Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Effect of 1-Hydroxyethane-1,1-diphosphonic Acid (HEDPA) on Partitioning of Np and Pu to Synthetic Boehmite

Brian A. Powell[a]; Linfeng Rao[b]; Kenneth L. Nash[c]
[a] Clemson University, Anderson, SC, USA [b] Lawrence Berkeley National Laboratory, Berkeley, CA, USA [c] Washington State University, Pullman, WA, USA

Online publication date: 22 March 2010

To cite this Article Powell, Brian A. , Rao, Linfeng and Nash, Kenneth L.(2010) 'Effect of 1-Hydroxyethane-1,1-diphosphonic Acid (HEDPA) on Partitioning of Np and Pu to Synthetic Boehmite', Separation Science and Technology, 45: 6, 721 — 731
To link to this Article: DOI: 10.1080/01496391003608397
URL: http://dx.doi.org/10.1080/01496391003608397

Separation Science and Technology, 45: 721–731, 2010

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496391003608397

Taylor & Francis
Taylor & Francis Group

Effect of 1-Hydroxyethane-1,1-diphosphonic Acid (HEDPA) on Partitioning of Np and Pu to Synthetic Boehmite

Brian A. Powell,[1] Linfeng Rao,[2] and Kenneth L. Nash[3]
[1]*Clemson University, Anderson, SC, USA*
[2]*Lawrence Berkeley National Laboratory, Berkeley, CA, USA*
[3]*Washington State University, Pullman, WA, USA*

The effect of 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) on the sorption of Np(V) and Pu(V) to synthetic boehmite (γ-AlOOH) was examined as a function of time and pH (between 4 to 11). The sorption of both elements in boehmite suspensions (1 M NaCl, 600 mg L^{-1} boehmite) increased with increasing pH. The sorption edges for neptunium and plutonium occurred at approximately pH 8.0 and 6.6, respectively. After steady state partitioning was reached, HEDPA was added to the neptunium-boehmite and plutonium-boehmite suspensions. Neptunium and plutonium partitioning appears to be primarily affected by the formation of soluble Np:HEDPA and Pu:HEDPA complexes, the dissolution of boehmite promoted by HEDPA, and the precipitation of Np:HEDPA and Pu:HEDPA colloids. The results are discussed in terms of applicability of HEDPA-promoted dissolution as a waste reduction method in the treatment of sludge phases contained within high-level nuclear waste storage tanks.

Keywords 1-hydroxyethane-1,1-diphosphonic acid; alumina; boehmite; HEDPA; neptunium; nuclear waste; plutonium

INTRODUCTION

Safe, efficient, and economical techniques are required for the treatment of high-level radioactive wastes. The nuclear wastes in the underground storage tanks at the Hanford Site in Washington State, U.S.A. present an extraordinary clean-up task. Approximately 1.7×10^8 curies of radioactivity are contained in 177 underground storage tanks at this site (1). Over time the waste from spent nuclear fuel reprocessing has stratified into a salt cake, a supernatant phase, and an underlying sludge phase. Most of the transuranics have partitioned to the sludge phase, of which aluminum oxides represent a large component. The current waste treatment strategy proposes vitrification of the sludge phase followed by disposal in a geologic repository (2). However, vitrification of the entire sludge phase is not economically feasible due to the large volume of the sludge and the high cost of vitrification. Therefore, studies have been performed to examine the possibility of reduction of the sludge volume through dissolution of the aluminum oxides with diphosphonic acids. In a companion paper to this work, 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) was shown to significantly enhance the solubility of Al in saturated boehmite suspensions (3). It was also found that HEDPA is capable of leaching uranium into the aqueous phase through solid phase dissolution and/or the formation of U(VI):HEDPA complexes (3). Across the pH range 4 to 11, HEPDA is expected to form anionic complexes based upon the stability constants reported by Reed et al. (4). As the pH was increased and the boehmite surface developed a net negative charge, these anionic U(VI):HEDPA complexes were repelled by the surface and remained in the aqueous phase (3). In contrast to the availability of the data on the U(VI):HEDPA aqueous complexes, no studies have been conducted with neptunium and plutonium, two other actinides of critical concern in nuclear waste sludges.

Previous studies examining Np(V) leaching from simulated waste sludges with increasingly aggressive solutions indicated that 25% of the Np was removed with 3 M NaOH, a further 50% was removed with 2.0 M HNO_3, and the remaining Np was removed with 0.5 M HEDPA (5). When performing similar leaching experiments with a REDOX process sludge simulant (high Al content), Bond et al. (6), observed 20–30% leaching of either Pu(IV) or Pu(VI) in 0.1 M HNO_3. However, the Pu was proposed to be associated with alumina colloids based upon filtration tests (6). Significantly greater leaching of Pu(IV) and Pu(VI) was observed from all simulated waste sludges using 2 M HNO_3 and 0.5 HEDPA. In that investigation, Pu was found to be a dissolved species rather than a radiocolloid (6).

Understanding actinide partitioning to minerals in the presence of natural or synthetic ligands is also necessary for the reliable prediction of hydrogeochemical behavior of the actinides. Sorption to mineral surfaces is an

Received 11 May 2009; accepted 4 January 2010.
Address correspondence to Brian A. Powell, Department of Environmental Engineering and Earth Sciences, Clemson University, Anderson, SC 29625, USA. E-mail: bpowell@clemson.edu

important mechanism for retarding the subsurface migration of the actinides. Aluminum oxides and oxyhydroxides are proposed to be a primary control of subsurface migration. Some data are available describing Np(V) and Pu interactions with various aluminum (oxyhydr)oxides (7–14). However, data describing Np and Pu sorption to mineral surfaces in the presence of natural or synthetic complexing ligands are limited (8,10,11). In natural systems, Np and Pu are typically found as hydrolyzed $An(OH)_x^{4-x}$ and $AnO_2(OH)_y^{1-y}$ species. The strong tendency to hydrolyze and the low solubility of tetravalent actinide hydroxides may constrain the aqueous phase concentrations of Np(IV) and Pu(IV). However, in oxic natural waters and in the absence of strong complexants, Np and Pu are found primarily as Np(V) and Pu(V) in the aqueous phase. Subsurface transport of pentavalent actinides is of particular concern because they generally have a lower affinity for solid phases relative to other actinide oxidation states due to their low effective charge of approximately +2.2 (15). Complexation with multidentate organic ligands, such as HEDPA used in this work, may affect the partitioning of Np(V) and Pu(V) and therefore affect subsurface transport rates.

The present study has been conducted to investigate the partitioning behavior of Np(V) and Pu in HEDPA-amended synthetic boehmite suspensions. This work seeks to provide a more detailed understanding of the mechanisms controlling Pu behavior than previous studies using bismuth phosphate, REDOX, and PUREX waste simulants (5,6). Quantitative sorption data were obtained to evaluate the applicability of HEDPA leaching as a technique to reduce the volume of the sludge phases contained within the Hanford waste tanks, and examine the sorption behavior of Np(V) and Pu organophosphorous complexes with regard to subsurface transport.

MATERIALS AND METHODS

Solid Phase Characterization

The alumina used in this work was obtained from SASOL (trade name CATAPAL® B). Details regarding the treatment and characterization of this material are presented elsewhere (3). The alumina was found to have a predominantly amorphous character with broad XRD peaks corresponding to boehmite (γ-AlOOH). The boehmite had a N_2(g)-BET surface area of $354\,m^2\,g^{-1}$ and a point-of-zero-salt-effect of 8.1 ± 0.1.

Chemicals and Stock Solutions of Neptunium and Plutonium

HEDPA was obtained as a 70% aqueous solution (Sigma) and purified by recrystallization from glacial acetic acid. Stock solutions of ^{237}Np(V) (0.038 M) and Pu(VI) (1.8 mM) were prepared from the inventory at the Lawrence Berkeley National Laboratory. The oxidation states of Np(V) and Pu(VI) in the stock solutions were verified using absorption spectroscopy on a Cary 5G spectrophotometer. Analysis by α-spectroscopy indicated that the alpha activity of the Pu stock was 24.6% ^{238}Pu and 75.4% ^{242}Pu.; on a molar basis, approximately 99.9% ^{242}Pu. All other chemicals were of ACS reagent grade quality and used as received. All experiments were performed in either 1.0 M NaCl or 1.0 M $NaClO_4$. The concentrations of Np and Pu were measured by liquid scintillation counting (LSC) using EcoLumeTM (MP Biomedicals Inc.) cocktail on a Wallac 1415 counter. Alpha-beta discrimination was used to separate the alpha counts of ^{237}Np from the beta activity of the ^{233}Pa daughter product. Error for all measurements was propagated using liquid scintillation counting statistics.

Preparation and Analysis of Oxidation States of Neptunium and Plutonium in Working Solutions

Working solutions of Np (94 μM) and Pu (19 μM Pu) were prepared by diluting the Np(V) and Pu(VI) stock solutions mentioned above in NaCl at pH 3. The oxidation state distribution of Pu in the working solution and control solutions of the sorption experiments (boehmite and HEDPA free) was determined using a procedure including lanthanum fluoride coprecipitation and sorption to silica gel. Details of the procedure have been described elsewhere (16,19). The ability of this procedure to separate pentavalent and hexavalent actinides was verified using Np(V) and U(VI) working solutions. The oxidation state of Np in the working solution and in the subsequent sorption experiments was found to remain as Np(V). Measurements of the oxidation state distribution of ^{242}Pu control solutions (no HEDPA or boehmite) in 1 M NaCl are shown in Table 1 along with the data from analysis of U(VI) and Np(V) solutions (as a validation test of the separation procedures). The data from Np(V) and U(VI) solutions indicate that the method is approximately 90% efficient under the conditions used. The LaF_3(s) coprecipitation step was assumed to be >99% efficient for Pu(IV) removal. It

TABLE 1
Oxidation state distribution of Pu in control solutions (1 M NaCl; 1.9 μM ^{242}Pu)

	An(IV)	An(V)	An(VI)
Pu control at pH 4[a]	4% ± 3%	83% ± 3%	13% ± 4%
Pu control at pH 8[a]	0% ± 4%	91% ± 4%	9% ± 5%
U(VI) stock[b]	5% ± 2%	5% ± 1%	90% ± 2%
Np(V) stock[b]	3% ± 1%	87% ± 2%	10% ± 3%

[a]Error propagated from counting statistics.
[b]Error represents standard deviation of 3 replicate measurements.

was assumed that no Pu(III) was present as it would be unstable in the oxic, circum-neutral pH solutions examined here. Based upon these efficiencies and assumptions, an error of approximately 10% could be used to describe the Pu oxidation state distributions rather than the lower error based upon counting statistics listed in Table 1.

The results indicate that, though all the Pu in the stock solution was initially Pu(VI), it was predominantly in the pentavalent state in the control solutions, which were much more dilute and less acidic than the stock solution. It appears that the Pu(VI) from the stock solution was reduced to Pu(V) after dilution in 1 M NaCl. This is consistent with the observed stability of Pu(V) in dilute and near neutral solutions (16–18). Therefore, the sorption experiments in this work are discussed in terms of Pu(V) sorption rather than Pu(VI).

Batch Sorption/Leaching Experiments

Initially, parallel experiments in 1.0 M NaCl and 1.0 M $NaClO_4$ were conducted to evaluate the effect of background electrolyte on the oxidation states of Np and Pu and their sorption/leaching behavior. Experiments in the 1 M $NaClO_4$ system were later discontinued as no significant difference between the two background solutions was observed. Only the results of experiments with 1.0 M NaCl are described below.

Np and Pu were first equilibrated with boehmite suspensions in 1.0 M NaCl (pH from 4 to 10, roughly 0.5 pH unit increments) for 10 days. Preliminary kinetic tests (in the absence of HEDPA) indicated steady state partitioning of Np and Pu was achieved between 1 to 3 days at pH 4, 7, and 10. To prepare the samples, 660 mg L^{-1} boehmite suspensions in 15 mL high-density polyethylene centrifuge tubes were adjusted to target the pH values using NaOH and HCl. After the boehmite suspensions reached a steady pH, an aliquot of Np(V) or Pu(V) working solution was added to achieve initial Np(V) or Pu(V) aqueous concentrations of 10.6 μM and 2.1 μM, respectively. After adjusting the pH of each suspension to the target pH, the suspensions were placed on an orbital shaker and mixed along their longitudinal axis. After 10 days, an aliquot was transferred to a centrifugal filter (30 k MWCO, Nanosep, Pall Life Sciences, estimated 12 nm pore size). Throughout this work, the filtrate passing through a 30 k MWCO filter is operationally defined as the soluble fraction. The first 100 to 200 μL of the filtrate were discarded to allow equilibration of the solution with the filter membrane. The Np or Pu concentration in a 200 μL aliquot of the filtrate was determined using LSC. Control solutions containing Np or Pu without boehmite were also prepared to monitor the loss of Np or Pu from the system due to precipitation or sorption to the vial walls.

After 10 days, the suspensions were amended with a small volume of a 50 mM HEDPA stock solution (pH 7) to yield a suspension containing 5.4 mM HEDPA, 600 mg L^{-1} boehmite, and 1 M NaCl. In parallel, the control solutions without boehmite were also amended to 5 mM HEDPA. The pH of the HEDPA stock solutions was adjusted to 7 to minimize the pH changes resulting from the addition of HEDPA to the suspensions. The Np(V) and Pu(V) concentrations after the addition of the HEDPA solutions were 9.4 μM and 1.9 μM, respectively. The pH of each suspension was adjusted to the target pH immediately after the addition of HEDPA and re-adjusted as necessary with HCl and NaOH throughout the experiment. Deviation from the initially fixed pH over the course of the experiment was found to be less than 0.2 pH units for all samples. The suspensions were mixed at 150 rpm on an orbital shaking platform. At specified intervals, aliquots were removed and passed through 30 k MWCO centrifugal filters as described above and the concentration of Np or Pu in the filtrate was measured using LSC.

Following the experiments, the aqueous phase was removed and the vials were rinsed with 1.0 M NaCl. Then a 1.0 M HCl solution was added to each vial to leach any sorbed Np or Pu from the vial walls. It was assumed that the amount of Np or Pu in this acid leached phase represents the amount of Np or Pu sorbed to the vial walls during the experiments. In experiments with boehmite present, no significant loss of Np or Pu to the vial walls was observed.

Pu-HEDPA and Np-HEDPA Solutions in the Absence of Boehmite

Based upon observations of the boehmite-free control samples described above, more detailed analysis of Np and Pu behavior in HEDPA/NaCl solutions without boehmite was required. Additional boehmite-free Np and Pu solutions in 1 M NaCl and 5 mM HEDPA were monitored over time at pH 4, 6, 8, 9, and 11. Aliquots were removed at various times and passed through 30 k MWCO centrifugal filters and the concentration of Pu and Np in the aqueous phase was measured using LSC. After 18 days, the size fractionation of Np and Pu was examined by measuring Np and Pu in an unfiltered sample as well as filtrate passed through 100 k MWCO and 30 k MWCO centrifugal filters (Nanosep, Pall Life Sciences). At the end of the experiments, the possibility of sorption of Np and Pu to the vial walls was tested by washing the vials with NaCl and HCl as discussed above.

RESULTS AND DISCUSSION

Examination of An(V)-HEDPA Solutions in the Absence of Boehmite

The concentrations of Np and Pu in boehmite-free, 5 mM HEDPA solutions at pH 4, 6, 8, 9, and 11 were

monitored using various filtration steps. The fractions of Np or Pu that passed through 30 k MWCO filters are shown as a function of time over an 18-day period in Fig. 1. Both Np and Pu were predominantly soluble at pH 8, 9, and 11 and the data at each time interval overlap and are difficult to differentiate as shown in Fig. 1. Interestingly, at pH 11 the concentration of Np and Pu in these systems is above the solubility limit for Np(V)-(hydr)oxide precipitates but no loss of Np or Pu was observed.

In control solutions without HEDPA after greater than 10 days of equilibration, a loss of 51% Np and 81% Pu was observed in boehmite-free solutions at pH 11 and a loss of 19% Pu was observed at pH 7. Np remained in the aqueous phase at pH 4 and 7 and Pu remained soluble at pH 4. This indicates that Np and Pu were either sorbing to the vial walls or precipitating at pH 11 (and pH 7 for Pu). Sorption to the vial walls was found to account for less than 2% of the Np and Pu loss using NaCl-HCl washing as described above. Therefore, it appears that Np and Pu precipitates were formed at pH 11 in solutions containing no HEDPA after 10 days. After 24 hours, no loss of aqueous Np and Pu was observed. Therefore, the precipitation discussed above appears to have occurred sometime after 24 hours of equilibration. The possible formation of Np and Pu precipitates must be carefully considered when evaluating the sorption data presented below.

It is noteworthy that the increased solubility of Np and Pu at pH 11 in the presence of HEDPA indicates that formation of Np:HEDPA and Pu:HEDPA complexes suppresses precipitation of hydroxides at high pH levels. However, at pH 4 and 6 in the presence of 5 mM HEDPA, a significant fraction of Np and Pu were removed upon passing through a 30 k MWCO filter. Sorption of Np and Pu to the filters was ruled out as complete recovery was obtained upon successive filtration of a single solution through new filters. Additionally, less than 2% of the total Np and Pu was sorbed to the vial walls in all systems with HEDPA present. Since two common experimental artifacts indicating loss of actinides were ruled out (sorption to filtration apparatus and sorption to reaction vessel walls), the loss of Np and Pu shown in Fig. 1 was likely due to formation of precipitates with HEDPA. After 18 days, aliquots of each suspension were passed through either 100 k MWCO (estimated 200 nm pore size) or 30 k MWCO centrifugal filters. The fraction of total Np and Pu in the filtrate is shown in Fig. 2, along with an unfiltered sample. As the filtration pore size decreased, the fraction of total Np and Pu in the filtrate also decreased, indicating removal of a Np:HEDPA or Pu:HEDPA colloidal precipitate. Precipitation of actinide-HEDPA solids at low pH was also reported in studies determining the thermodynamic parameters of U:HEDPA complexes, but only at low HEDPA:U(VI) ratios (7). Furthermore, an Al:HEDPA precipitate was also observed in a similar study and

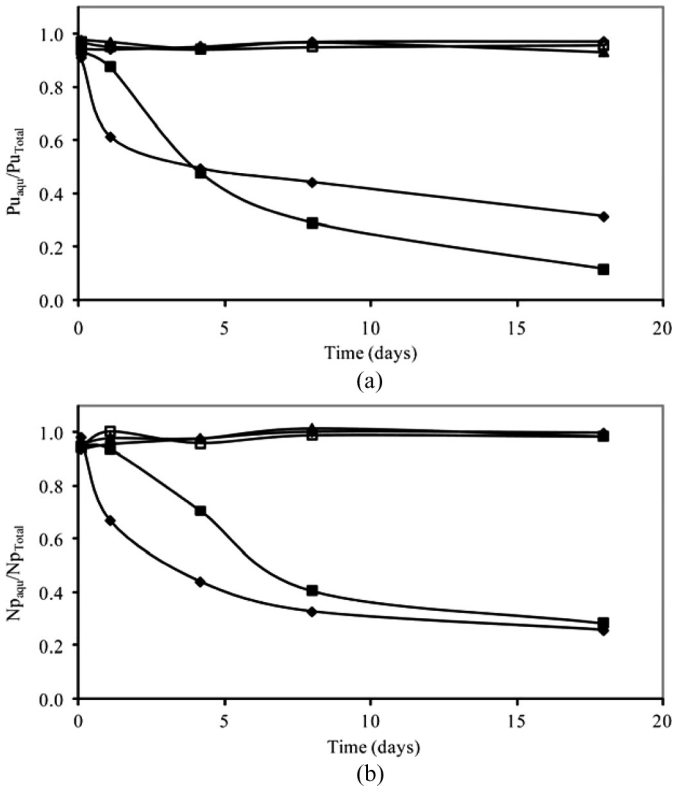

FIG. 1. Fractions of aqueous Np (top) and Pu (bottom) in HEDPA solutions after filtration with 30 k MWCO filters. Symbols: pH 4 (◆), pH 6 (■), pH 8 (▲), pH 9 (◇), pH 11 (□). System Parameters: [HEDPA] = 5 mM; [Np(V)] = 9.4 μM; [Pu(V)] = 1.9 μM; [NaCl] = 1.0 M. Error bars not shown for clarity; average $2\sigma = 4\%$.

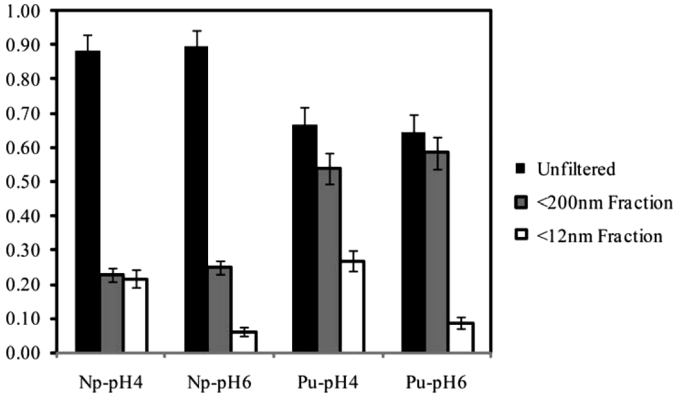

FIG. 2. Fractions of Pu and Np remaining in 5 mM HEDPA solutions at pH 4 and pH 6 after filtration with 100 k MWCO (200 nm) and 30 k MWCO (12 nm) filters after 18 days, in comparison with those of unfiltered. System Parameters: [HEDPA] = 5 mM; [^{237}Np(V)] = 9.4 μM; [^{242}Pu(V)] = 1.9 μM; [NaCl] = 1.0 M. 2σ error propagated from counting statistics.

found to be facilitated by relatively high (>0.1 M) sodium concentrations (3).

Sorption of Np(V) and Pu(V) to Boehmite in the Absence of HEDPA

The pH dependant sorption of Np and Pu to boehmite is shown in Fig. 3. Generally, the sorption of both Np and Pu increased with increasing pH. Sorption edges for Pu(V) and Np(V) (defined as the point at which 50% is sorbed) occurred at approximately pH 6.6 and 8.0, respectively, in good agreement with previous studies examining Np(V)/Pu(V) sorption to metal oxides (8,10,13,14,18,20,21). The sorption edge and sorption behavior in general for Pu(V) in 1.0 M NaCl or 1.0 M $NaClO_4$ are quite similar, suggesting that there is little effect of chloride on the sorption behavior in 1.0 M ionic strength solutions and that the perchlorate medium did not prevent autoreduction of Pu(VI) to Pu(V) as observed in 1.0 M NaCl.

At low pH values, the boehmite surface hydroxyl sites are protonated resulting in an overall positive surface charge. Within this pH region, NpO_2^+ and PuO_2^+ are the predominant species. Repulsion between the free dioxycations and the positively charged surface limits sorption of Np and Pu in low pH suspensions. As the pH increases, boehmite surface hydroxyl sites deprotonate resulting in a decrease in the net positive surface charge. As the pH approaches and exceeds the pzse (8.1) the surface generated a net negative surface change. Therefore, the cationic NpO_2^+ and PuO_2^+ species are attracted to the negative surface and sorption increases. At higher pH values it is noteworthy that hydrolysis of Np(V) and Pu(V) starts to occur and gradually becomes significant—about 50% of Np(V) or Pu(V) would be hydrolyzed around pH 9 to 10 if estimated by using the first hydrolysis constants $\left(\log \beta_{11}^*\right)$ of −8.98 for Np(V) (22) and −9.7 for Pu(V) (23), respectively. The extent of hydrolysis in the presence of mineral solids could be even higher than this estimation. As shown by the study of Np(V) sorption by hematite (20), the hydrolysis of NpO_2^+ on the mineral surface occurs approximately 2 pH units lower that in solution, likely due to relatively high concentration of hydroxide sites on the mineral surface. The hydrolysis of Np(V) and Pu(V) with increasing pH was coincident with the transition of the mineral surface from a net positive surface charge to a net negative surface charge. This allows for greater interaction between cationic NpO_2^+/PuO_2^+ and neutral $NpO_2OH(aq)/PuO_2OH(aq)$ species with the neutral or negatively charged mineral surface as shown in Fig. 3.

It is important to note that possible formation of precipitates was observed in boehmite free control solutions as discussed above (particularly for Pu). The formation of precipitates or surface precipitates cannot be explicitly ruled out in these data. However, as discussed above, precipitation of Np or Pu was not observed within the first 24 hours of the experiment (as demonstrated by a constant aqueous phase concentration). Furthermore, kinetic sorption experiments in the presence of boehmite indicated that sorption reached greater than 90% of the observed equilibrium sorption condition within one hour. Therefore, it appears that sorption occurs at a faster rate than precipitation was observed. From these observations it can be assumed that sorption of Np and Pu should be the dominant process removing Np and Pu from the aqueous phase as opposed to precipitation. This is further supported by the observation that the fraction of Np and Pu remaining in solution of boehmite-free controls was greater than that remaining in solution in the presence of boehmite. This indicates that precipitation cannot be the only mechanism influencing the systems at high pH. To this end, consideration of discrete Np and Pu precipitates cannot be explicitly ruled out in the high pH systems but does not appear to be a dominant process. Therefore, the discussion of the effects of HEDPA on Np and Pu sorption to boehmite below will consider both sorption/desorption and precipitation/dissolution processes.

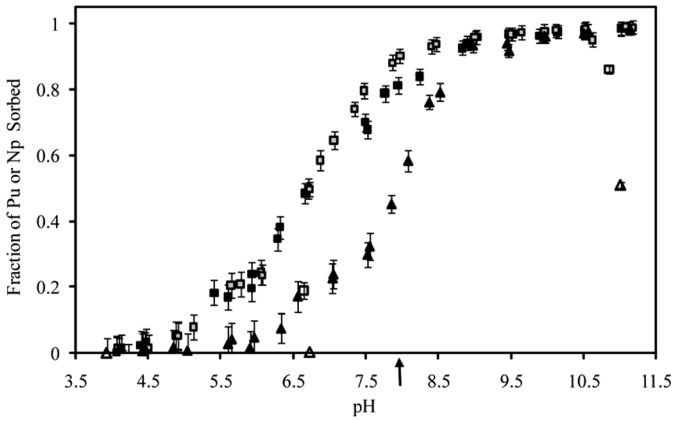

FIG. 3. Sorption of Pu(V) (■,□) and Np(V) (▲) on boehmite after 10 days, in the absence of HEDPA. Open symbols represent boehmite-free control solutions. Background solution was 1 M NaCl (■) or 1 M $NaClO_4$ (□). The bold arrow indicates the boehmite point-of-zero-salt-effect. Additional solution conditions: [γ-AlOOH] = 660 mg L^{-1}; [Pu(V)] = 2.1 μM; [Np(V)] = 10.6 μM.

Effect of HEDPA on Sorption of Np and Pu on Boehmite

Data describing the effect of HEDPA on Pu and Np sorption to boehmite are shown in Figs. 4 and 5. For comparison, the data from Fig. 3 describing steady-state Pu and Np sorption to boehmite in the absence of HEDPA are re-plotted using a smoothed dashed line in Figs. 4 and 5, respectively. Generally, for both Np and Pu systems the addition of HEDPA enhances Np and Pu sorption to the solid phase at low pH values and reduces the sorption of Np and Pu at high pH values as compared with the HEDPA-free systems. However, notable differences

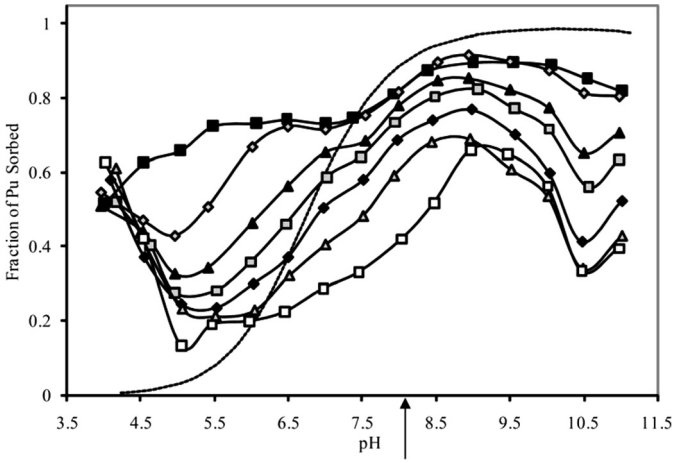

FIG. 4. Effect of HEDPA on Pu sorption to boehmite (γ-AlOOH). For comparison, a smoothed dashed line representing data from Fig. 3 showing steady state distribution (10 day equilibrium) of Pu without HEDPA present is shown. The bold arrow indicates the boehmite point-of-zero-salt-effect. Symbols: 0.1 days (■), 1 day (◇), 8 days (▲), 15 days (□), 30 days (◆), 60 days (▲), 97 days (□). System parameters: [HEDPA] = 5.4 mM; [γ-AlOOH] = 600 mg L^{-1}; [NaCl] = 1.0 M; $[Pu(V)]_{initial}$ = 1.9 μM. Error bars removed for clarity, average $2\sigma = 2\%$ propagated from counting statistics. The bold arrow indicates the boehmite point-of-zero-salt-effect. Solid lines are to aid in visualization of the data and do not represent a model fit.

between the Np and Pu systems appear in the data. In the presence of HEDPA and after extended equilibration time periods, the fraction of Pu sorbed was lower than the fraction of Np sorbed at similar pH values. To aid in comparison of the Pu and Np datasets, the results describing sorption at selected pH values from Figs. 4 and 5 were re-plotted in Fig. 6 as a function of reaction time. The fraction of Pu sorbed decreased at most pH values during the 100 days of the experiment. The fraction of Np sorbed changes little over a longer (~200 day) time period. The increased aqueous phase concentrations of Pu at pH 4.5–6.5 and above pH 8 suggest the formation of soluble Pu(IV/V)-HEDPA complexes. The relative similarity of Np sorption behavior at high pH in the presence and absence of the ligand indicate that Np probably remains in the pentavalent oxidation state throughout these experiments. The presence or absence of Np(V) – HEDPA complexes cannot be confirmed based on these results. The addition of HEDPA clearly influences the partitioning of Np and Pu relative to the HEDPA-free

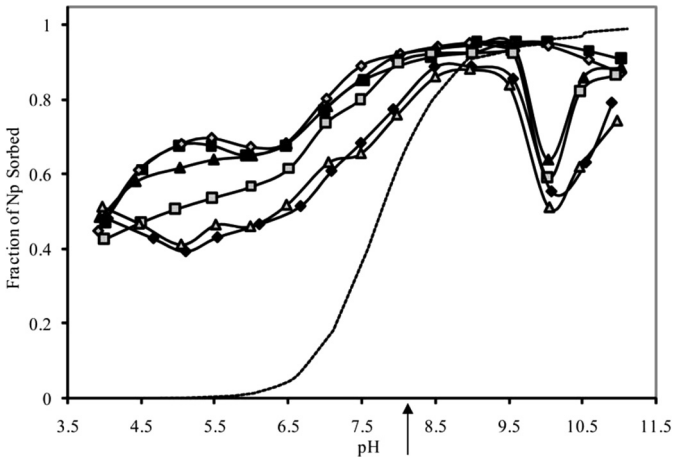

FIG. 5. Effect of HEDPA on Np sorption to boehmite (γ-AlOOH). For comparison, a smoothed dashed line representing data from Fig. 3 showing steady state distribution (10 day equilibrium) of Np without HEDPA present is shown. Symbols: 0.1 days (■), 1 day (◇), 7 days (▲), 21 days (□), 102 days (◆), 135 days (▲). System parameters: [HEDPA] = 5.4 mM; [γ-AlOOH] = 600 mg L^{-1}; [NaCl] = 1.0 M; $[Np(V)]_{initial}$ = 9.4 μM. Error bars removed for clarity, average $2\sigma = 2\%$ propagated from counting statistics. The bold arrow indicates the boehmite point-of-zero-salt-effect. Solid lines are to aid in visualization of the data and do not represent a model fit.

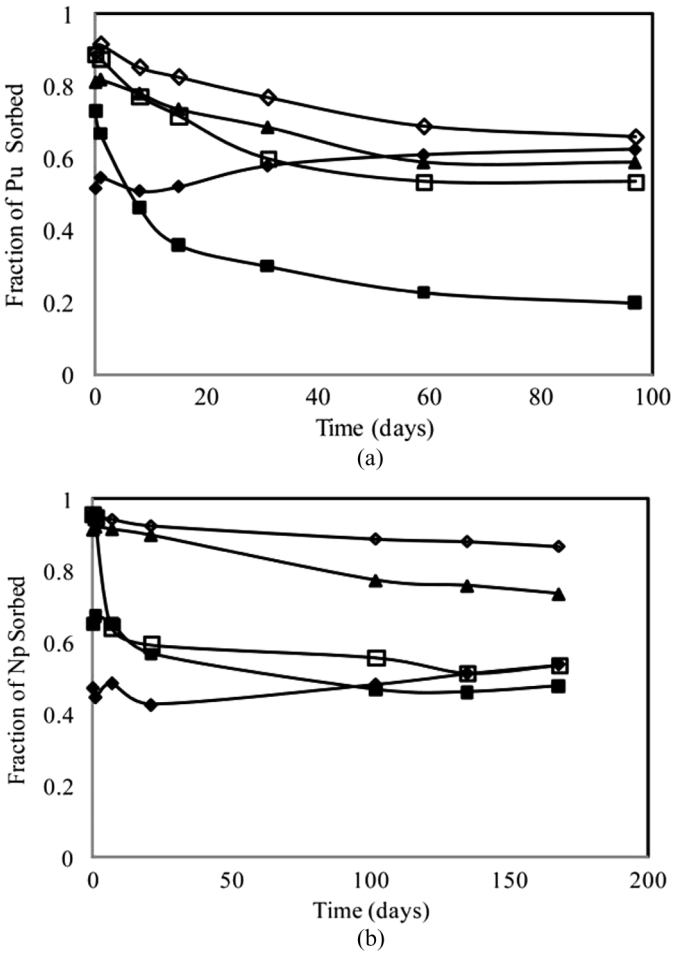

FIG. 6. Effect of HEDPA on Np and Pu sorption to boehmite (γ-AlOOH) versus time. Selected data at constant pH values shown in Figs. 4 and 5 at fixed pH values has been replotted-versus time for comparison (symbols representing the data at different time are the same as in Figs. 4 and 5).

systems. The predominant factors influencing these systems are:

1. dissolution of boehmite solids promoted by HEDPA,
2. sorption of Np and Pu by boehmite as free cationic, hydrolyzed, or HEDPA complexed species, and
3. precipitation of Np:HEDPA or Pu:HEDPA colloids as discussed above and shown in Figs. 1 and 2.

The possibility of Pu(V) reduction to Pu(IV) also must be considered. However, experimental evidence verifying this reduction is not included as part of this study. Each of these factors will be discussed below as they apply to the data shown in Figs. 4 and 5.

A brief discussion of the results from previous studies examining HEDPA-promoted boehmite dissolution (3) must be considered when examining the Np and Pu partitioning data presented below. In a study of the partitioning of U(VI) on boehmite in the presence of HEDPA (3), the ability of HEDPA to dissolve boehmite was examined under conditions similar to those used in this work (5 mM HEDPA, 1 M NaCl, 600 mg L^{-1} boehmite). It was found that the formation of Al-HEDPA complexes and $Al(OH)_4^-$ promotes boehmite dissolution in acidic and basic pH regions, with maximum boehmite dissolution occurring at pH 4 and 11 (3). As the pH increased from pH 4 or decreased from pH 11, the Al concentration decreased monotonically until achieving minimum at pH 7.5. With respect to the influence of dissolution on the sorption of Np and Pu as discussed below, it is reasonably assumed that dissolution of one Al surface site by HEDPA results in the exposure of another site that may be available for sorption. Complete dissolution of a 600 mg L^{-1} (0.01 M as Al^{3+}) boehmite suspension did not occur in 5 mM HEDPA within 135 days (3). Additionally, a 1:1 Al:HEDPA solid phase with a molar ratio of 1:1 Al:HEDPA was observed across the pH range 6 to 9 (3). Therefore, the effects of the dissolution of boehmite and possible coprecipitation of the actinides with Al:HEDPA precipitates must be considered.

Clearly, these ternary HEDPA-actinide-boehmite systems are particularly complex. To aid in discussion, the effects of HEDPA amendment on Np and Pu partitioning to boehmite were defined by distinct pH regions as discussed in detail below.

pH Region from 4.0 to 5.5

Amendment of a Pu-boehmite suspension with HEDPA promoted rapid sorption of Pu below the "HEDPA-free" sorption edge (pH range 4.0 to 7.5) within the first 2 hours (Figs. 4 and 5). This was followed by a two step desorption process where initial rapid desorption was observed in the first 15 days, followed by slow desorption for the remainder of the experiment. After 30 days the fraction of aqueous Pu was greater in 5 mM HEDPA than the HEDPA-free system at all pH values above 5.5.

Immediately after amendment with HEDPA, Np and Pu partitioning are similar consistent with the expected similar behavior of pentavalent actinides. However, some subtle differences were observed that may indicate Pu(V) reduction to Pu(IV). As shown in Fig. 6, the fraction of Np sorbed after addition of HEDPA shows relatively little change over time compared with the Pu dataset. Additionally, the fraction of Np sorbed was much greater than that of Pu at extended times. This situation could arise from a kinetic limitation of the detachment of Np:HEDPA complexes from the mineral surface, a difference in the oxidation state distribution, or in the nature of the complexes formed within the two systems. Assuming Np remains in the pentavalent state, it is conceivable that reduction of Pu(V) to Pu(IV) could explain these differences.

The decrease in aqueous Np and Pu concentrations at low pH values following the addition of HEDPA may be, in part, due to precipitation of Np:HEDPA or Pu:HEDPA colloids as described above. Interestingly, the aqueous concentration of Np and Pu were higher in the boehmite suspensions than in the boehmite-free control solutions. After 18 days at pH 4, less than 25% of the Np or Pu was soluble in the control experiments (Fig. 1). However, the data in Figs. 4 and 5 show that after 15 days 48% of the Pu was soluble and after 21 days 58% of the Np was soluble. In the presence of boehmite, the concentration of HEDPA available for complexation with Np or Pu is likely decreased due to sorption of HEDPA to the mineral surface and complexation with dissolved Al(III). Previous studies indicated that sorption of HEDPA is similar to that of other anionic species where high degrees of sorption are observed at low pH and the fraction sorbed decreases with increasing pH (24). Powell et al. (25) observed a maximum of 20% sorption of HEDPA to boehmite across a wide pH range under similar experimental conditions. Additionally, complexation of HEDPA by Al during boehmite dissolution may also decrease the amount of free HEDPA available to complex Np or Pu. There is some disagreement in the reported Al-HEDPA stability constants reported in the literature (26,27). However, using either set of stability constants, the expected concentration of soluble Al in the presence of 5 mM HEDPA could result in complexation of between 20% to 100% of the available HEDPA. Therefore, in the presence of boehmite, Np:HEDPA and Pu:HEDPA colloids may not have formed to the extent observed in boehmite-free controls due to the decreased "available" concentration of HEDPA.

The partitioning of Np and Pu at low pH may also be influenced by sorption of ternary Np:HEDPA and Pu:HEDPA surface complexes. Ternary surface complexes with HEDPA could be present if one phosphonic group of HEDPA binds the surface (≡S−OH) while the other binds

Np or Pu. Schindler (28) has characterized these complexes as type A and type B complexes as described below. A type B surface complex can be envisioned as HEDPA acting as a bridging ligand between the surface and Np or Pu as shown in the generalized reaction below.

$$\equiv S-OH + An^{x+} + LH_y^{-4} \Leftrightarrow ([\equiv S-LH_x-An]^{x+y-3} + OH^-$$

It is noteworthy that type B complexes can form with polydentate ligands, such as HEDPA. Therefore, if reduction of Pu(V) to Pu(IV) occurs as proposed above and a bidentate complex results, type B complexes with HEDPA are less probable. This would lead to an increase in the aqueous Pu concentration as is seen in Fig. 4. At high pH values where the cationic metal species may be attracted to the negatively charged surface, a type A complex could form through metal-bridging as:

$$\equiv S-OH + An^{x+}LH_y^{y-4} \Leftrightarrow ([\equiv SO^- - An - LH_y]^{x+y-5} + H^+$$

Formation of ternary surface complexes in which bonding with the surface occurs either through the metal (metal-bridging) or ligand (ligand-bridging) have been proposed to describe the partitioning of trace metals to surfaces that contain adsorbed ligands (29–31). There is a growing body of spectroscopic evidence describing these two types of ternary complexes, including recent spectroscopic studies on the effect of soil fulvic acid on Ni sorption to boehmite (32). The ligand-bridging complex dominated at low pH conditions while under high pH conditions both metal-bridging ternary complexes as well as binary metal-surface complexes are possible (32). The sorption behavior of the complex is generally similar to the sorption behavior of the bridging species. Therefore, in systems with low pH values where sorption of HEDPA is stronger than sorption of Np or Pu, an HEDPA-bridging ternary surface complex would be expected. However, the formation of such a complex is speculative and must be verified through future spectroscopic measurements.

pH Region from 5.5 to 9.0

The addition of HEDPA to the Pu-boehmite suspensions at pH 5.5 to 7.5 resulted in an increase in the fraction of Pu sorbed within the first 2 hours. Minimal changes were observed within the first 2 hours for systems at pH 7.5 to 9.0. However, during the next 97 days the fraction of the sorbed Pu decreased across the entire pH range. Generally, the fraction of Pu sorbed increased as the pH increased from 5 to 9. Similar results were observed in the Np system. However, more Np was sorbed in 5 mM HEDPA than in HEDPA-free systems at circum-neutral pH values. At all pH values lower than 8.5, the addition of HEDPA enhanced sorption of Np.

Similar to the low pH systems, the partitioning behavior in the circumneutral pH range may be influenced by precipitation of Pu:HEDPA and Np:HEDPA colloids, sorption reactions, and boehmite dissolution. Additionally, coprecipitation of Np and Pu with Al:HEDPA solids that form across the pH range 6 to 9 must also be considered. The available data do not allow explicit identification of the dominant processes. However, the observed increase in the aqueous concentration of both Np and Pu are not consistent with the precipitation of An:HEDPA and Al:HEDPA colloids. Therefore, two possible mechanisms are proposed which may explain the increasing Np and Pu concentration over time after HEDPA amendment,

1. dissolution of discrete Np and Pu precipitates and
2. binary and ternary sorption processes.

If discrete Np and Pu precipitates are formed as discussed above then the dissolution of these precipitates by HEDPA would result in an increase in the aqueous Np and Pu concentrations as observed in Figs. 4 and 5. Based on the sorption kinetics discussed above it is proposed that the formation of discrete Np and Pu precipitates is minimal in systems containing boehmite. However, additional supporting data for this proposal is provided by boehmite-free control solutions amended with HEDPA. The boehmite-free control solutions discussed above indicated a loss of Np and Pu in high pH systems. After amending these systems with 5 mM HEDPA, Np and Pu were quantitatively solubilized at pH 7 and 11 within 8 days. Therefore, if Np and Pu precipitates are formed, dissolution promoted by HEDPA will have occurred within 8 days. The data in Figs. 4 and 5 indicated that the desorption process occurs over 97 days indicating that dissolution of Np and Pu precipitates is likely not controlling the behavior of Np and Pu in these systems.

Therefore, the sorption processes and boehmite dissolution are proposed to be the dominant processes across the pH range 5.5 to 9.0. Thermodynamic data describing Np:HEDPA and Pu:HEDPA complexes are unavailable at present. However, studies of U(VI):HEDPA complexation showed a series of anionic species with increasingly higher charges dominating the U(VI) speciation at high pH values (7). If the Np(V):HEDPA, Pu(V):HEDPA, and possibly Pu(IV):HEDPA complexes are similarly anionic, desorption due to electrostatic repulsion would be expected as the pH increased and an overall negative surface charge developed above pH ~8.5, as observed in Figs. 4 and 5.

Since Np, Pu, and HEDPA all sorb to boehmite at circumneutral pH values, the formation of ternary surface complexes as well as binary metal-surface complexes are possible in this region. As discussed above, Strathmann and Myneni (32) observed both metal-bridging boehmite-Ni-fulvic acid ternary complexes as well as binary

Ni-boehmite surface complexes at high pH conditions. Fitts et al. (33) observed both binary and ternary complexes in Cu(II)-glutamate-γ-Al_2O_3 suspensions at high pH conditions and concluded that the binary Cu(II)-aluminol surface complex was dominant. Similarly, the increased sorption of Np and Pu with increasing pH as shown in Figs. 4 and 5 is indicative of complexation of Np and Pu with the surface. Within this pH range in HEDPA-free solutions, both Np and Pu are predominantly sorbed. Therefore, the sorption behavior within this pH range is proposed to be due to the sorption of Np and Pu either as binary surface complexes or as Np:HEDPA and Pu:HEDPA surface complexes. Again, the formation of such surface complexes is speculative and must be verified with spectroscopic data.

pH Region above 9.0

Above pH 9.0, both Np and Pu were predominantly associated with the solid phase in HEDPA free suspensions (Figs. 4 and 5). This could indicate sorption or possible precipitation of insoluble hydroxides. However, as discussed above, the influence of discrete Np and Pu precipitates is not expected to be significant in this system. Therefore the predominant factors affecting Np and Pu partitioning in this range are sorption reactions and boehmite dissolution. It is noteworthy that the change in Np and Pu partitioning in this system was concurrent with significant boehmite dissolution by HEDPA (3). The rate of Np and Pu leaching into the aqueous phase was consistent with the rate of boehmite dissolution observed in previous work, thus suggesting boehmite dissolution was an influencing factor across this pH range (3).

The fraction of Np and Pu sorbed decreased with increasing pH between pH 8.5 and 10. Within this pH region, the surface transitions from a net positive surface charge to a net negative surface charge. Again assuming anionic Np:HEDPA and Pu:HEDPA complexes form at these pH levels, the anionic complexes will be repelled by the negative surface and partition into the aqueous phase. This is consistent with a decreasing sorption of Np and Pu across this pH range. At extended time periods above pH 10.0 and 10.5, for Np and Pu respectively, the partitioning trend reversed and the fraction of Np and Pu sorbed increased with increasing pH. In this pH region it is reasonable to assume that some competition between HEDPA and hydroxide ions for Np and Pu will occur. However, without available stability constants for Np:HEDPA and Pu:HEDPA species, quantitative distribution between HEDPA and hydroxide complexes cannot be calculated. Furthermore, as shown in Fig. 3, complete sorption of Np and in HEDPA-free systems occurs above pH 9.5 where the predominant species are $AnO_2OH(aq)$ and $AnO_2(OH)_2^-$ (22,23). Therefore the increase in sorption observed above pH 10 is likely indicative of sorption of An-hydroxide complexes rather than leaching of An:HEDPA complexes. This effect was much more pronounced for Np relative to Pu. Regardless of the primary influence, HEDPA promotes desorption of both Np and Pu from the solid phase relative to a ligand free system.

CONCLUSIONS

This work has shown that the addition of HEDPA affects the sorption of Np and Pu to boehmite in a complex manner. Np and Pu partitioning appears to be primarily affected by the formation of Np:HEDPA and Pu:HEDPA complexes, the dissolution of boehmite promoted by HEDPA, the precipitation of Np:HEDPA and Pu:HEDPA colloids in low pH regions, and possibly reduction of Pu(V) to Pu(IV). At low pH values, HEDPA initially promotes sorption of Np and Pu, relative to the minimal sorption observed in ligand free systems. This effect is due to the sorption of aqueous Np:HEDPA and Pu:HEDPA complexes and/or precipitation of Np:HEDPA and Pu:HEDPA solids. However, as the systems equilibrate for greater than 90 days, both Np and Pu leach back into the aqueous phase in the pH range 5.5 to 9.0. The fraction of Np leached back into solution over time is considerably lower than the fraction of Pu.

Generally the fraction of Np sorbed was greater in the presence of HEDPA when compared with the HEDPA free system across the pH region 5.5 to 9.0 even after 135 days. Following the addition of HEDPA, the fraction of Pu sorbed was less than that observed in the absence of HEDPA at pH 5.5 to 9.0 after 90 days. Sorption at circumneutral pH values is proposed to be due to the formation of ligand bridging and metal-bridging Np-HEDPA and Pu-HEDPA ternary surface complexes. At pH greater than 9, HEDPA leaches Np and Pu from the solid phase, relative to an HEDPA free system. Within this basic pH range, Np and Pu partitioning are proposed to be influenced by both HEDPA and hydroxide complexes as well as boehmite dissolution.

The enhanced solubilization of Pu relative to Np under acidic and basic conditions observed in this work could also indicate that the reduction of Pu(V) to Pu(IV) may be occurring in these systems. Reduction of Pu(V) to Pu(IV) facilitated by stronger Pu(IV)-HEDPA complexes and a more favorable reduction potential may explain the observed differences between Np and Pu behavior. However, experimental data verifying this reduction is not available. If reduction of Pu(V) to Pu(IV) were occurring, it is interesting that this effect is associated with an increase in the aqueous phase concentration of Pu. This may indicate a structural rearrangement of the Pu(IV):HEDPA complex relative to Pu(V):HEPDA complexes which hinders the formation of type A and type B surface

complexes. Presumably this would be due to the formation of a bidentate Pu(IV):HEDPA complex which will prevent the formation of a type B surface complex.

These results show that the use of a strong complexing agent such as HEDPA to reduce the volume of aluminum bearing sludges may cause significant leaching of Np and Pu. It is unlikely that the precipitation of Np:HEDPA and Pu:HEDPA colloids at low pH levels can be exploited during waste treatment processes as the increased phosphate concentration within the solids will be problematic during the vitrification process. At high pH levels, HEDPA was found to significantly enhance the solubility of aluminum and therefore may accomplish significant waste volume reduction. However, some leaching of Np and Pu was observed. Additional experiments at high pH levels are required to determine whether significant fractions of Np and Pu will remain associated with the solid phase, as the trend in this work shows.

It is important to note that many of the proposed mechanisms in this work are not supported by spectroscopic data, hence they allow for other possible interpretations. Furthermore, the lack of available thermodynamic data describing Np:HEDPA and Pu:HEDPA complexes restricts the interpretation of these data. Future efforts should focus on spectroscopic characterization of ternary metal-ligand-mineral systems and further quantification of solution thermodynamics. Only with these data can reliable and accurate predictions of actinide behavior in natural and engineered systems be achieved.

ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences and Office of Biological and Environmental Research of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 at the Lawrence Berkeley National Laboratory. The authors also acknowledge the helpful comments provided during the review of this manuscript.

REFERENCES

1. Closing the Circle on the Splitting of the Atom: The Environmental Legacy of Nuclear Weapons Production in the United States and What the Department of Energy is doing about it. DOE/EM-0266 (1996).
2. Kupfer, M.J. (1995) Disposal of Hanford Site Tank Wastes. In: *Chemical Pretreatment fo Nuclear Waste for Disposal*, Shultz, W.W.; Horwitz, E.P., eds.; Plenum Press: New York, 25–37.
3. Powell, B.A.; Rao, L.; Nash, K.L. (2008) Examination of Uranium(VI) Leaching during ligand promoted dissolution of waste tank sludge surrogates. *Separation Science and Technology*, 15: 3798–3812.
4. Reed, W.A.; Rao, L.; Zanonato, P.; Garnov, A.Yu.; Powell, B.A.; Nash, K.L. (2007) Complexation of U(VI) with 1-hydroxy-1,1-ethanediphosphonic acid (HEDPA). *Inorg. Chem.*, 46: 2870–2876.
5. Nash, K.L.; Gelis, A.V.; Jensen, M.P.; Bond, A.H.; Sullivan, J.C.; Rao, L.; Garnov, A.Yu. (2002) Actinides in alkaline media: dissolution, mineral associations, and speciation in Hanford Waste tank sludge simulants. *J. Nucl. Sci. Tech., Supplement*, 3: 512–515.
6. Bond, A.H.; Nash, K.L.; Gelis, A.V.; Sullivan, J.C.; Jensen, M.P.; Rao, L. (2001) Plutonium mobilization and matrix dissolution during experimental sludge washing of bismuth phosphate, redox, and purex waste simulants. *Sep. Sci. Tech.*, 36: 1241–1256.
7. Allard, B.; Olofsson, U.; Torstenfelt, B.; Kipatsi, H.; Andersson, J. (1982) Sorption of Actinides in Well-Defined Oxidation States on Geologic Media. In: *Scientific Basis for Radioactive Waste Management–V*, Lutze, W., ed.; Elsevier Science Pub. Co., New York, 775–782.
8. Righetto, L.; Bidoglio, G.; Marcandalli, B.; Bellobono, I.R. (1988) Surface interactions of actinides with alumina colloids. *Radiochim. Acta*, 44/45: 73–75.
9. Nakayama, S.; Sakamoto, Y. (1991) Sorption of neptunium to naturally-occurring iron-containing minerals. *Radiochim. Acta*, 52–3 (P1): 153–157.
10. Righetto, L.; Bidogllo, G.; Azimonti, G.; Bellobono, I. (1991) Competitive actinide interactions in colloidal humic acid-mineral oxide systems. *Environ. Sci. Tech.*, 25: 1913–1919.
11. Kung, K.S.; Triay, I.R. (1994) Effect of natural organics on Cs and Np sorption. *Radiochim. Acta*, 66/67: 421–426.
12. Tochiyama, O.; Yamazaki, H.; Mikami, T. (1996) Sorption of neptunium(V) on various aluminum oxides and hydrous aluminum oxides. *Radiochim. Acta*, 73: 191–198.
13. Del Nero, M.; Madé, B.; Bontems, G.; Clément, A. (1997) Adsorption of neptunium(V) on hydrargillite. *Radiochim. Acta*, 76: 219–228.
14. Turner, D.R.; Pabalan, R.T.; Bertetti, F.P. (1998) Neptunium(V) sorption on montmorillonite: An experimental and surface complexation modeling study. *Radiochim. Clays and Clay Minerals*, 46 (3): 256–269.
15. Choppin, G.R.; Rao, L. (1984) Complexation of pentavalent and hexavalent actinides by fluorides. *Radiochim. Acta*, 37: 143–146.
16. Orlandini, K.A.; Penrose, W.R.; Nelson, D.M. (1986) Pu(V) as the stable form of oxidized plutonium in natural waters. *Mar. Chem.*, 18: 49–57.
17. Morse, J.W.; Choppin, G.R. (1986) Laboratory studies of plutonium in marine systems. *Mar. Chem.*, 20: 73–89.
18. Sanchez, A.L.; Murray, J.W.; Sibley, T.H. (1985) Adsorption of plutonium IV and V on goethite. *Geochim. Cosmo. Acta*, 49: 2297–2307.
19. Kobashi, A.; Choppin, G.R.; Morse, J.W. (1988) A study of the techniques for separating plutonium in different oxidation states. *Radiochim. Acta*, 43: 211–215.
20. Kohler, M.; Honeymann, B.D.; Leckie, J.O. (1999) Neptunium(V) sorption on hematite (α-Fe_2O_3) in aqueous suspension: The effect of CO_2(g). *Radiochim. Acta*, 85: 33–48.
21. Powell, B.A.; Fjeld, R.A.; Kaplan, D.I.; Coates, J.T.; Serkiz, S.M. (2005) $Pu(V)O_2^+$ adsorption and reduction on synthetic goethite (α-FeOOH) and hematite (α-Fe_2O_3). *Environ. Sci. Tech.*, 37: 2107–2114.
22. Rao, L.; Srinivasan, T.G.; Garnov, A.Yu.; Zanonato, P.; Di Bernardo, P.; Bismondo, A. (2004) Hydrolysis of neptunium(V) at variable temperatures (10–85°C). *Geochim. et Cosmochim. Acta*, 68: 4821–4830.
23. Lemire, R.J.; Fuger, J.; Nitsche, H.; Potter, P.; Rand, M.H.; Rydberg, J.; Spahiu, K.; Sullivan, J.C.; Ullman, W.J.; Vitorge, P.; Wanner, H. (2001) Chemical thermodynamics of neptunium and plutonium, (edited by OECD Nuclear Energy Agency, Data Bank), Elsevier Science Publishers B.V.: Amsterdam.
24. Nowack, B.; Stone, D. (1999) The influence of metal ions on the adsorption of phosphonates onto goethite. *Env. Sci. Tech.*, 33: 3627–3633.
25. Powell, B.A.; Rao, L.; Nash, K.L.; Martin, L. (2005) Characterization of Actinides during HEDPA leaching for Aluminum Dissolution in Tank Waste Sludges. In: *Basic Science, Applications, and Technology*,

Sarrao, J.; Schwartz, A.; Antonio, M.; Burns, P.; Haire, R.; Nitsche, H., eds.; (Mat. Res. Soc. Symp. Proc. Vol. 893, Warrendale, PA), 0893-JJ07-02.

26. Lacour, S.; Deluchat, V.; Bollinger, J.; Serpaud, B. (1998) Complexation of trivalent cations (Al(III), Cr(III), Fe(III)) with two phosphonic acids in the pH range of fresh waters. *Talanta*, 46: 999–1009.
27. Gumienna-Kontecka, E.; Silvagni, R.; Lipinski, R.; Lecouvey, M.; Marincola, F.C.; Crisoni, G.; Nurchi, V.M.; Leroux, Y.; Koslowski, H. (2002) Bisphosphonate chelating agents: Complexation of Fe(III) and Al(III) by 1-phenyl-1-hydroxymethylene bisphosphonate and its analogues. *Inorg. Chim. Acta.*, 339: 111–118.
28. Schindler, P.W. (1990) Co-Adsorption of Metal Ions and Organic Ligands: Formation of Ternary Surface Complexes. In: *Mineral-Water Interface Geochemistry*, Hochella, M.F., Jr.; White, A.F., eds.; Mineralogical Society of America: Washington, DC, 281–307.
29. Davis, J.A.; Leckie, J.O. (1978) Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides. *Environ. Sci. Tech.*, 23: 1309–1315.
30. Elliott, H.A.; Huang, C.P. (1979) The adsorption characteristics of Cu(II) in the presence of chelating agents. *J. Colloid. Inter. Sci.*, 70: 29–45.
31. Benjamin, M.M.; Leckie, J.O. (1981) Conceptual model for metal-ligand-surface interactions during adsorption. *Environ. Sci. Tech.*, 15: 1050–1057.
32. Strathmann, T.J.; Myneni, C.B. (2005) Effect of soil fulvic acid on nickel(II) sorption and bonding at the aqueous-boehmite (γ-AlOOH) interface. *Environ. Sci. Tech.*, 39: 4027–4034.
33. Fitts, J.P.; Persson, P.; Brown, G.E.; Parks, G.A. (1999) Structure and bonding of Cu(II)-glutamate complexes at the γ-Al_2O_3-water interface. *J. Colloid. Inter. Sci.*, 220: 133–147.