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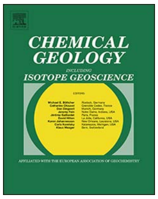

Neptunium(V) sorption to vadose zone sediments: Reversible, not readily reducible, and predictable based on Fe-oxide content

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ABSTRACT

Neptunium (Np) is among the key risk-drivers at the Savannah River Site's (SRS) low-level waste disposal facility located in South Carolina. A series of studies were undertaken to identify and to model the key geochemical processes controlling Np sorption to SRS vadose zone sediments. The approach was to conduct Np(V) laboratory batch and flow studies using two sediments representing end-member depositional facies recovered beneath the disposal facility. Baseline distribution coefficients (K_d values; Np concentration ratio of sediment:porewater) were 9.05 ± 0.61 $L\,kg^{-1}$ and 4.26 ± 0.24 $L\,kg^{-1}$ for the clayey and sandy end-member sediments, respectively. The addition of natural organic matter (NOM) to the sediment resulted in only a two fold increase in the K_d values, most likely due to the formation of ternary sediment-NOM-Np complexes. None of the reduction treatments (ascorbic acid, dithionite, zero valent iron, hydrogen peroxide, and anaerobic atmosphere), including some long-term (71-day) equilibration experiments, resulted in significant increases in K_d values. This indicated that little to no reduction of Np(V) to the more strongly sorbing Np(IV) occurred. Among the key novel findings in this research was that batch desorption tests and stop-flow stir-cell kinetic experiments indicated that the Np (V) sorption was completely reversible. These observations were used to develop a simple conceptual model describing Np(V) sorption. The conceptual model described NpO_2^+ reversibly complexation to iron oxide coatings on the sediments. The model was successfully applied without any adjustable parameters to an independent set of experimental data, requiring only the dithionite-extractable Fe concentration from the independent dataset. There is no standard approach for quantifying reactive sorption site concentrations on composite materials (e.g., soils and sediments). In this study we proposed such a method based on an operationally defined fraction of the extractable iron. This parameterization approach was calibrated with two sediments then used to blindly and successfully predict sorption on another end-member soil. The successful modeling approach taken in this work 1) identified key reactions that are or are not influencing the system to develop a simple but appropriate conceptual model and 2) calibrated the fraction of extractable iron required for surface site density determination and used the calibrated model for blind predictions. This modeling approach could be used for other composite materials to allow for comparisons of the fraction of surface reactive extractable metals.

1. Introduction

Neptunium-237 contamination is of major concern due to its long half-life, 2.14 million years, and its tendency to be highly mobile in oxic natural waters. Other Np isotopes exist but are short lived and pose little risk to the public. The Solid Waste Management Facility, located on the Savannah River Site (SRS; near Aiken, South Carolina) is tasked with safely disposing of low-level radioactive waste in the subsurface vadose zone. Along with other radionuclides, this facility contains approximately 74 GBq of disposed ^{237}Np (Hiergesell et al., 2008). The ^{237}Np is among the major long-term risk drivers at the facility, and as such it is paramount to understand the geochemical controls on Np subsurface migration to ensure accurate estimates of radiological risk to the public.

The predominant oxidation state for Np in low E_H waters is Np(IV), while under more oxidizing conditions, as expected in most vadose zone, the estimated predominant oxidation state is Np(V) (Supplemental information, Fig. S1). The standard redox potential for Np(V) + e- < = > Np(IV) is +0.604 V lies below the standard redox potential of Fe(III) reduction (Fe(III) + e- < = > Fe(II)) of +0.77 V.

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Thus, under standard conditions, reduction of Np(V) by Fe(II) will not be favorable. However, Nakata et al. (2002) showed that Fe(II) on the surface of magnetite reduces Np(V) to Np(IV) while Fe(II) in solution did not. This indicates the importance of surficial iron leading to Np reduction. Furthermore, (Boyanov et al., 2007) demonstrated that reduction of U(VI) by surface bound Fe(II) is highly pH dependent.

The subsurface transport of Np can be retarded if it is reduced to the more strongly sorbing tetravalent oxidation state. Lieser and Muhlenweg (1988) reported a sharp increase in Np sorption at E_H levels below 0.20 (V). Additionally, Icopini et al. (2007) reported the biotic reductive precipitation by *Shewanella oneidensis* in the presence of citrate of aqueous Np(V) to an insoluble Np(IV) phase. The addition of citrate also allowed *Geobacter metallireducens* to carry out Np reduction. Unexpectedly, the reduced Np(IV) formed soluble and potentially mobile Np(IV)-citrate complexes. Comparisons between Np(V)/Np(IV) reduction and Pu(V)/Pu(IV) reduction demonstrate the relative sorption affinities of tetravalent and pentavalent actinides. Powell et al. (2014) showed that for Pu sorption to a Savannah River Site (SRS) subsurface Clayey Sediment, Pu(IV) sorbed much more strongly than Pu (V). However, after a 33-day contact period, the sorption edge of the Pu (V) mirrored that of the Pu(IV) with nearly 100% sorption in all systems with a pH > 3. This shift in sorption was attributed to reduction of Pu (V) to Pu(IV) due to interactions with the sediment. The reduction of Pu (V) to Pu(IV) has a much high standard reduction potential (~1.1 V) than Np(V) reduction to Np(IV). Therefore, reduction of Pu(V) is generally more likely to occur than Np(V). Thus, strongly reducing conditions must be maintained to stabilize tetravalent Np species.

Most natural waters have pH values between 4.5 and 9.0 (Becking et al., 1960) and at these values pentavalent actinide sorption can vary widely (Silva and Nitsche, 1995). Sorption can be described by the sediment-water distribution coefficient (K_d):

$$K_d = \frac{[Np]_{sediment}}{[Np]_{aq}} \tag{1}$$

where $[Np]_{sediment}$ is the sediment Np concentration ($mol/kg_{sediment}$) and $[Np]_{aq}$ is the aqueous Np concentration ($mol\,L^{-1}$). K_d values for Np(V) have been calculated for a variety of soil types. Sheppard et al. (1979) found a K_d value of $200\,L\,kg^{-1}$ for Np(V) sorption to a Fuquay sand from Barnwell, South Carolina at a pH of 5.2 over an equilibration period of 94 days. Kohler et al. (1999) that Np(V) had a K_d of $20\,L\,kg^{-1}$ for sorption to hematite at a pH of 5.5. In the same pH range, Bertetti et al. (1998) showed that Np(V) sorption to quartz, α-alumina, and montmorillonite had K_d values at pH 5 of 0.1, 2, and $10\,L\,kg^{-1}$, respectively. These K_d values support the conclusion that pentavalent actinides sorb weakly.

Another factor that can alter Np sorption is the presence of natural organic matter (NOM). Schmeide and Bernhard (2009) demonstrated that humic substances may abiotically reduce Np(V) to Np(IV). Reduction to Np(IV) was initially fast, in the 5–10 day range, and was dependent on the type of humic material as well as pH. Humic substances and other NOM can also increase sorption by forming ternary surface-metal-ligand complexes (Schindler, 1990). These complexes can form in two ways. Type A complexes form when the metal binds directly with the surface ($\equiv$SO-M$^+$-NOM). Type B complexes form when the NOM binds directly with the surface ($\equiv$SO-NOM-M$^+$). For a system containing Np, the diphosphonic acid chelating ligand HEDPA (1-hydroxyethane-1,1-diphosphonic acid) and boehmite (γ-AlOOH), Type A complexes were proposed to predominate at higher pH values when surface charges are negative due to deprotonation which attracts the positively charged metal. Conversely, under lower pH conditions, the Type B complexes occurred (Powell et al., 2010). Khasanova et al. (2007) explored the influence of ternary species by varying the order of addition of each component in a system containing hematite or goethite, a leonardite humic acid (HA), and Np. They showed increased Np sorption when the soil and aqueous Np were allowed to pre-equilibrate before humic acid addition than when the soil was pre-equilibrated with humic acid before Np addition. This difference was attributed to the humic acid saturating the mineral surfaces and hindering Np binding. Np(V) still exists predominantly as the free neptunyl ion when mixed with humate solutions with the NpO_2HA species forming at pH 5.8 up to pH 9 and the colloidal $NpO_2(OH)HA$ forming above pH 9 (Schmeide and Bernhard, 2009) while Np(IV) complexes strongly with the humic acid resulting in higher solubility even at elevated pH values.

After Np potentially migrates through the engineered barriers at the SRS E-Area Low Level Waste Disposal Facility, risk models predict that the Np will reside ~95% of its time in the vadose zone and ~5% of its time in the underlying aquifer before it poses a potential health risk (WSRC, 2008). The general objective of this study was to study Np(V) sorption to SRS vadose zone sediments. The intent of this research was to first identify the key processes influencing Np sorption to these sediments and then to develop a numerical model that could be used in model transport/risk. More specifically, the objectives of this study were to 1) quantify the impact of NOM on Np sorption, 2) quantify the impact of various reducing treatments on Np sorption, 3) quantify the reversibility and hysteresis of Np sorption, and finally 4) develop a surface complexation model to describe the key geochemical processes influencing Np sorption to SRS vadose zone sediments.

2. Method and materials

2.1. Sediments

Two sediment samples were collected approximately 3 m below grade (approximately 123 m above sea level) from E-Area (coordinates: 33.285685, −81.663038) on the SRS along the wall of a borrow pit trench. The SRS is located within the Atlantic Coastal Plains and these sediments were deposited in a variety of neritic marine, marginal marine, and nonmarine environments. The two sediment samples used in this study were selected to represent end members, with respect to sorption properties, depositional facies within the vadose zone; they were referred to as the Sandy Sediment and Clayey Sediment (Table 1). These two facies are readily identified based on their texture (sand and silt clay) and color (yellow and red). Prior to collecting samples, the surface 10 cm of sediment along the trench walls were scraped away to remove potential foreign materials. Samples were brought to the lab, air dried, and passed through a 2-mm sieve. < 3% of field sample were > 2-mm. The < 2-mm sediment was used in these studies.

2.2. ^{237}Np(V) solution preparation

Before using the ^{237}Np stock solution (purchased from Isotope Products, Valencia, CA), it was purified of radiological decay products and all the Np was converted to the +5 oxidation state. To convert it to Np(V), the stock solution was evaporated to dryness then the residue was brought up in approximately 5 mL 8.0 M HNO_3. Then 1.0 M hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$, EMD Chemicals, ACS grade) and water were added to achieve a 3 M HNO_3/0.3 M $NH_2OH{\cdot}HCl$ solution. This solution was purified by extraction chromatography using Eichrom TEVA resin packed in a Bio-Rad poly-prep column. The 3 M HNO_3/0.3 M $NH_2OH{\cdot}HCl$ Np solution was loaded on a 2 mL column and washed with three column volumes of 3 M HNO_3. The Np(IV) was eluted with 0.02 M HCl + 0.2 M HF. The effluent was evaporated to dryness then redissolved in 1.0 M HNO_3. The sample was brought up in 10 mL of 1.0 M HNO_3 then evaporated to incipient dryness and redissolved in 5.0 mL of 1.0 M HNO_3. The fuming in HNO_3 performed at the end of the purification procedure drove Np to the soluble pentavalent state.

An aliquot of the stock solution was evaporated to dryness on a stainless steel planchet and counted on the EG&G Ortec Alpha Spectrometer (Octete PC Detectors). The resulting alpha spectra showed only ^{237}Np and no other alpha emitting isotope impurities. The exact