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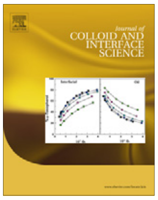

Neptunium(V) sorption to goethite at attomolar to micromolar concentrations

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ABSTRACT

Sorption of 10^{-18}–10^{-5} M neptunium (Np) to goethite was examined using liquid scintillation counting and gamma spectroscopy. A combination approach using ^{239}Np and long lived ^{237}Np was employed to span this wide concentration range. ^{239}Np detection limits were determined to be 2×10^{-18} M and 3×10^{-17} M for liquid scintillation counting and gamma spectroscopy, respectively. Sorption was found to be linear below 10^{-11} M, in contrast to the non-linear behavior observed at higher concentrations both here and in the literature. 2-site and 3-site Langmuir models were used to simulate sorption behavior over the entire 10^{-18}–10^{-5} M range. The 3-site model fit yielded Type I and II site densities of 3.56 sites/nm^2 (99.6%) and 0.014 ± 0.007 sites/nm^2 (0.4 ± 0.1%), consistent with typical "high affinity" and "low affinity" sites reported in the literature [21]. Modeling results for both models suggest that sorption below $\sim 10^{-11}$ M is controlled by a third (Type III) site with a density on the order of $\sim 7 \times 10^{-5}$ sites/nm^2 ($\sim$0.002%). While the nature of this "site" cannot be determined from isotherm data alone, the sorption data at ultra-low Np concentrations indicate that Np(V) sorption to goethite at environmentally relevant concentrations will be (1) linear and (2) higher than previous (high concentration) laboratory experiments suggest.

1. Introduction

Kilogram quantities of Np have been introduced into the environment as a result of nuclear weapons testing and nuclear power [1–4]. While initially present in relatively small quantities in spent nuclear fuel (0.02–0.1%) [5], its in-growth from ^{241}Am, coupled with its long half life (2.14×10^6 yrs) and relatively weak sorption, results in ^{237}Np becoming a major dose contributor in a geological repository after 10,000 years [6,7].

Under oxidizing conditions prevalent throughout much of the subsurface, Np exists primarily in the pentavalent oxidation state [6]. As a result of the low charge/size ratio of its dominant cationic species in aqueous solutions (NpO_2^+), Np(V) sorbs weakly to most mineral surfaces and is thus expected to be the most environmentally mobile actinide [8,9].

Np(V) sorption to mineral surfaces can both retard as well as increase migration. Np(V) is effectively removed from the mobile phase if it is sorbed to immobile minerals in soil or on fracture surfaces. However, the transport of Np(V) can also be enhanced if sorbed to a mobile colloid [10–12]. Iron oxides are thought to play an important role in the environmental transport of low solubility actinides because of their ubiquity, high metal sorption affinities, and high sorption capacities [13–15]. Thus, understanding the sorption/desorption behavior of Np to iron oxides is important for developing accurate environmental transport models.

Many of the studies on the sorption of Np have been performed via radiometric counting (i.e. liquid scintillation counting and gamma spectroscopy) of ^{237}Np which, as a result of the long half life of ^{237}Np (2.14×10^6 yrs), has restricted such studies to relatively high aqueous Np concentrations (>10^{-10} M) [8,27–30]. However, Np concentrations in the environment are typically much lower. For example, at the Nevada National Security Site (formerly known as the Nevada Test Site), Np concentrations are routinely measured at 10^{-13}–10^{-17} M in groundwater [31]. Thus, new methods to study the sorption of Np at ultra-low, femto-molar concentrations are necessary.

Several radiotracers for ^{237}Np have been utilized in the literature for low-level environmental Np analyses and include ^{235}Np ($t_{1/2}$ = 396.1 days) [13,32], ^{236}Np ($t_{1/2} = 1.54 \times 10^5$ yrs) [4], and ^{239}Np ($t_{1/2}$ = 2.3565 days), of which ^{239}Np is most common owing to its much greater availability [7,32–33]. However, to our knowledge only one sorption study using short-lived ^{239}Np isotopes is reported in the literature [7], compared to the many high concentration sorption studies reported using ^{237}Np [18,28–30].

Experimental and modeling studies of metal ion sorption to iron oxides have shown that sorption cannot always be explained as binary adsorption at a single type of surface group or "site". As a result, multi-site sorption models are frequently employed [16–21]. In such models, the iron oxide surface is modeled as

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containing a relatively large quantity (∼90–99%) of "low affinity" sites which characterize bulk sorption behavior and smaller quantities (∼1–10%) of "high affinity" sites which control sorption behavior at low mineral surface loads [21]. Spectroscopic studies suggest that the observed "high affinity" sites can potentially result from heterogeneity in the mineral surface and can include structural features such as "edges" [22,23] and "corners" [22,24] of the iron octahedra, adatom sites [25], and defect sites in the mineral surface. Further variability in the sorption behavior has also been shown to result from differing affinities toward different exposed iron oxide crystal faces [22,23]. However, in the absence of spectroscopic or other information, "sites" identified based on fitting isotherm data do not necessarily imply specific reaction mechanisms [16,34,35].

Studies of Np sorption at moderate concentrations (10^{-6}–10^{-8} M) have suggested Freundlich-like behavior, in that as the Np concentration increases, the distribution coefficient (K_d, defined as the concentration of Np associated with the solid divided by the concentration in the aqueous phase) decreases [18]. Fundamentally, the Freundlich isotherm has been shown to be equivalent to a multi-site Langmuir model in which a Gaussian-like distribution of site affinities exists [47]. Thus, the Freudlich model can be considered an end-member in the multi-site modeling approach. The use of Freundlich isotherms is commonly employed in order to describe experimentally observed increasing K_d values with decreasing sorbate concentration at relatively high concentrations ($>10^{-10}$ M). However, one consequence of the application of a Freundlich model is that K_ds are predicted to continuously increase as the sorbate concentration decreases, resulting in extremely high K_ds when extrapolated to ultra-low concentrations. Observations made by Girvin et al. [13] with respect to Np sorption to amorphous iron oxyhydroxides indicate that Np sorption will transition to linear behavior at trace concentrations (10^{-12}–10^{-14} M). A similar change to linear sorption behavior at low concentrations for Cd, Cu and Zn on amorphous iron oxyhydroxides was observed by Dzombak and Morel [16] and Benjamin and Leckie [26]. It is reasonable to expect that this same transition will occur for Np on goethite. However, the aqueous concentration or surface loading at which this occurs is not known. The objectives of this study were to (1) examine Np–goethite interactions over a wide concentration range (10^{-18}–10^{-5} M) in order to compare Np behavior at high concentrations to Np behavior at ultra-low concentrations more commonly observed in the field, (2) develop a radioanalytical method utilizing ^{239}Np tracers for sorption studies at ultra-low concentrations, and (3) develop a consistent model to describe Np–goethite sorption behavior over a wide range of concentrations and surface loading.

2. Experimental

All chemicals used in this work were ACS reagent grade unless otherwise specified. Goethite was synthesized based on methods described by Schwertman and Cornell [36]. Characterization data of the goethite stock solution used in these experiments was recently reported by Tinnacher et al. [18]. The goethite had a low BET surface area of 15.8 $m^2\,g^{-1}$. The point of zero charge was 8.5 ± 0.1 as determined using the potentiometric titration method.

2.1. Np stock preparations

^{239}Np was purified from an Am stock available at LLNL which contained 90% (by activity) ^{243}Am and 10% ^{241}Am [31]. Briefly, a small aliquot of the Am stock was baked to near dryness and reconstituted in a solution of concentrated HCl + HI (50:1 v/v). Columns (2 mL, AG BioRad 50–100 mesh resin) were pre-conditioned with several column volumes of HCl + HI prior to loading the stock. Americium was eluted using several column volumes of HCl + HI. The Np fraction was eluted using several column volumes of 6 M HCl + 0.05 M HF.

Maximum purification of ^{239}Np was essential in order to lower the background count rate resulting from two major factors: (1) ^{239}Np in-growth during the sorption experiment resulting from incomplete separation from ^{243}Am, and (2) possible small quantities of ^{237}Np contamination, in-grown from ^{241}Am in the Am stock solution [31]. To minimize the ^{237}Np background, an initial purification of the Am stock solution was performed and the Np fraction discarded (Fig. EA-4). The first usable ^{239}Np separation was performed 24 h later using the Am stock from the initial purification. In addition, the ^{239}Np fraction underwent a second column separation, after which no Am or ^{237}Np was detected by gamma spectroscopy or liquid scintillation counting.

^{237}Np was obtained from a ^{237}Np stock available at LLNL. Separation of ^{237}Np from ^{233}Pa was performed using the procedure of Pickett et al. [37]. Briefly, the stock solution was baked to near dryness and reconstituted in concentrated HCl three times (to drive off an residual HF that may have been initially present in the stock solution). Np was dissolved in 1 mL of HCl + HI. Columns (2 mL, AG BioRad 100–200 mesh resin) were pre-conditioned with several column volumes of concentrated HCl, followed by three column volumes of HCl + HI prior to loading the stock. ^{233}Pa was eluted using five column volumes of 9 M HCl + 0.05 M HF. ^{237}Np was eluted using five column volumes of 6 M HCl + 0.05 M HF. The purified ^{237}Np solution was slowly heated until the volume was reduced to one drop. The procedure was then repeated a second time, resulting in 99 + % pure ^{237}Np solution determined by gamma spectroscopy and liquid scintillation counting.

Oxidation of the purified Np solutions to the +5 and +6 oxidation states was performed by heating the solution and reducing the volumes to one drop and then reconstituting the Np in 5 M HNO_3 three times. Reduction to the +5 state was subsequently performed by adding one to three drops of H_2O_2, covering the solutions, and very lightly heating for ∼30 min. Small aliquots of high concentration ^{237}Np solutions were taken and analyzed using a Cary 500 UV–Vis spectrophotometer. The oxidation/reduction cycle was repeated as necessary until 100% of the neptunium was confirmed to be in the Np(V) oxidation state.

For the lowest concentration solutions of pure ^{239}Np, the oxidation state was verified indirectly via extraction chromatography using an EICHROM UTEVA column. Since UTEVA strongly retains actinides in the +4 and +6 state, but not the +5, a pure solution of Np(V) passes un-retained through the column. A small aliquot of the ^{239}Np solution was diluted in 5 M HNO_3 and eluted. Liquid scintillation counting showed that 95 ± 10% of the ^{239}Np was collected in the effluent.

2.2. Sorption experiments

All sorption experiments were performed in 5 mM NaCl/0.7 mM $NaHCO_3$ (pH ∼ 8) solution prepared by adding appropriate amounts of each salt to 18 MΩ cm H_2O and filtering through a 0.45 μm filter. This solution composition was chosen to provide a direct comparison to sorption experiments reported in Tinnacher et al. [18]. Under these solution conditions, aqueous Np(V) speciation is dominated by NpO_2^+ as determined using stability constant data from NEA [38] (Fig. EA-5).

For batch sorption experiments, a 20 g/L goethite stock solution was prepared in 5 mM NaCl/0.7 mM $NaHCO_3$. To remove any colloidal goethite particles, the stock was sonicated, centrifuged at 3000 rpm for 1 h (particles < ∼100 nm remain suspended),