 1999; Novikov et al., 2006). Notably, preliminary models of these field sites could not predict the transport distances observed and transport was under predicted by as much as 1200 times (Nyhan et al., 1985; Penrose et al., 1990; Ryan and Elimelech, 1996). In response to the lack of understanding of these systems, multiple review papers have called attention to the importance of colloids as a transport vector for the strongly sorbing, reduced oxidation states of the actinides and suggested a need for a better description of the mechanisms leading to enhanced transport (McCarthy and Zachara, 1989; Ryan and Elimelech, 1996; Kersting, 2012; Kersting, 2013; Zanker and Hennig, 2014). Therefore, colloid facilitated transport of the actinides must be systematically investigated to develop more realistic transport and risk assessment models.

To further understand actinide transport in complex environmental systems with sediments as well as organic and inorganic colloids; laboratory work on simpler systems must first be considered. The majority of the experiments completed to date have investigated sorption to simple binary systems (mineral or organic + actinide). These experiments have proven that sorption is strong for Pu and Th and that the tetravalent oxidation state dominates in the presence of natural soils and sediments (Duff et al., 1999; Kaplan et al., 2004; Powell et al., 2006; Kaplan et al., 2007; Hixon et al., 2010; Melson et al., 2012), minerals (Keeney-Kennicutt and Morse, 1985; Hunter et al., 1988; Lu et al., 2003; Powell et al., 2004, 2005; Zavarin et al., 2012; Begg et al., 2013; Hixon et al., 2013), and organic colloids (Murphy et al., 1999; Artinger et al., 2002; Santschi et al., 2002; Artinger et al., 2003; Marquardt et al., 2004; Blinova et al., 2007;

Shcherbina et al., 2007; Reiller et al., 2008; Roberts et al., 2008; Xu et al., 2008). Further, the field experiments discussed previously highlight tetravalent actinides as most likely to be associated with colloids due to their strong sorption and low solubility. Emphasis in this work is placed on iron oxide minerals and organic colloids due to their particularly strong complexation affinity for the tetravalent actinides and abundance in the natural environment which may lead to a greater likelihood for enhanced transport if present as mobile colloids.

Laboratory batch experiments investigating Th sorption to hematite (Fe_2O_3) systems (Cromieres et al., 1998; Melson et al., 2012) have shown that interactions are strong with a sorption edge near pH 3. Pu exhibits similarly strong sorption to iron oxide minerals and the tetravalent oxidation state dominates at equilibrium due to surface mediated reduction (Sanchez et al., 1985; Keeney-Kennicutt and Morse, 1985; Lu et al., 1998; Lu et al., 2003; Powell et al., 2004, 2005; Hixon et al., 2010; Romanchuk et al., 2011; Hixon and Powell, 2014). Powell *et al.* (2005) reported greater than 99% of Pu sorbed at equilibrium at pH 8 for hematite and goethite minerals.

Moreover, Lu *et al.* observed <1% desorption of Pu from hematite colloids after 150 and 293 days leading to the conclusion that there is a strong irreversibly sorbed fraction of Pu (Lu et al., 1998; Lu et al., 2003). Irreversible sorption was claimed based on the observation that desorption of Pu did not reach the expected equilibrium conditions based on the forward reaction after long periods (Lu et al., 1998; Lu et al., 2003). Due to the strong sorption of tetravalent actinides, desorption may be both small and kinetically hindered. Tinnacher *et al.* (2011) and Wong *et al.* (2015) discuss several mechanisms by which actinides may age on a surface and alter the desorption behavior. This could occur through truly irreversible sorption, hysteretic sorption, or aging via reversible transition between two surface species (i.e. transition from a weaker to a

more strongly sorbing species or a stronger sorption site). The exact mechanisms controlling this behavior are not fully understood and are the subject of ongoing work. However, in the case of strong sorption of Th to mobile iron oxide colloids, it could lead to a significant increase in transport.

The tetravalent actinides also sorb strongly to organic humic substances with an increase in sorption with increasing pH. Therefore, it is necessary to examine previous experiments investigating sorption of actinides to binary systems in the presence of only organic matter and actinides. Zimmerman *et al.* (2014) reported > 50% sorption of Pu and Th for pH 4.0 – 7. Further, Th(IV) and Pu(IV) have been shown to complex similarly in the presence of humic substances. However, Zimmerman *et al.* (2014) measured only slightly greater sorption for Th than Pu after 10 days in batch experiments with 10 mg_C/L as humic acid. Further, complexation constants have been measured to be up to three orders of magnitude greater for Pu(IV) as compared to Th(IV) as measured in 0.1 M NaCl and 10 mg_C/L of humic acid for pH 4-7 (Artinger et al., 2003; Zimmerman et al., 2014). It is clear that the interactions between tetravalent actinides and humic substances are very strong and are likely formed through carboxylate groups (Schild and Marquardt, 2000; Geckeis et al., 2002; Reiller et al., 2003; Sachs et al., 2005; Choppin, 2007; Reiller et al., 2008). For further discussion, Reiller *et al.* (2008) presents a review of previous work investigating tetravalent actinide sorption to humic substances.

Previous work has shown that humic substances have a significant impact on sorption and transport of inorganic mineral colloids (Davis and Leckie, 1978; Tipping, 1982; Kretzschmar and Sticher, 1997; Schrick et al., 2004 Baalousha et al., 2008; Baalousha, 2009) with particularly strong interactions for iron oxides. Specifically, humic substances may lead to mobilization of

iron oxide colloids through coating via sorption (Seijo et al., 2009) and by controlling the electrophoretic mobility of the colloids (Tipping, 1982). Yang *et al.* (2013) showed that hydrous ferric oxide interacted with humic acids by electrostatic interactions and association with aliphatic/aromatic carbon and inner-sphere complexation with carboxyl groups, while colloidal SiO₂ and ZnO interactions were only by relatively weak interactions like van der Waals or hydrogen bonding. It is possible that strong sorption of humic acids to iron oxides may hinder sorption of the actinides to iron oxide colloids through loss of available sorption sites to the humic acid. Because humic substances may increase the mobility and exhibit strong complexation of inorganic colloids and actinides, it is also important that researchers investigate systems including actinides, organic humic substances and inorganic colloids (ternary systems).

Researchers have shown that ternary systems with humic substances can have a significant impact on sorption and transport of actinides and inorganic minerals and colloids (Davis and Leckie, 1978; Tipping, 1982; Kretzschmar and Sticher, 1997; Murphy et al., 1999; Takahashi et al., 1999; Takahashi et al., 2002; Reiller et al., 2002; Reiller et al., 2003; Schrick et al., 2004; Baalousha et al., 2008; Reiller et al., 2008; Baalousha, 2009; Bryan et al., 2012). For example, work with trivalent actinides and lanthanides reported that in the presence of humic substances, the dissolved species are controlled by humic substances from pH 4.0 – 8.0 and exist as primarily humic species. However, the species complexed with humic substances also constituted a significant fraction of the species sorbed to inorganic particulates with increased sorption in the acidic pH range (Takahashi et al., 1999; Takahashi et al., 2002; Bryan et al., 2012). Bryan *et al.* (2012) concluded that as the importance of the ternary complex increases, the metal cations will behave more like the humic substance itself. Tetravalent actinides exhibit similar behavior to trivalent metals.

Laboratory batch experiments have considered tetravalent actinide sorption in ternary systems with mineral and citrate, mineral and phosphate, and mineral and humic substances (Murphy et al., 1999; Reiller et al., 2002, 2003; Banik et al., 2007; Tanaka et al., 2009; Zimmerman et al., 2014). In ternary systems with the presence of humic substances and minerals, actinide sorption to minerals is increased at low pH and decreased at high pH with respect to binary actinide-mineral systems (Banik et al., 2007; Murphy et al., 1999; Reiller et al., 2002, 2003; Righetto et al., 1991; Zimmerman et al., 2014). For example, at pH <4 the sorption of Th to hematite is significantly increased with 11 mg/L humic acid and decreased with respect to the absence of humic acid (Reiller et al., 2002). Therefore, ternary complex formation is most likely under slightly acidic conditions as suggested previously by Righetto *et al.* (1991) for alumina and humic acid. The Pu – humic acid – alumina system at 50 mg/L humic acid and 200 mg/L alumina exhibited significant sorption (>80 %) across the pH range investigated (pH 6 – 10) as compared to >80% sorption of Pu to alumina in a humic acid – free system only above pH 8 (Righetto et al., 1991). However, the specific ternary complexes forming in these systems have not yet been identified and experiments investigating the transport capabilities have only recently begun.

Column experiments are needed to investigate the specific conditions that may lead to enhanced mobilization for ternary systems under relevant field conditions with both mineral colloids and humic substances (Begg et al., 2013; Zanker and Hennig, 2014). There is a possibility for the formation of two different types of ternary complexes, including: 1) humic molecules acting as a bridge between a metal ion and mineral/colloid surface or 2) the metal ion acting as a bridge between humic molecules and mineral/colloid surface (Bryan et al., 2012). However, recently published laboratory studies have examined colloid-facilitated transport of

actinides in the presence of only inorganic colloids. For example, Xie *et al.* (2013, 2014) conducted colloid-facilitated transport experiments of Pu with natural colloids isolated from a Sandy soil in Lop Nor at variable colloid concentration (0-2000 mg/L), ionic strength (0.01-0.96 mol/L NaCl) and flow rate (0.472-4.56 mL/min) (Xie et al., 2013; Xie et al., 2014). The optimum colloid concentration for colloid facilitated transport of Pu was 375 mg/L with greater than 50% of Pu within the mobile colloid fraction (Xie et al., 2013). Although this work significantly increases our understanding of colloidal transport of Pu on inorganic colloids, it does not include any investigation of the transport capabilities of ternary complexes. Experiments are still needed to investigate transport in ternary systems with inorganic colloids, humic substances and tetravalent actinides.

This work examines the transport of strongly sorbing Th in the presence of hematite colloids and Suwannee River fulvic acid (SRFA) through columns packed with quartz and natural sediments. The tetravalent oxidation state is the focus because it is expected to be the dominant state for Pu and Th in natural systems (Choppin, 2007) and to be the oxidation state for U and Np in deep groundwaters exhibiting reducing conditions (Degueldre et al., 1996; Kim and Grambow, 1999). Further, the tetravalent oxidation state of the actinides' unique chemical properties including their low solubility and strong sorption affinity to mineral surfaces and organics creates conditions that are particularly susceptible to colloidal transport in subsurface systems (Choppin, 2007; Geckeis et al., 2013). Moreover, Th is used as an oxidation state analog for tetravalent actinides; because it is a stable oxidation state for the investigation of tetravalent actinides and because Pu, Np, and U often exist in multiple oxidation states in environmental systems (Kraskopf, 1984; Choppin, 1999, 2007).

The experimental design was guided by the hypothesis that humic substances can enhance An(IV) migration by coating and stabilizing colloids and enhancing sorption to mobile colloids. This mechanism is expected to dominate under acidic pH conditions where organic matter can adsorb and coat colloid surfaces and facilitate formation of ternary colloid-ligand-actinide complexes. Several previous studies have demonstrated that 1) humic substances can potentially enhance tetravalent actinide sorption to mineral surfaces and 2) humic substances can stabilize mineral colloids by coating the surfaces and minimizing aggregation. This work combines both of these processes and investigates the enhanced transport of tetravalent actinides in the presence of both fulvic acid and hematite colloids. It is likely that the ternary system transport is a manifestation of the stabilization of the inorganic (hematite) colloids by the fulvic acid coatings and the formation of mobile ternary colloid-ligand-actinide complexes.

Hematite colloids were chosen as a model particle to describe previous field measurements suggesting iron oxide colloids as a transport vector and due to its natural abundance in environmental systems. Fulvic acid was chosen as it is a significantly smaller size range and fraction of natural organic material that could be separated from the larger hematite nanoparticles by filtration. The objective is to systematically compare transport of tetravalent actinides in ternary systems (actinide + hematite + fulvic acid) to transport of systems with combinations of these components building to the ternary system. In this manner, laboratory-scale experiments investigate the following systems: dissolved actinide ion, precipitated intrinsic actinide colloid, binary systems including iron oxide colloids or fulvic acid, and the ternary system (hematite + fulvic acid + Th).

2.0 MATERIALS AND METHODS

2.1 Materials

Hematite colloids were synthesized with a low concentration Fe(III) (1.25×10^{-3} M) from $\text{Fe}(\text{NO}_3)_3$ at a temperature of 100°C to create a small, homogenous size fraction (Wang et al., 2008). A fraction of the particles were labeled with ^{55}Fe by adding an aliquot of $^{55}\text{Fe}(\text{NO}_3)_3$ during synthesis. Characterization of the particles by HRTEM (Hitachi 9500) as well as particle size and zeta potential (Brookhaven 90Plus) is summarized in Table S1 and Figure S1 in the

2.2 Batch experiments

2.2.1 Hematite and SRFA Systems

Preliminary batch experiments examining the sorption of SRFA to hematite colloids and the particle size/zeta potential of bare and SRFA-associated hematite colloids as a function of pH were used to identify the optimum conditions for transport of hematite colloid suspensions. Particle size and zeta potential measurements (Brookhaven 90Plus) were taken at variable ionic strength ($0.01 - 0.0001$ M NaClO_4) and pH ($3 - 9$) for 0.03 g/L (1.9×10^{-4} M) hematite colloid suspensions in the presence and absence of 25 mg_C/L SRFA. Additional experiments in 0.01 and 0.001 M NaCl yielded similar results (not shown).

Further experiments utilized ^3H – SRFA to investigate sorption of 5 mg_C/L SRFA (6700 Bq/mL, ^3H) to 0.03 g/L hematite colloid at pH $4.1 - 5.9$ over a three day period followed by desorption over a five day period (Figure 1). The fraction of SRFA sorbed to the hematite colloids was measured based on filtration through 10kDa molecular weight cut-off filters (MWCO, Pall Nanosep) which removed the hematite and any bound SRFA but allowed soluble SRFA to pass through the membrane. The SRFA concentration in the filtrate was measured via ^3H by liquid scintillation counting (LSC) in Optiphase HiSafe III Cocktail (Perkin Elmer) with a minimum detectable concentration (MDC) of 5.6 Bq/mL or 0.02 mg_C/L (LSC, Hidex SL300). The detection limits are significantly higher for these experiments due to a greater dilution for measurements. Error bars are calculated based on counting statistics. Following the three day

sorption period, hematite colloids were washed with pH adjusted ultrapure water and resuspended. A ThermoScientific Orion DualStar pH/ISE meter and 81033BN ThermoScientific micro combination electrode were used after a three point calibration prior to each measurement period. Desorption samples were analyzed following filtration as described above at 20 minutes, 1 hour, 6 hours, 24 hours, and 5 days (118 hours).

2.2.2 Quartz – Hematite – SRFA – Thorium Systems

Batch sorption experiments were conducted at 200 $\mu\text{g/L}$ (8.6×10^{-7} M) ^{232}Th in quadruplicate at 50 g/L (0.54 M) quartz, 45 mg hematite/L (2.8×10^{-4} M), 25 mg/L SRFA and 0.001 M NaCl at pH 5.5 in 50 mL polypropylene tubes (VWR). Three sample sets were prepared in the presence of ^{232}Th including: 1) Quartz + SRFA, 2) Quartz + hematite, and 3) Quartz + hematite + SRFA. It must be noted that these suspensions were prepared with a specific order of addition to minimize the likelihood of Th precipitation. Reiller *et al.* reported that there is no influence of addition order on sorption in the presence of humic acid (HA) until the ratio of HA:SOH is greater than 30 based on measurements of proton exchange capacity (Reiller et al., 2005). However, these experiments included a pre-equilibration period prior to introduction of the final component. The addition of components proceeded in the following order and were completed within 30 minutes: (1) Quartz, (2) hematite, (3) SRFA, then (4) ^{232}Th . Both hematite and SRFA suspensions were pH adjusted prior to addition. The ^{232}Th stock solution was not pH adjusted prior to addition (stored in 2% HNO_3) as only a small aliquot (~ 20 μL) was added and there were concerns over precipitation and sorption to vial walls in the stock suspension at elevated pH. Final stock suspensions were re-adjusted to ~ 5.5 after addition of each of the components. The aqueous phase was removed for analysis on days 1, 6 and 12 and subject to a centrifugation step for quartz or filtration step for hematite. The centrifugation step included centrifugation at

46,250 rcf for 20 min (Beckman Coulter Allegra 22XR, F2402 rotor). This is calculated to remove particles <100 nm by Stokes law as described by Jackson (1985). The filtration step utilized 10 kDa MWCO filters and is assumed to retain all hematite colloids and associated Th. The MDC using ICP-MS is 0.6 ppb (2.6×10^{-9} M) ^{232}Th and 80 ppb (1.4×10^{-6} M) ^{56}Fe under these sampling conditions. Sorption coefficients (K_d) are calculated based on equations presented in the *Supplementary Materials*.

2.3 Column experiments

2.3.1 Hematite – SRFA Systems

Laboratory-scale, saturated column experiments were conducted at a flow rate of 1 mL/min (~6.5 minute residence time) or 0.1 mL/min (~65 minute residence time) using a peristaltic pump (Masterflex, model 7720-60) and Tygon tubing (Masterflex, size 16) attached to columns (polycarbonate columns, 8.5 cm length x 1.5 cm ID; pore volume ~6.3 mL) packed with either high purity quartz or Savannah River Site surface sandy sediment. The columns received the following influent treatments: (1) Conditioning with at least 100 pore volumes of 0.001 M NaCl at pH 5.5, (2) Amendment with approximately one pore volume of spike solutions, (3) Flushing with at least 38 pore volumes of 0.001 M NaCl at pH 5.5. The effluent was collected into a fraction collector (Eldex) in 2 mL aliquots for the first 4-5 pore volumes followed by collection of 6 mL aliquots for the remainder of the experiments.

Seven column experiments were designed to investigate the transport of tetravalent actinides in the presence and absence of hematite colloids and SRFA (major characteristics of spike solutions in Table 1 and TEM imaging in *Supplementary Materials* Figure S4-S5). Five of these seven columns were packed with quartz to investigate the transport of Th at pH 5.5 in 0.001 M NaCl and 1 mL/min flow rate with the following spike solutions: (1) dissolved Th, (2)

precipitated Th, (3) Hematite + Th, (4) SRFA + Th, and (5) Hematite + SRFA + Th. The sixth column was subjected to the same conditions as column five with the exception of a lower flow rate of 0.1 mL/min. The final column compares the ternary complex conditions in quartz with a natural SRS sandy sediment at 1 mL/min flow rate. In this manner, the different column experiments investigate all possible combinations of colloidal transport of Th in a system with fulvic acid and hematite colloids. The specifics for the column experiments are further described in Table 1.

Each spike solution also contained a nonreactive tracer (rhenium at 5 µg/L or ^3H at 2500 Bq/mL). Although Re is not commonly used as a tracer, previous work has shown that perhennate (ReO_4^-) does not react with inorganic minerals (montmorillonite) and humic substances (Takahashi et al., 1999). Further, a compilation of conservative tracers for all columns is included in the *Supplementary Materials* Figure S6 for comparison and shows similar results for both Re and ^3H tracers. It should be noted that the order of addition in these spike suspensions was the same as in batch sorption experiments (Hematite + SRFA + ^{232}Th). Due to the relatively high concentrations of stable ^{56}Fe in the SRS sediment column, experiments were completed with colloids labeled with ^{55}Fe to distinguish native Fe from sediments and hematite colloids. A total iron detection limit based on ^{55}Fe via LSC was 13 ppb compared with 80 ppb using ICP-MS for determination of ^{56}Fe . Initial spike concentrations were determined based on LSC or ICP-MS where appropriate. However, ^3H -labeled SRFA was not used in this experiment as it could not be effectively differentiated from ^{55}Fe by LSC. Therefore, recovery of SRFA in the SRS sediment column was not tracked. Transmission electron microscopy (Hitachi 9500 TEM and HD2000 STEM) was also completed on the initial spike solutions by air-drying 10 µL

322 of the spike solutions (Table 1) onto a Formvar coated or lacey carbon grids (Ted Pelco) with
323 storage in a low humidity chamber prior to analysis.

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Table 1: Initial spike chemical characteristics

Spike ID ^a	Flow Rate, mL/min	Hematite, g/L [mol/L]	Th, ppb [mol/L]	Th Isotope	SRFA, mg _C /L [³ H, Bq/mL]	Zeta Potential, mV ^d	Diameter, nm	% of Spike as Dissolved Th ^e
²³⁰ Th	0.94±0.17	0	0.72 ^c [3.1x10 ⁻⁹]	²³⁰ Th	0	NM	NM	85%
²³² Th	0.98±0.07	0	10 [4.3x10 ⁻⁸]	²³² Th	0	NM	NM	15%
Hematite-Th	0.97±0.14	0.1 [6.25x10 ⁻⁴]	289 [1.3x10 ⁻⁶]	²³² Th	0	23±4	152±1	<1%
SRFA-Th	0.94±0.02	0	274 [1.2x10 ⁻⁶]	²³² Th	25 [250]	NM	NM	NM
Hematite-SRFA-Th	1.02±0.01	0.04 [2.5x10 ⁻⁴]	147 [6.3x10 ⁻⁷]	²³² Th	25 [32.6]	-52±12	176±4	24.8%
Hematite-SRFA-Th	0.11±0.014	0.1 [6.25x10 ⁻⁴]	311 [1.3x10 ⁻⁶]	²³² Th	25 [64.6]	-52±9	98±6	16.1%
SRS Sandy - Hematite-Th-SRFA	1.01±0.02	0.05 ^b [3.1x10 ⁻⁴]	238 [1.0x10 ⁻⁶]	²³² Th	25	-41±2	350±38	15.3%

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327 ^aAll columns except for the last column were run in columns packed with high purity quartz, the final column is packed with SRS

328 sandy sediment

329 ^bConcentration of ⁵⁵Fe of 2250 Bq/mL330 ^cConcentration of ²³⁰Th of 0.55 Bq/mL331 ^dMeasured at the pH of the experiments (~ 5.5)332 ^eRepresents the percent dissolved based on filtration through a 10 MWCO filter

Effluent collection included analysis of ^{187}Re , ^{56}Fe and ^{232}Th via ICP-MS and ^3H , ^{55}Fe , and ^{230}Th using LSC (with an MDC of 0.02 Bq/mL for ^{230}Th , an alpha emitting radionuclide, and 0.6 Bq/mL for ^{55}Fe and ^3H , beta emitting radionuclides). In addition, samples with a sufficient concentration and remaining volume were analyzed for the dissolved fraction by measurement of the filtrate passed through 10kDa MWCO filter (Pall Gelman Microsep). Additional analysis of particle size and zeta potential (Brookhaven 90Plus) were also completed on samples with sufficient volume and concentration. It is noteworthy that previous experiments showed that > 90% of dissolved Pu(IV) passed through the 10kDa MWCO filters in the presence of 5 mgC/L SRFA at pH 5, 7 and 9 (*Supplementary Materials*, Table S3) (Simpkins, 2011). Moreover, all An(IV) that passes through filters is likely associated with SRFA due to the low solubility of An(IV) in the absence of SRFA.

Following collection of the column effluent, columns were sectioned into 1 cm slices and leached in 8 M HNO_3 for two weeks to leach Fe and Th from the solid phase and then measured on either ICP-MS or LSC as discussed above. Samples from the 8 M HNO_3 leach step were prepared for LSC in Ultima Gold AB (Perkin Elmer) cocktail following a centrifuge step as described above. Error bars for elements analyzed by ICP-MS are based on triplicate measurements and by LSC are based on counting statistics. Retardation factors were calculated for effluent breakthrough of each component based on equations presented previously (Clark, 1996; Powell et al., 2014) and outlined in the *Supplementary Materials*.

3.0 RESULTS

3.1 Batch Experiments

3.1.1 Hematite – SRFA Systems

Preliminary batch work investigated the ability of SRFA to stabilize and adsorb to hematite colloids in suspension as well as the stability of hematite colloids themselves (*Supplementary Materials*, Figures S7-S10, Figure 1-2). The colloid stability experiments presented in *Supplementary Materials*, Figure S7 show that minimal aggregation occurs with the SRFA at 25 mg_C/L across the pH range (3-9) investigated. Furthermore, presence of SRFA causes the zeta potential of the hematite – SRFA suspensions to remain negative in the range of -25 – -35 mV without considerable variation with regard to ionic strength (*Supplementary Materials*, Figures S9). In this respect, the SRFA controls the surface charge of the hematite in agreement with previous work (Davis, 1982; Tipping, 1982; Righetto et al., 1991).

Figure 1: Batch sorption (3 days, *open symbols*, right y-axis) followed by desorption (*closed symbols*, left y-axis) of 4.5 mg_C/L ³H-SRFA to 0.03 g/L hematite at pH 4.1 (*diamonds*), 5.2 (*triangles*) and 5.9 (*squares*) measured via removal of ³H associated with SRFA from the aqueous phase, error bars based on counting statistics are within the size of the symbols.

However, without the presence of the SRFA ligand, hematite particle size increases (*Supplementary Materials*, Figure S8) with ionic strength and pH towards the point of zero charge near pH 7-8 (Kosmulski, 2002, 2011) and particles are no longer stable in suspension by pH 6.0. This was confirmed by visible aggregation in the samples. In addition, the hematite zeta potential is positive under acidic conditions and decreases with increasing pH across the range investigated. Near the point of zero charge of hematite the zeta potential in the absence of SRFA reach zero and enter the negative range indicating that the surface of the colloids transitions from a net positive to a net negative charge (*Supplementary Materials*, Figure S10).

At the pH and ionic strength chosen for the column experiments presented below (pH 5.5 and ionic strength of 0.001 M NaCl, respectively), the hematite colloids in the absence of SRFA had a positive zeta potential and exhibited some aggregation in suspension. However, they were stable in suspension over the length of the experiments based on particle size measurements taken before and after the duration of the experiments in the range of 150-200 nm. Because the quartz is expected to exhibit a negative surface charge at pH 5.5, the positively charged hematite colloids in the absence of SRFA may be attracted to the quartz. The hematite colloids in the presence of SRFA are expected to exhibit minimal aggregation and a negative zeta potential based on the data presented in the *Supplementary Materials* Figure S7. These parameters were chosen for the column transport experiments presented below to exhibit ideal conditions for colloid-facilitated transport with parameters that are still relevant to natural systems.

A hypothesis of this work is that SRFA may enhance colloid-facilitated transport of Th by increasing the mobility of Th-bearing hematite colloids. However, in order for this to be the case, the SRFA must remain adsorbed to the hematite colloids, thereby reducing the likelihood of (1) desorption of Th and (2) aggregation of the hematite colloid suspension due to its negative

zeta potential. Therefore, batch sorption and desorption of SRFA to hematite colloids was monitored to ensure that the SRFA would remain sorbed to the hematite colloid surfaces over the experimental timeframe of this work. Batch sorption and desorption experiments investigating ^3H -SRFA sorption to 0.03 g/L hematite (Figure 1, methods described in 2.2.1) in the presence of 4.5 mg_C/L SRFA show that approximately 54% of the SRFA was sorbed to the hematite colloids within three days (based on filtration through 10kDa MWCO filters) and minimal desorption (< 6%) occurred over ~100 hours. Therefore, minimal desorption of SRFA is expected to occur over the timescale of the column experiments presented below as they are all less than 100 hours in length. It is expected that the hematite will be coated with a layer of SRFA as previously theorized by Seijo *et al.* (2009) using Brownian dynamics simulations for low ionic strength systems. The fulvic acid adsorption to hematite is expected to be limited by electrostatic repulsion at the surface leading to formation of a monolayer at low ionic strength. This is consistent with the negative zeta potentials of SRFA-coated hematite relative to uncoated hematite as shown in Figures S9 and S10 in the *Supplementary Materials*. Further, sorption of SRFA to quartz sand is not expected to outcompete sorption to hematite due to the weak adsorption of humic substances to quartz (Righetto et al., 1991) and the negative surface charge of quartz at pH 5.5 (Kosmulski, 2002; 2011).

3.1.2 Quartz – Hematite – SRFA – Thorium Batch Systems

Batch sorption experiments for ^{232}Th sorption to quartz and hematite colloids at pH 5.5 in 0.001 M NaCl show that sorption was reduced by at least one order of magnitude in the presence of 25 mg_C/L SRFA relative to SRFA-free systems (Figure 2). The greatest reduction was observed with the hematite colloids as equilibrium K_d values differed by approximately two orders of magnitude at equilibrium. At equilibrium (12 days) the average K_d based on triplicate

measurements for ^{232}Th sorption to hematite and quartz without SRFA was 27200 and 620 L/kg, respectively. However, in the presence of SRFA, those K_d values dropped at least an order of magnitude to 230 and 22 L/kg at equilibrium (12 days), respectively (K_d calculations in *Supplementary Materials*). It must be noted that the aqueous Th concentrations measured by ICP-MS were below the MDC for the hematite-Th system. Therefore, while these values appear to decrease with time, they cannot be differentiated as they are all below analytical detection limits.

In previous work, we have extensively characterized tetravalent actinide sorption to experimental apparatus (Powell et al., 2014; Zimmerman et al., 2014). Due to the strong hydrolysis and low solubility, loss to the vial walls frequently occurs. However, we have shown that in the presence of other sorbing surfaces, competition for sorption sites leads to a low association of the actinides with the vessels. We have verified this by acid leaching the vessels following sorption experiments. However, it is likely that precipitation occurred in experiments in the absence of fulvic acid as they are above solubility and recoveries from filtered (10k MWCO) samples was below analytical detection limits as compared to centrifuged and settled sampling procedures.

Each spike solution prepared for the column experiments presented below was equilibrated for approximately three days prior to introduction to the columns for consistency. Therefore, it is expected that the Th is in equilibrium with both hematite colloids and SRFA prior to introduction to the columns. In addition, the dissolved fraction was measured immediately prior to spiking the columns presented in Table 1 above with 10-25% of ^{232}Th initially in the dissolved phase (i.e. the ternary SRFA-Th-hematite system). It is assumed that any ^{232}Th in the dissolved fraction is associated with the SRFA due to its strong complexation affinity with

organic matter and low solubility. For comparison, in the SRFA-free system, greater than 99.5% of Th is adsorbed to hematite colloids versus approximately 90% in the SRFA system with hematite colloids.

Figure 2: Batch sorption results for experiments at pH 5.5 in 0.001 M NaCl with the following constituents: 200 $\mu\text{g/L}$ ^{232}Th , 50 g/L quartz or 45 mg/L hematite colloids, with/without 25 mg_C/L SRFA, K_d (L/kg) values are calculated for systems for ^{232}Th :hematite (*white*), ^{232}Th :Quartz (*gray*), ^{232}Th :hematite in the presence of SRFA (*striped*), and ^{232}Th :Quartz in the presence of SRFA (*black*), error bars are based on measurement error of triplicate samples.

3.2 Column Experiments

Figure 3 below presents the elemental effluent breakthrough for each of the 1 mL/min columns run in high purity quartz for Th, hematite colloids as ^{56}Fe , and SRFA as ^3H . Furthermore, each of the components have similar breakthrough times and retardation factors when SRFA is present. Therefore, aqueous effluent data will be represented by only the Th elemental breakthrough for additional figures. Nonetheless full effluent and solid phase analysis for each column is included in the *Supplementary Materials* Figures S11-S17 and aqueous (effluent), overall recovery and retardation factors for Th are in Table 2. A summary of physical parameters and retardation factors for each component are presented in *Supplementary Materials* Table S4-S5. Table 3 summarizes the effluent analysis conducted in addition to elemental analysis by ICP-MS and LSC during collection for hematite-SRFA-Th columns for select samples. This includes effluent filtration followed by elemental analysis as well as particle size analysis and zeta potential measurements as discussed in the Materials and Methods section (disaggregated effluent filtration data is presented in Table S6 in the *Supplementary Materials*). However, filtration and particle size analysis was not completed on all column effluents due to lack of sufficient volume and detection limitations.

The quartz columns with SRFA present [Hematite-SRFA-Th and SRFA-Th] have similar retardation factors (1.0-1.6) for both 0.1 and 1.0 mL/min flow rates with effluent recovery >60% (Figure 6, Table 2, retardation factor calculations in *Supplementary Materials*, Table S5). Therefore, even under relatively fast flow rates, the 1 mL/min system does not appear to have been kinetically limited. For comparison, Figure 4 presents only effluent Th breakthrough for each of the 1 mL/min flow rate, quartz columns. The presence of SRFA led to nearly unretarded transport of both hematite colloids and Th (Hematite-SRFA-Th and SRFA-Th). It is important

to note that these columns represent two different species transporting through the column, one as a particulate (Hematite-SRFA-Th) and one as a dissolved species (Th-SRFA) with similar mobility observed for both. This confirms that SRFA is controlling the transport.

The ^{230}Th and ^{232}Th columns at 1 mL/min flow rate in quartz had retardation factors of 1.9 and 3.4. Further, the ^{232}Th -hematite column did not have sufficient effluent recovery to calculate a retardation factor as most aqueous measurements were below the MDC as described above in the Materials and Methods. The ^{230}Th and ^{232}Th -hematite columns had effluent recoveries of 51.6 and 1.3%, respectively (Table 2). Moreover, the effluent recovery of the hematite-Th column is negligible as compared to >60% recovery in the hematite-SRFA-Th spike in quartz media at a 1 mL/min flow rate. Therefore, it is clear that the SRFA led to a drastic enhancement of transport of the hematite colloids and Th in this system. However, although the hematite-SRFA-Th column did not appear to be kinetically limited (based on a comparison of 0.1 and 1.0 mL/min flow), these columns were likely not in kinetic equilibrium with respect to Th sorption to the quartz due to the fast flow rate. Therefore, the calculated retardation factors are not necessarily representative of equilibrium partitioning to the solid phase.

For comparison, the distribution of the components recovered within the solid phase of the hematite-SRFA-Th column represents a smaller fraction of the total input (<40%) and is evenly distributed throughout the column, while for the hematite-Th column the majority of the recovered Th is in the solid fraction (~60%). It must be noted that the overall recovery is lower for the hematite-Th column (~62% overall) likely due to incomplete leaching of Th during the 8M HNO_3 step showing that these complexes are likely very strongly sorbed to the solid phase. Moreover, the solid phase distribution shows the majority of influent Th was deposited within the first 2 cm from the solid phase (~40%) (Figure 5). This shows that the hematite-Th was

removed quickly from the aqueous phase as much of the colloids did not reach the end of the column. The opposite occurred in the hematite-SRFA-Th column as shown by the significant breakthrough in the effluent and even distribution throughout the solid phase of the column. A small amount of the hematite-SRFA-Th colloids were removed as the spike solution moved along the quartz column with the majority moving through the column with interaction with the solid phase.

The colloids in the hematite-Th spike solution (without SRFA) exhibited negligible aggregation prior to introduction to the column and there were no significant changes in the stock solution on the time scale of the experiments. An average particle size of 152 ± 1 nm was measured prior to input which is similar to hematite-SRFA-Th column spike solutions also at pH~5.5 (measurements ranging from 95-190 nm throughout the experiments, Table 1). However, the hematite-Th spike solution had a positive zeta potential 70 ± 4 mV which may have been attracted towards the negatively charged quartz based on its point of zero charge near pH 2 (Kosmulski, 2002, 2011). This electrostatic interaction likely led to strong attenuation of the hematite-Th colloids with the quartz and, therefore, limited mobility in the columns. Further, the hematite-SRFA-Th solutions had a zeta potential of -42 to -55 mV and were expected to be repelled by the bulk quartz sand leading to a greater likelihood of transport than the hematite-Th colloids.

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513 Figure 3: Effluent breakthrough for quartz columns under four different spike conditions (noted within the text box of each figure) at 1
 514 mL/min flow rate at pH 5.5 and 0.001 M NaCl. The breakthrough of Th (*black triangles*), hematite as ^{56}Fe (*gray squares*), SRFA as
 515 ^3H (*white circles*), and Re tracer (*gray diamonds*): (A) ^{230}Th , (B) ^{232}Th , (C) SRFA-Th, (D) Hematite-Th, (E) Hematite-SRFA-Th.

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Note: Re tracer is not shown for 'B' and 'D' to allow for greater detail in Fe and Th breakthrough in y-axis.

517
 518 Figure 4: Effluent breakthrough of Th at pH 5.5 in 0.001 M NaCl with 1 mL/min flow rate within the following column experiments
 519 in high purity quartz: ^{230}Th (1 ppb, *gray triangles*), ^{232}Th (10 ppb, *black triangles*), Hematite-Th (*gray squares*), Th-SRFA (*white*
 520 *circles*) and Hematite-SRFA-Th (*black circles*) with the tracer (Re, *gray diamonds*) included for comparison, error bars are based on
 521 triplicate measurements for ^{232}Th and counting statistics for ^{230}Th .

522 Table 2: Summary of aqueous (effluent) recovery and overall (effluent + solid phase) recovery for all column experiments.

Spike ID	Flow Rate (mL/min)	Aqueous Recovery (%)			Overall Recovery (%)			Retardation Factor (Th)
		Th	Fe	SRFA	Th	Fe	SRFA	
²³⁰ Th	0.94 ± 0.17	51.6	N/A	N/A	97.7	N/A	N/A	1.9
²³² Th	0.98 ± 0.07	2.1	N/A	N/A	90.6	N/A	N/A	3.4
Hematite-Th	0.97 ± 0.14	1.3	1.9	N/A	61.6	86.4	N/A	BDL
SRFA-Th	0.94 ± 0.02	97.3	N/A	98.2	97.3	N/A	98.2	1.0
Hematite-SRFA-Th	1.02 ± 0.01	60.3	70.5	92	99.9	84.8	92	1.4
SRS Sandy – Hematite-SRFA-Th	1.01 ± 0.02	<1	<1	NM	88	78.7	NM	BDL
Hematite-SRFA-Th	0.107 ± 0.014	85.1	93.9	92.3	104.5	106.6	92.3	1.5

Note: N/A – not applicable, NM – not measured, BDL – below detection limits

Table 3: Summary of effluent analysis for select column experiments including particle size, zeta potential and % dissolved (average of at least 3 effluent samples).

Spike ID	Flow Rate (mL/min)	Zeta (mV)	Diameter (nm)	Fraction Dissolved An(IV) (%)
Hema-SRFA-Th	1	-52 ± 12	176 ± 3	$28 \pm 22\%$
Hema-SRFA-Th	0.1	-69 ± 8	153 ± 17	$18 \pm 1\%$

The SRS sandy sediment column with the hematite-SRFA-Th spike solution did not exhibit effluent Th breakthrough above the MDC. However, Figure 7 shows the recovery of Th and hematite (as Fe) in the solid phase following leaching. It demonstrates that the majority of the colloids did not reach the middle of the column. This confirms the importance of using environmentally relevant soils and sediments in column experiments because these are significantly different results than those for hematite-SRFA-Th in quartz columns. Minimal transport of the hematite colloids and ^{232}Th was observed within the column based on leaching of the solid phase with the largest fraction in sections 2 and 3 cm from the influent. It is significant that the quartz and SRS sandy sediment are different because the SRS sandy sediment is composed largely of quartz with small coatings of kaolinite and iron oxides. Therefore, it is likely that the hematite-SRFA-Th colloids are interacting strongly with these coating minerals.

To examine the influence of nanoparticle filtration, experiments were conducted with non-reactive polystyrene microspheres for comparison (ThermoScientific, summarized in *Supplementary Materials*). Unretarded breakthrough of the polystyrene nanoparticles occurred in quartz columns, but negligible breakthrough was observed in the SRS sandy sediment (*Supplementary Materials*, Figure S18-S19). Further, results with the polystyrene microspheres are comparable to those with hematite-SRFA-Th spike solutions in both quartz and SRS sandy sediment. This is significant because it shows that the non-reactive polystyrene microspheres are

transporting similarly to our hematite-SRFA-Th colloids. The decrease in mobility in the SRS sandy sediment could be due to either filtration based on particle size or a greater reactivity of the microspheres than expected. Fluorescence microscopy of the SRS sandy sediment shows that particles are strongly associated with the coatings on the quartz grains (*Supplementary Materials, Figure S20*). Results are inconclusive as to whether it is a reaction with coatings or physical filtration of particles although the polystyrene particles appear to have been reactive with the SRS sandy sediment coatings based on association.

Figure 5: Recovery of ^{232}Th per centimeter of column length from quartz sand columns for hematite-Th (*black*) and hematite-SRFA-Th (*gray*) column experiments at 1 mL/min flow rate based on leaching in 8 M HNO_3 , error bars based on triplicate measurements.

Figure 6: Comparison of hematite colloid facilitated transport of Th [as hematite-SRFA-Th] through quartz columns at 0.1 and 1.0 mL/min flow rate, 1.0 mL/min quartz column with hematite-SRFA-Th (*gray triangles*), 0.1 mL/min flow rate, quartz column with hematite-SRFA-Th (*black circles*) spike solutions, column conditions for all experiments: pH 5.5 in 0.001 M NaCl.

Figure 7: Recovery from the sediments within the SRS sandy columns for hematite colloids as ^{55}Fe (gray) and ^{232}Th (black) following leaching in 8 M HNO_3 for hematite-SRFA-Th spike at pH 5.5 in 0.001 M NaCl

4.0 DISCUSSION

4.1 Batch Experiments

Initial batch experiments were designed to investigate the optimal conditions for colloid-facilitated transport of An(IV) on hematite colloids. These data presented in Figures 1 and 2 demonstrate the ability of SRFA to adsorb to hematite colloids in suspension and change sorption of tetravalent actinides. Further, electrophoretic mobility and particle size data confirms that SRFA stabilizes hematite colloids in suspension (*Supplementary Materials*, Figure S7 – S10). Based on these experiments, a low ionic strength (0.001 M NaCl) and pH of 5.5 were chosen to reduce aggregation but still represent environmentally relevant conditions. In addition, ³H-SRFA and hematite colloid batch sorption/desorption experiments proved that significant desorption of the SRFA from hematite colloids is not expected over the time span of the column transport experiments as <6% desorbed over 118 hours in batch sorption experiments (Figure 1). It is expected that hematite particles are coated with a layer of SRFA at low ionic strength as described previously (Seijo et al., 2009).

The batch sorption experiments showed that ²³²Th adsorbs much more strongly to hematite versus quartz based on equilibrium K_d values of 27200 vs. 620 L/kg. However, SRFA can form aqueous complexes with Th and decrease Th sorption to hematite colloids and quartz with time. However, this is likely not occurring over the timeframe of this work since all spike solutions were pre-equilibrated. In addition, the filtration data presented in Table 3 and predicted by the K_d values from the batch sorption results (section 3.2) provide further evidence of stability over the time span of the column experiments because there is no significant change in the fraction of Th sorbed to the hematite over the time span of these experiments. Further, previous work by Zhao *et al.* (2011) showed that sorption K_d values of Pu in natural water from the

Nevada Test site in the presence of dissolved organic matter were approximately two orders of magnitude lower than without ($<0.4 \text{ mg}_C/\text{L}$) in the same water. It is assumed that Pu in this system was in the tetravalent oxidation state and will act similarly to Th as shown previously with humic acid (Zimmerman et al., 2014). This data and previous work shows that the SRFA may be capable of desorbing ^{232}Th from the hematite due to the strong interaction of Th with organic matter (Reiller et al., 2005; Reiller et al., 2008; Reiller et al., 2003). However, the K_d value of 230 L/kg measured for ^{232}Th sorption to hematite colloids in the presence of SRFA still represents greater than 90% sorption at equilibrium. Moreover Bouby *et al.* observed $>80\%$ association of Th with bentonite colloids over a period of ~ 400 days with minimal desorption (Bouby et al., 2011).

4.2 Quartz columns at 1.0 mL/min flow rate

The overall mobility of Th through quartz columns with respect to each of the experimental conditions followed the trend:

$\text{Th} - \text{SRFA} > \text{Hematite} - \text{SRFA} - \text{Th} > \text{soluble } ^{230}\text{Th} > \text{saturated } ^{232}\text{Th} > \text{Hematite} - \text{Th}$

The Th – SRFA column exhibited the earliest and most significant effluent breakthrough. These results are consistent with previous work reporting a strong association of Th with humic substances (Reiller et al., 2003; Reiller et al., 2008; Zimmerman et al., 2014) and increased transport in the presence of humic substances (but not specifically fulvic acid) (Artinger et al., 2003). Moreover these results follow the trends expected based on batch experiments presented in Figure 2. It is not expected that the An(IV) species affected the transport of the hematite colloids in these experiments due to the low mass relative to that of the colloid (mass ratio of colloid:An(IV) of at least 150). However, significantly greater retardation was expected based on K_d values measured in batch experiments. Previous work has often shown that batch experiments

overestimate sorption (Ivanovich, 1993; Serkiz et al., 2007) for two important reasons (1) drastically different solid to liquid ratios and (2) significantly greater available surface areas in batch experiments. Further, the consistency between the 0.1 and 1.0 mL/min flow rates for hematite-Th-SRFA columns shows that equilibrium was reached in column experiments in the presence of SRFA. However, it is likely that equilibrium was not reached in experiments without SRFA where the stronger sorption was expected.

Transport of Th and hematite in the presence of SRFA (i.e. likely present as Th sorbed to hematite colloids which remained in suspension due to SRFA coating) was significantly greater than the system without SRFA. However, in the absence of hematite where Th was transported as soluble Th-SRFA complexes, transport was slightly enhanced relative to the ternary Th-hematite-SRFA system (1.0 versus 1.4 retardation factor, note the error is ~ 0.3). These observations are supported by previous data showing that iron oxide nanoparticles can be stabilized in suspension by humic substances (Baalousha, 2009; Baalousha et al., 2008; Davis and Leckie, 1978; Kretzschmar and Sticher, 1997; Reiller et al., 2008; Reiller et al., 2002, 2003; Schrick et al., 2004). Based on the data discussed above, SRFA can either solubilize Th and create a mobile aqueous species or coat hematite colloids and produce a mobile Th-hematite particle. These two mobile species have relatively similar retardation factors. The influence of SRFA on Th mobility is clearly demonstrated by the low mobility of Th in the absence of SRFA (Figure 3). However, Th transport in the absence of complexing ligands such as SRFA can also be impacted by precipitation of Th hydrolysis products.

Due to the insolubility of Th, column experiments were run with isotopes ^{230}Th and ^{232}Th to enable experiments at different molar concentrations but still detectable analytically by LSC or ICP-MS, respectively. The ^{230}Th and ^{232}Th columns represent both dissolved and precipitated

Th, respectively. Solubility calculations based on work by Neck and Kim predict a solubility of 4.3 $\mu\text{g/L}$ at pH 5.5 with $\text{Th}(\text{OH})_2^{2+}$ as the major species with ionic strength corrections approximated using the Debye-Huckel method (*Supplementary Materials*, Figure S21) (Neck and Kim, 2001). However, it must be noted that the error on the solubility constant (K_{sp}) is 0.8 log units. Therefore, introduction of one sigma error of the K_{sp} leads to a solubility range at pH 5.5 of 0.7 to 25.3 $\mu\text{g/L}$. Because insignificant breakthrough occurred for the ^{232}Th [10 $\mu\text{g/L}$] column in the presence of quartz at pH 5.5 and 0.001 M NaCl at 1 mL/min flow rate and 85% of the ^{232}Th in the initial spike solution was in the colloidal size fraction (15% in the dissolved fraction) based on filtration, it is likely that precipitation occurred and led to immobilization of the majority of the ^{232}Th within the column.

However, the ^{230}Th column [0.72 $\mu\text{g/L}$] in quartz at pH 5.5 and 0.001 M NaCl at a 1 mL/min flow rate recovered approximately 52% of the total ^{230}Th within the effluent breakthrough with 72% of the ^{230}Th associated with the dissolved size fraction in the initial spike solution. Assuming the colloidal size fraction that was removed by the 10kDa MWCO filter as described in Materials and Methods is precipitated Th and that precipitated Th is not mobile within the columns, it is likely that the true solubility of Th is on the lower end of the estimated range. In addition, it is notable that a large fraction of the dissolved Th is mobile in these systems due to the fast flow rate (1 mL/min), low reactivity and nonequilibrium with the quartz sand.

The effluent recovery in the hematite-Th column is <2% as compared to >60% recovery in the hematite-SRFA-Th column. These findings are corroborated by previous works suggesting that humic substances may have a significant impact on the sorption and transport of inorganic minerals and their co-associated contaminants (Baalousha, 2009; Baalousha et al.,

2008; Davis and Leckie, 1978; Kretzschmar and Sticher, 1997; Murphy et al., 1999; Reiller et al., 2008; Reiller et al., 2002, 2003; Schrick et al., 2004; Takahashi et al., 2002). The majority of the hematite and Th were quickly sequestered within the column in the absence of SRFA (Figure 5). This is likely due to deposition of the hematite-Th colloids on the quartz. In this system, the Th is strongly associated with hematite based on (1) sorption of greater than 99% of the ^{232}Th with the hematite colloids in the hematite-Th column spike solution, resulting in a K_d value of 27200 L/kg (based on filtration as described in Materials and Methods, section 2.3), and (2) ^{56}Fe and ^{232}Th being correlated in their distribution in the solid phase (based on elemental leaching of the solid phase, Figure 5). In addition to a correlation between Fe and Th in the effluent measurements, the solid phase concentration of ^{55}Fe and ^{232}Th as a function of distance in the column were also correlated (Figure 5 and *Supplementary Materials*, Figure S13).

A critical finding of this work is that colloid facilitated transport of Th was only observed in the presence of SRFA. In the binary Th-hematite system, negligible transport of Th was observed with only 1.3% of Th eluting from the column (Table 2). The negligible transport of hematite-Th complexes confirms batch sorption experiments in this work and previously which show a strong sorption of tetravalent actinides to hematite (Cromieres et al., 1998; Hixon et al., 2010; Hixon and Powell, 2014; Lu et al., 1998; Lu et al., 2003; Melson et al., 2012; Powell et al., 2005; Romanchuk et al., 2011). Systems with extremely low organic carbon may be able to effectively sequester Th (or other tetravalent An) via sorption to metal oxide minerals. However, it is important to note that for these simplified systems hematite colloids could both increase or decrease Th transport with respect to the dissolved species depending on the presence or absence of SRFA.

It is suggested that a ternary hematite-SRFA-Th complex is present and mobile in the column experiments with the ternary hematite-SRFA-Th spike, because (1) each of the components (hematite as Fe, SRFA as ^3H , and Th) had similar breakthrough times and retardation factors and (2) 70-85% of the ^{232}Th was associated with the colloidal size fraction in the effluent and initial spike solutions (based on filtration Table 3). The ternary complex is likely a SRFA coated hematite with Th bound to the SRFA coating due to the lower pH consistent with greater sorption of humic materials. This is a type 1 complex in which the fulvic acid acts as a bridge between the Th ion and the hematite surface as described previously by Bryan *et al.* (2012). This ternary complex is especially likely considering the significant sorption and limited desorption of SRFA to hematite in preliminary batch experiments (Figure 1) and low pH (~5.5) of these systems.

For the Th-SRFA column spike solutions where no hematite colloids are present, it is expected that Th exists as a mobile Th-SRFA complex. This is also based on the strong sorption of Th to humic substances (Reiller *et al.*, 2008; Reiller *et al.*, 2003) and the ability of humic substances to control the aqueous speciation of the contaminant as seen previously with trivalent lanthanides (Takahashi *et al.*, 1997; Yamamoto *et al.*, 2005) and tetravalent actinides (Artinger *et al.*, 2003). In these experiments, either a mobile binary (Th-SRFA) or an immobile binary (hematite-Th) complex exists where mobility is dependent upon whether or not SRFA is present.

Because of the strong complexation affinity of Th with both hematite colloids and humic substances (Cromieres *et al.*, 1998; Reiller *et al.*, 2002, 2003) and the increased solubility of Th in the presence of humic substances (Artinger *et al.*, 2003; Choppin, 2007; Reiller *et al.*, 2008), it is likely that precipitation of Th did not occur within spike solutions with hematite and/or SRFA. Reiller *et al.* (2008) estimated a 60 fold increase in Th solubility in the presence of humic acid at

pH 6. With respect to the solubility range estimated above, a 60 fold increase in solubility would lead to a range of 40-1500 ppb at pH 5.5. However, these are estimates for humic acid and not fulvic acid. Moreover, it must be noted that concentrations were above theoretical solubility of Th without the presence of humic substances. Electron microscopy was attempted on spike solutions but could not rule out precipitation of Th due to the small size of hematite colloids (likely similar in size as possible Th precipitates) and difficulty imaging in the presence of SRFA. While precipitation of Th cannot be ruled out in the systems with hematite colloids and SRFA present, it is not expected based on the above discussion.

4.3 Quartz Columns at 0.1 mL/min flow rate

Because the 1 mL/min flow rate resulted in a retention time of only ~6.5 minutes, additional column experiments were conducted at a 0.1 mL/min flow rate (~65 minute retention time) for comparison. These experiments were conducted to investigate whether or not the fast flow rate could be a significant factor impacting transport in these systems. It was considered that the fast flow rate could induce shear forces great enough to lead to break up of deposited and/or aggregated colloids followed by re-mobilization as discussed previously (Dunphy Guzman et al., 2006). Gao *et al.* (2006) also noted that faster flow rates led to greater mobilization of colloids under unsaturated conditions. However, the similarity of hematite colloid, Th and SRFA from the hematite-SRFA-Th spike solution through quartz columns at 0.1 and 1.0 mL/min show that it is unlikely that shear forces affected the colloid transport in these systems (Figure 3). Further, the breakthrough is slightly earlier in the 1.0 mL/min flow rate (retardation factors of 1.4 versus 1.5 for 1.0 and 0.1 mL/min flow rates, respectively, Table 2 and Table S5 in *Supplementary Materials*), but the resolution of the breakthrough peaks is not great enough to confirm differences as the error on the retardation factors was 0.2-0.3. In addition, the

hematite-Th spike solution at 1.0 mL/min demonstrates that the fast flow rate was not capable of breaking up and re-mobilizing hematite colloids with flushing of over 40 pore volumes of 0.001 M NaCl at pH 5.5.

4.4 SRS Sandy columns at 1.0 mL/min flow rate

It is critical to note that the two media (quartz versus SRS sandy) exhibited dramatically different transport of the ternary hematite-SRFA-Th spike input. Previous work investigating dissolved Pu(IV) in the same sediment from Savannah River Site and similar column setup at pH 3 reported no breakthrough of Pu(IV) and that the largest fraction of Pu was associated with the first cm of the column (Powell et al., 2014). The current experiments with Th associated with hematite colloids and SRFA exhibit the greatest solid phase recovery between 2-4 cm in the column (>20% recovery of the total in each slice as determined by a leaching step of 1cm slices). Therefore, while effluent concentrations of hematite, Th or SRFA from the SRS sandy sediment column were below detection limits, the post-experiment solid phase analysis indicated that some transport of the hematite-SRFA-Th ternary complex occurred. Further, in a qualitative comparison with previous work, greater Th transport was observed in this ternary hematite-SRFA-Th column at pH 5.5 relative to an experiment with only dissolved Pu(IV) in the same soil at pH 3.5 (Powell et al., 2014). This observation of Th transport as a Th-hematite-SRFA ternary species is consistent with the experiments with quartz packed columns showing high mobility of the same ternary species.

Because the SRS sandy is a natural sediment composed of quartz sand as well as sediment coatings mostly composed of kaolinite and goethite, it is likely that the sediment coatings (and not the quartz sand) led to the reduction in transport. Previous experiments with environmentally relevant sediments have reached similar conclusions that naturally occurring, colloidal-sized

particles can contribute to removal of nanoparticles (Emerson et al., 2014; Quik et al., 2012).

The following multiple working hypotheses describe the potential mechanisms behind the reduction in transport in the SRS sandy sediment relative to the quartz columns:

1. Clay coating-mediated destabilization of the particles
2. Aggregation of particles with the clay-sized coating minerals
3. Physical entrapment of particles in smaller pores due to heterogeneities in the natural sediment

However, it is likely that these theorized mechanisms are not independent but interconnected processes leading to immobilization of the particles.

Nonetheless, additional experiments were conducted with presumably stable, 100 nm polystyrene nanoparticles to further investigate these mechanisms (*Supplementary Materials*, Figure S18-S19). However, similar results were observed with quartz versus SRS sandy sediment columns for the polystyrene microspheres as noted with the hematite-SRFA-Th columns (*Supplementary Materials* Figure S19). Fluorescence microscopy shows that particles are associated with the sediment grains specifically with the coatings (*Supplementary Materials*, Figure S20). Based on the microscopy results, it appears that interactions with sediment coatings and possibly filtration were responsible for sequestration of the polystyrene nanoparticles within the sandy sediment columns. Filtration does not appear to be a significant mechanism for the removal of the polystyrene nanoparticles in the quartz columns but drawing a conclusion from the SRS sandy sediment columns from that data is not possible since the pore structures could not be quantitatively compared.

5.0 CONCLUSIONS

This work demonstrates a complex influence of natural organic matter on Th transport. SRFA can enhance Th transport as either (1) a soluble Th-SRFA complex or (2) as a Th-amended hematite colloid where SRFA coats and enhances the particle mobility. Due to strong sorption of Th or precipitation of Th hydrolysis products, Th is only sparsely mobile in the absence of SRFA. Thus, the introduction of SRFA led to nearly unretarded transport of Th in both Th-SRFA and hematite-SRFA-Th columns. Even at the low pH (~5.5) of these experiments where some sorption of organic matter is expected, enhanced mobility of Th was observed. In addition, the enhanced mobilization of colloidal hematite facilitated by SRFA clearly demonstrates the importance of SRFA in transport but also highlights the likelihood of immobilization of tetravalent actinides by hematite colloids in the absence of a sorbing organic ligand which can alter the surface of the colloid. This work illustrates that colloids can enhance or retard transport of the actinides depending on the conditions.

The transport of Th, SRFA, and hematite was dramatically decreased within the SRS sandy column as compared to the quartz sand. This demonstrates the importance of natural sediment coatings on contaminant immobilization and shows that experiments using pure phases may not properly represent real sediments. These ternary systems should be investigated further to better understand the mechanisms of colloid facilitated transport of the tetravalent actinides in complex matrices. There are important implications with respect to environmental systems as inorganic colloids and organic matter are fairly ubiquitous in environmental systems with reported colloid concentrations of 0.1 – 260 mg/L (Buddemeier and Hunt, 1988; Vilks et al., 1988; Moulin and Ouzounian, 1992; McCarthy and Degueldre, 1993; Degueldre et al., 1996; Roberts et al., 2004; Kersting, 2013) and 0.1 – 200 mg organic carbon/L (Choppin and Allard, 1985; Thurman, 1986; Short et al., 1988; Vilks et al., 1997; Artinger et al., 2000; Buckau et al.,

2000). Future work should be concentrated on environmentally relevant sediments and soil coatings to further investigate their interactions with these ternary complexes.

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REFERENCES

1. Artinger, R., Buckau, G., Geyer, S., Fritz, P., Wolf, M., Kim, J.I., 2000. Characterization of groundwater humic substances: influence of sedimentary organic carbon. *Appl Geochem* **15**, 97-116.
2. Artinger, R., Buckau, G., Zeh, P., Geraedts, K., Vancluyse, J., Maes, A., Kim, J.I., 2003. Humic colloid mediated transport of tetravalent actinides and technetium. *Radiochim Acta* **91**, 743-750.
3. Artinger, R., Schuessler, W., Schafer, T., Kim, J.-I., 2002. A kinetic study of Am(III)/Humic colloid interactions. *Environ Sci and Technol* **36**, 4358-4363.
4. Baalousha, M., 2009. Aggregation and disaggregation of iron oxide nanoparticles: Influence of particle concentration, pH and natural organic matter. *Sci Total Environ* **407**, 2093-2101.
5. Baalousha, M., Maniculea, A., Cumberland, S., Kendall, K., Lead, J.R., 2008. Aggregation and Surface Properties of Iron Oxide Nanoparticles: Influence of pH and Natural Organic Matter. *Environ Toxicol Chem* **27**, 1875-1882.
6. Banik, N.L., Buda, R.A., Burger, S., Kratz, J.V., Trautmann, N., 2007. Sorption of tetravalent plutonium and humic substances onto kaolinite. *Radiochim Acta* **95**, 569-575.
7. Begg, J.D., Zavarin, M., Zhao, P.H., Tumey, S.J., Powell, B., Kersting, A.B., 2013. Pu(V) and Pu(IV) Sorption to Montmorillonite. *Environ Sci Technol* **47**, 5146-5153.
8. Blinova, O., Novikov, A., Perminova, I., Goryachenkova, T., Haire, R., 2007. Redox interactions of Pu(V) in solutions containing different humic substances. *J Alloys Compd* **444**, 486-490.
9. Bouby, M., Geckeis, H., Lutzenkirchen, J., Mihai, S., Schafer, T., 2011. Interaction of bentonite colloids with Cs, Eu, Th and U in presence of humic acid: A flow field-flow fractionation study. *Geochim Cosmochim Acta* **75**, 3866-3880.

10. Bouby, M., Manh, T.N., Geckeis, H., Scherbaum, F., Kim, J.I., 2002. Characterization of aquatic colloids by a combination of LIBD and ICP-MS following the size fractionation. *Radiochim Acta* **90**, 727-732.
11. Brunhauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. *JACS* **60**, 309-319.
12. Bryan, N.D., Abrahamsen, L., Evans, N., Warwick, P., Buckau, G., Weng, L.P., Van Riemsdijk, W.H., 2012. The effects of humic substances on the transport of radionuclides: Recent improvements in the prediction of behaviour and the understanding of mechanisms. *Appl Geochem* **27**, 378-389.
13. Buckau, G., Artinger, R., Geyer, S., Wolf, M., Fritz, P., Kim, J.I., 2000. Groundwater in-situ generation of aquatic humic and fulvic acids and the mineralization of sedimentary organic carbon. *Appl Geochem* **15**, 819-832.
14. Buddemeier, R.W., Hunt, J.R., 1988. Transport of colloidal contaminants in groundwater: radionuclide migration at the Nevada Test Site. *Applied Geochemistry* **3**, 535-548.
15. Choppin, G.R., 1999. Utility of Oxidation State Analogs in the Study of Plutonium Behavior. *Radiochim Acta* **85**, 89-95.
16. Choppin, G.R., 2007. Actinide speciation in the environment. *J Radioanal Nucl Chem* **273**, 695-703.
17. Choppin, G.R., Allard, B., 1985. Complexes of actinides with naturally occurring organic compounds. *Application of Geochemical Models to High-level Nuclear Waste Repository Assessment: Conference Proceedings* **16**, 24.
18. Clark, M.M., 1996. Transport Modeling for Environmental Engineers and Scientists. John Wiley and Sons, New York, NY.
19. Cromieres, L., Moulin, V., Fourest, B., Guillaumont, R., Giffaut, E., 1998. Sorption of thorium onto hematite colloids. *Radiochim Acta* **82**, 249-255.
20. Davis, J.A., 1982. Adsorption of natural dissolved organic matter at the oxide/water interface. *Geochim Cosmochim Acta* **46**, 2381-2393.
21. Davis, J.A., Leckie, J.O., 1978. Effect of Adsorbed Complexing Ligands on Trace-Metal Uptake by Hydrous Oxides. *Environ Sci Technol* **12**, 1309-1315.
22. Degueldre, C., Pfeiffer, H.-R., Alexander, W., Wernli, B., Bruetsch, R., 1996. Colloid properties in granitic groundwater systems. I. Sampling and characterization. *Appl Geochem* **11**, 677-695.
23. Duff, M.C., Hunter, D.B., Triay, I.R., Bertsch, P.M., Reed, D.T., Sutton, S.R., Shea-McCarthy, G., Kitten, J., Eng, P., Chipera, S.J., Vaniman, D.T., 1999. Mineral Associations and Average Oxidation States of Sorbed Pu on Tuff. *Environ Sci Technol* **33**, 2163-2169.
24. Emerson, H.P., Hart, A.E., Baldwin, J.A., Waterhouse, T.C., Kitchens, C.L., Mefford, O.T., Powell, B.A., 2014. Physical transformations of iron oxide and silver nanoparticles from an intermediate scale field transport study. *J Nanoparticle Res* **16**, 14.
25. Geckeis, H., Lutzenkirchen, J., Polly, R., Rabung, T., Schmidt, M., 2013. Mineral-water interface reactions of actinides. *Chem Rev* **113**, 1016-1062.
26. Geckeis, H., Rabung, T.H., Ngo Manh, T., Kim, J.I., Beck, H.P., 2002. Humic colloid-borne natural polyvalent metal ions: Dissociation experiment. *Environ Sci Technol* **36**, 2946-2952.

27. Hixon, A.E., Arai, Y., Powell, B.A., 2013. Examination of the effect of alpha radiolysis on plutonium(V) sorption to quartz using multiple plutonium isotopes. *J Colloid Interface Sci* **403**, 105-112.
28. Hixon, A.E., Hu, Y.J., Kaplan, D.I., Kukkadapu, R.K., Nitsche, H., Qafoku, O., Powell, B.A., 2010. Influence of iron redox transformations on plutonium sorption to sediments. *Radiochim Acta* **98**, 685-682.
29. Hixon, A.E., Powell, B.A., 2014. Observed changes in the mechanism and rates of Pu(V) reduction on hematite as a function of total plutonium concentration. *Environ Sci Technol* **48**, 9255-9262.
30. Hunter, K.A., Hawke, D.J., and Choo, L.K., 1985. Equilibrium adsorption of thorium by metal oxides in marine electrolytes. *Geochim Cosmochim Acta*, **52**, 627-636.
31. Ivanovich, M., 1993. Assessment of Radionuclide Retardation – Uses and Abuses of Natural Analog Studies – Response. *J Contam Hydrol* **13**, 263-266.
32. Jackson, M.L., 1985. Soil Chemical Analysis - Advanced Course, 2nd ed., Soil Chem. Anal.-Adv. course. Parallel Press, Madison, WI.
33. Kaplan, D.I., Bertsch, P.M., Adriano, D.C., Orlandini, K.A., 1994. Actinide association with groundwater colloids in a coastal plain aquifer. *Radiochim Acta* **66/67**, 181-187.
34. Kaplan, D.I., Powell, B.A., Demirkanli, D.I., Fjeld, R.A., Molz, F.J., Serkiz, S.M., Coates, J.T., 2004. Influence of Oxidation States on Plutonium Mobility during Long-Term Transport through an Unsaturated Subsurface Environment. *Environ Sci Technol* **38**, 5053-5058.
35. Kaplan, D.I., Powell, B.A., Duff, M.C., Demirkanli, D.I., Denham, M.E., Fjeld, R.A., Molz, F., 2007. Influence of Sources on Plutonium Mobility and Oxidation State Transformations in Vadose Zone Sediments. *Environ Sci Technol* **41**, 7417-7423.
36. Keeney-Kennicutt, W.L., Morse, J.W., 1985. The redox chemistry of Pu(V)O₂⁺ interaction with common mineral surfaces in dilute solutions and seawater. *Geochim Cosmochim Acta* **49**, 2577-2588.
37. Kersting, A.B., 2012. Impact of colloidal transport on radionuclide migration in the natural environment. Radionuclide Behaviour in the Natural Environment: Science, Implications and Lessons for the Nuclear Industry, 384-410.
38. Kersting, A.B., 2013. Plutonium transport in the environment. *Inorgan Chem* **52**, 3533-3546.
39. Kersting, A.B., Efurnd, D.W., Finnegan, D.L., Rokop, D.J., Smith, D.K., Thomspn, J.L., 1999. Migration of plutonium in groundwater at the Nevada Test Site. *Nature* **397**, 56-59.
40. Kim, J.I., Grambow, B., 1999. Geochemical assessment of actinide isolation in a German salt repository environment. *Eng Geol* **52**, 221-230.
41. Kosmulski, M., 2002. The pH-dependent surface charging and the points of zero charge. *J Colloid Interface Sci* **253**, 77-87.
42. Kosmulski, M., 2011. The pH-dependent surface charging and points of zero charge: V. Update. *J Colloid Interface Sci* **353**, 1-15.
43. Krauskopf, K.B., 1984. Thorium as an Analogue for Plutonium and Rare-Earth Metals as Analogues for Heavier Actinides, in: Smellie, J.A.T. (Ed.), Natural Analogues to the Conditions around a Final Repository for High-Level Radioactive Waste. Swedish Geological Company, Uppsala, Sweden.
44. Kretzschmar, R., Sticher, H., 1997. transport of humic-coated iron oxide colloids in a sandy soil: influence of Ca²⁺ and trace metals. *Environ Sci Technol* **31**, 3497-3504.

45. Lu, N., Cotter, C.R., Kitten, H.D., Bentley, J., Triay, I.R., 1998. Reversibility of Sorption of Plutonium-239 onto Hematite and Goethite Colloids. *Radiochim Acta* **83**, 167-173.
46. Lu, N., Reimus, P.W., Parker, G.R., Conca, J.L., Triay, I.R., 2003. Sorption kinetics and impact of temperature, ionic strength and colloid concentration on the adsorption of plutonium-239 by inorganic colloids. *Radiochim Acta* **91**, 713-720.
47. Marquardt, C.M., Seibert, A., Artinger, R., Denecke, M., Kuczewski, B., Schild, D., Fanghanel, T., 2004. The redox behavior of plutonium in humic rich groundwater. *Radiochim Acta* **92**, 617-623.
48. McCarthy, J.F., Degueldre, C., 1993. In Characterization of Environmental Particles: Sampling and characterization of colloids in groundwater for studying their role in contaminant transport. Lewis Publishers, Chelsea, MI.
49. McCarthy, J.F., Zachara, J.M., 1989. Subsurface transport of contaminants. *Environ Sci Technol* **23**, 496-502.
50. Melson, N.H., Haliene, B.P., Kaplan, D.I., Barnett, M.O., 2012. Adsorption of tetravalent thorium by geomedia. *Radiochim Acta* **100**, 827-832.
51. Moulin, V., Ouzounian, G., 1992. Role of colloids and humic substances in the transport of radio-elements through the geosphere. *Appl Geochem* **1**, 179-186.
52. 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. *Colloid Surf* **157**, 47-62.
53. Neck, V., Kim, J.I., 2001. Solubility and hydrolysis of tetravalent actinides. *Radiochim Acta* **89**, 1-16.
54. Nelson, D. M., W. R. Penrose, J. O. Karttunen and P. Mehlhaff (1985). "Effects of Dissolved Organic Carbon on the Adsorption Properties of Plutonium in Natural Waters." *Environ Sci Technol* **19**(2): 127-131.
55. Novikov, A.P., Kalmykov, S.N., Utsunomiya, S., Ewing, R.C., Horreard, F., Merkulov, A., Clark, S.B., Tkachev, V.V., Myasoedov, B.F., 2006. Colloid Transport of Plutonium in the Far-Field of the Mayak Production Association, Russia. *Science* **314**, 638-641.
56. Nyhan, J. W., B. J. Drennon, W. V. Abeele, M. L. Wheeler, W. D. Purtymun, B. Trujillo, W. J. Herrera and J. W. Booth (1985). "Distribution of Plutonium and Americium Beneath a 33-yr-old Liquid Waste Disposal Site." *J Environ Qua* **14**(4): 501-509.
57. Penrose, W.R., Polzer, W.L., Essington, E.H., Nelson, D.M., Orlandini, K.A., 1990. Mobility of Plutonium and Americium through a Shallow Aquifer in a Semiarid Region. *Environ Sci Technol* **24**, 228-234.
58. Powell, B.A., Duff, M.C., Kaplan, D.I., Fjeld, R.A., Newville, M., Hunter, D.B., Bertsch, P.M., Coates, J.T., Eng, P., Rivers, M.L., Serkiz, S.M., Sutton, S.R., Triay, I.R., Vaniman, D.T., 2006. Plutonium oxidation and subsequent reduction by Mn(IV) minerals in Yucca Mountain Tuff. *Environ Sci Technol* **40**, 3508-3514.
59. Powell, B.A., Fjeld, R.A., Coates, J.T., Kaplan, D.I., Serkiz, S.M., 2003. Plutonium Oxidation State Geochemistry in the SRS Subsurface Environment (U). Westinghouse Savannah River Company.
60. Powell, B.A., Fjeld, R.A., Kaplan, D.I., Coates, J.T., Serkiz, S.M., 2004. Pu(V)O₂⁺ adsorption and reduction by synthetic magnetite (Fe₃O₄). *Environ Sci Technol* **38**, 6016-6024.

61. Powell, B.A., Fjeld, R.A., Kaplan, D.I., Coates, J.T., Serkiz, S.M., 2005. Pu(V)O₂⁺ adsorption and reduction by synthetic hematite and goethite. *Environ Sci Technol* **39**, 2107-2114.
62. Powell, B.A., Kaplan, D.I., Serkiz, S.M., Coates, J.T., Fjeld, R.A., 2014. Pu(V) transport through Savannah River Site soils - an evaluation of a conceptual model of surface-mediated reduction to Pu (IV). *J Environ Rad* **131**, 47-56.
63. Quik, J.T., Stuart, M.C., Wouterse, M., Peijnenburg, W., Hendriks, A.J., van de Meent, D., 2012. Natural colloids are the dominant factor in the sedimentation of nanoparticles. *Environ Toxicol Chem / SETAC* **31**, 1019-1022.
64. Reiller, P., Casanova, F., Moulin, V., 2005. Influence of addition order and contact time on thorium(IV) retention by hematite in the presence of humic acids. *Environ Sci Technol* **39**, 1641-1648.
65. Reiller, P., Evans, N.D.M., Szabo, G., 2008. Complexation parameters for the actinides(IV)-humic acid system: a search for consistency and application to laboratory and field observations. *Radiochim Acta* **96**, 345-358.
66. Reiller, P., Moulin, V., Casanova, F., Dautel, C., 2002. Retention behavior of humic substances onto mineral surfaces and consequences upon thorium (IV) mobility: case of iron oxides. *Appl Geochem* **17**, 1551-1562.
67. 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.
68. 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.
69. Roberts, K.A., Santschi, P.H., Leppard, G.G., West, M.M., 2004. Characterization of organic-rich colloids from surface and ground waters at the actinide-contaminated Rocky Flats Environmental Technology Site (RFETS), Colorado, USA. *Colloids Surfaces A* **244**, 105-111.
70. Romanchuk, A.Y., Kalmykov, S.N., Aliev, R.A., 2011. Plutonium sorption onto hematite colloids at femto- and nanomolar concentrations. *Radiochimica Acta* **99**, 137-144.
71. Ryan, J.N., Elimelech, M., 1996. Colloid Mobilization and Transport in Groundwater. *Colloids Surface A* **107**, 1-56.
72. Sachs, S., Schmeide, K., Reich, T., Brendler, V., Heise, K.H., Bernhard, G., 2005. EXAFS study on neptunium(V) complexation by various humic acids under neutral pH conditions. *Radiochim Acta* **93**, 17-25.
73. Sanchez, A.L., Murray, J.W., Sibley, T.H., 1985. The adsorption of plutonium IV and V on goethite. *Geochim Cosmochim Acta* **49**, 2297.
74. Santschi, P.H., Roberts, K.A., Guo, L.D., 2002. Organic nature of colloidal actinides transported in surface water environments. *Environ Sci Technol* **36**, 3711-3719.
75. Schild, D., Marquardt, C.M., 2000. Analysis of Th(IV)-humate by XPS. *Radiochim Acta* **88**, 587-591.
76. Schrick, B., Hydutsky, B.W., Blough, J.L., Mallouk, T.E., 2004. Delivery vehicles for zerovalent metal nanoparticles in soil and groundwater. *Chem Mater* **16**, 2187-2193.
77. Seijo, M., Ulrich, S., Filella, M., Buffle, J., Stoll, S., 2009. Modeling the Adsorption and Coagulation of Fulvic Acids on Colloids by Brownian Dynamics Simulations. *Environ Sci Technol* **43**, 7265-7269.

78. Serkiz, S.M., Johnson, W.H., Wile, L.M.J., Clark, S.B., 2007. Environmental availability of uranium in an acidic plume at the Savannah River Site. *Vadose Zone Journal* **6**, 354-362.
79. Shcherbina, N.S., Kalmykov, S.N., Perminova, I.V., Kovalenko, A.N., 2007. Reduction of actinides in higher oxidation states by hydroquinone-enriched humic derivatives. *J Alloys Compd* **444**, 518-521.
80. Short, S.A., Lowson, R.T., Ellis, J., 1988. $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ activity ratios in the colloidal phases of aquifers in lateritic weathered zones. *Geochim Cosmochim Acta* **52**, 2555.
81. Silva, R.J., Nitsche, H., 1995. Actinide Environmental Chemistry. *Radiochim Acta* **70/71**, 377-396.
82. Simpkins, L., 2011. The Influence of Natural Organic Matter on Plutonium Sorption to Gibbsite, Environmental Engineering and Earth Science. Clemson University.
83. Takahashi, Y., Kimura, T., Minai, Y., 2002. Direct observation of Cm(III)-fulvate species on fulvic acid-montmorillonite hybrid by laser-induced fluorescence spectroscopy. *Geochim Cosmochim Acta* **66**, 1-12.
84. Takahashi, Y., Minai, Y., Ambe, S., Makide, Y., Ambe, F., 1999. Comparison of adsorption behavior of multiple inorganic ions on kaolinite and silica in the presence of humic acid using the multitracer technique. *Geochim Cosmochim Acta* **63**, 815-836.
85. Takahashi, Y., Yoshitaka, M., Ambe, S., Makide, Y., Ambe, F., Tominaga, T., 1997. Simultaneous determination of stability constants of humate complexes with various metal ions using multitracer technique. *Sci Tot Environ* **198**, 61-71.
86. Tanaka, K., Suzuki, Y., Ohnuki, T., 2009. Sorption and Oxidation of Tetravalent Plutonium on Mn Oxide in the Presence of Citric Acid. *Chem Lett* **38**, 1032-1033.
87. Thurman, E.M., 1986. Organic Geochemistry of Natural Waters. Martinus Nijhoff/Dr W. Junk Publishers, Dordrecht.
88. Tinnacher, R.M., Honeyman, B.D., 2007. A new method of radiolabel natural organic matter by chemical reduction with tritiated sodium borohydride. *Environ Sci Technol* **41**, 6776-6782.
89. Tinnacher, R.M., Powell, B.A., Kersting, A.B., Zavarin, M., 2011. Kinetics of Neptunium(V) Sorption and Desorption Reactions on Goethite: Experiment and Modeling. *Geochim Cosmochim Acta*, **75**, 6854-6599.
90. Tipping, E. and Higgins, D.C., 1982. The effect of adsorbed humic substances on the colloid stability of haematite particles. *Colloids and Surf* **5**, 85-92.
91. Vilks, P., Cramer, J.J., Shewchuk, T.A., Larocque, J.P.A., 1988. Colloid and particulate matter in Cigar Lake natural analog program. *Radiochim Acta* **44/45**, 305-310.
92. Vilks, P., Frost, L.H., Bachinski, D.B., 1997. Field-scale colloid migration experiments in a granite fracture. *J Contam Hydrol* **26**, 203-214.
93. Wahlgren, M.A. and Orlandini, K.A., 1982. Comparison of the geochemical behaviour of plutonium, thorium and uranium in selected North American lakes. In *Environmental Migration of Long-lived Radionuclides*, 757-774. IAEA-SM-257/89.
94. Wang, W., Howe, J.Y., Gu, B., 2008. Structure and morphology evolution of hematite (Fe_2O_3) nanoparticles in forced hydrolysis of ferric chloride. *J Phys Chem* **112**, 9203-9208.
95. Wong, J.C., Zavarin, M., Begg, J.C., Kersting, A.B., Powell, B.A., 2015. Effect of Equilibration Time on Pu Desorption from Goethite. *Radiochim Acta*, In press.

96. Xie, J.C., Lu, J.C., Lin, J.F., Zhou, X.H., Li, M., Zhou, G.Q., Zhang, J.H., 2013. The dynamic role of natural colloids in enhancing plutonium transport through porous media. *Chem Geol* **360**, 134-141.
97. Xie, J.C., Lu, J.C., Lin, J.F., Zhou, X.H., Xu, Q.C., Li, M., Zhang, J.H., 2014. Insights into transport velocity of colloid-associated plutonium relative to tritium in porous media. *Scientific Reports* **4**, 8.
98. Xu, C., Santschi, P.H., Zhong, J.Y., Hatcher, P.G., Francis, A.J., Dodge, C.J., Roberts, K.A., Hung, C.C., Honeyman, B.D., 2008. Colloidal Cutin-Like Substances Cross-Linked to Siderophore Decomposition Products Mobilizing Plutonium from Contaminated Soils. *Environ Sci Technol* **42**, 8211-8217.
99. Yamamoto, Y., Takahashi, Y., Shimizu, H., 2005. Systematics of stability constants of fulvate complexes with rare earth ions. *Chem Lett* **34**, 880-881.
100. Yang, Y., Saiers, J.E., Barnett, M.O., 2013. Impact of Interactions between Natural Organic Matter and Metal Oxides on the Desorption Kinetics of Uranium from Heterogeneous Colloidal Suspensions. *Environ Sci Technol* **47**, 2661-2669.
101. Zanker, H., Hennig, C., 2014. Colloid-borne forms of tetravalent actinides: a brief review. *J Contam Hydrol* **157**, 87-105.
102. Zavarin, M., Powell, B.A., Bourbin, M., Zhao, P., Kersting, A.B., 2012. Np(V) and Pu(V) ion exchange and surface-mediated reduction mechanisms on montmorillonite. *Environ Sci Technol* **46**, 2692-2698.
103. Zhao, P., Zavarin, M., Leif, R.N., Powell, B.A., Singleton, M.J., Lindvall, R.E., Kersting, A.B., 2011. Mobilization of actinides by dissolved organic compounds at the Nevada Test Site. *Appl Geochem* **26**, 308-318.
104. Zimmerman, T., Zavarin, M., Powell, B.A., 2014. Influence of humic acid on plutonium sorption to gibbsite: Determination of Pu-humic acid complexation constants and ternary sorption studies. *Radiochim Acta* **102**, 629-643.