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Author
Powell, Brian A.

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

Brian A. Powell*a, Linfeng Rao, Kenneth. L. Nashc

aClemson University, Anderson, SC 29625 USA
bLawrence Berkeley National Laboratory, Berkeley, CA 94720 USA
cWashington State University, Pullman, WA 99164 USA

*Corresponding author: email: bpowell@clemson.edu, Department of Environmental Engineering and Earth Sciences, Clemson University, Anderson, SC 29625

ABSTRACT

The effect of 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) on sorption of Np(V) and Pu(V) to synthetic boehmite (\(\gamma\)-AlOOH) was examined a function of time and pH (between 4 to 11). Sorption of both elements in boehmite suspensions (1 M NaCl, 600 mg L\(^{-1}\) boehmite) increased with increasing pH. 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: plutonium, neptunium, alumina, boehmite, 1-hydroxyethane-1,1-diphosphonic acid, HEDPA, nuclear waste

1. 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 x 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 3M NaOH, a further 50% was removed with 2.0 M HNO₃, 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 HNO₃. 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 2M
HNO₃ 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 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)₄₋₄ₓ and AnO₂(OH)₁₋₁ᵧ 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.
2. Materials and Methods

2.1 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 ($\gamma$-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.

2.2 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 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 $\alpha$-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.

2.3 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 1M 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 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 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).

### 2.4 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 NaClO₄ 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 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 (30k MWCO, Nanosep, Pall Life Sciences, estimated 12 nm pore
size). Throughout this work, the filtrate passing through a 30k MWCO filter is operationally defined
as the soluble fraction. The first 100-200 μL of 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 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
1M 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 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 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 30k 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.

2.5 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 1M 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 30k 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 100k MWCO and 30k 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.

3. Results and Discussion

3.1 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 30k MWCO filters are shown as a function of time over an 18-day period in Figure 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 Figure 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, a loss of 51% Np and 98% Pu was observed in boehmite free solutions at pH 11 and a loss of 44% Pu was observed at pH 7 (data not shown). 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. 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.

At pH 4 and 6, a significant fraction of Np and Pu were removed upon passing through a 30k 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 Figure 1 was likely due to formation of precipitates with HEDPA. After 18 days, aliquots of each suspension were passed through either 100k MWCO (estimated 200nm pore size) or 30k MWCO centrifugal filters. The fraction of total Np and Pu in the filtrate is shown in Figure 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 found to be facilitated by relatively high (> 0.1 M) sodium concentrations (3).

### 3.2 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 Figure 3. Generally, 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 NaClO₄ 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, boehmite surface hydroxyl sites are protonated resulting in an overall positive surface charge. Within this pH region, NpO₂⁺ and PuO₂⁺ 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, 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 (log $\beta_{11}$) 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 NpO₂⁺ on the mineral surface occurs approximately 2 pH units lower than 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$_2$OH(aq)/PuO$_2$OH(aq) species with the neutral or negatively charged mineral surface as shown in Figure 3.

3.3 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 Figures 4 and 5. For comparison, the data from Figure 3 describing steady-state Pu and Np sorption to boehmite in the absence of HEDPA are re-plotted using a smoothed dashed line in Figures 4 and 5, respectively. Generally, for both Np and Pu systems, the addition of HEDPA enhances the of Np and Pu partitioning to the solid phase at low pH values and reduces the sorption of Np and Pu partitioning at high pH values as compared with the HEDPA-free systems. However, notable differences between the Np and Pu systems appear in the data. In the presence of HEDPA and after extended equilibrating time periods, the fraction of Pu sorbed was lower than the fraction of Np sorbed at similar pH values. This could suggest a higher affinity of HEDPA for Pu in the aqueous phase, than is seen for Np. Assuming that the partitioning behavior of pentavalent actinides will be similar and that Np remained as Np(V) throughout the experiment, the difference in behavior between the Np(V) system and the Pu system (initially as Pu(V)) could indicate that Pu(V) to Pu(IV) is more readily reduced under most circumstances, more so in the presence of strong chelating agents.

To aid in comparison of the Pu and Np datasets, results describing sorption at selected pH values from Figures 4 and 5 were re-plotted in Figure 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 probably suggests the formation of soluble Pu(IV)-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
Addition of HEDPA clearly influences the partitioning of Np and Pu relative to the
HEDPA-free 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 in section 3.1 and shown in Figures 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 Figures 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)_{3}^{-} 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. 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. The effects of HEDPA amendment on Np and Pu partitioning were defined by distinct
pH regions as discussed in detail below.

3.3.1 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 (Figures 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. Preliminary experiments also indicated the initial
sorption of HEDPA, Np, and Pu to boehmite was rapid relative to the rate of change observed in Np
and Pu partitioning shown in Figures 4 and 5. Therefore, the reaction rates within these multi-
component systems are likely surface controlled. When examining HEDPA promoted boehmite
dissolution, Powell et al., (3) proposed that detachment of the Al:HEDPA may be a rate limiting step
when examining boehmite dissolution. If this mechanism of surface control is important in the
Pu:HEDPA and Np:HEDPA systems examined here, the detachment of Al:HEDPA species could
also control sorption of Np and Pu through occupation of available sorption sites.

The effect of HEDPA on Np sorption to boehmite is similar to its effect in the Pu system,
consistent with the expected similar behavior of pentavalent actinides. However, the effects were
more subtle and the reaction rates appeared considerably slower. As shown in Figure 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 either 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. Similar to the Pu
system, rapid sorption of Np was observed at pH values below the HEDPA-free sorption edge
immediately following addition of HEDPA (pH range 4 to 9, Figure 6). Following this initial uptake,
Np began to desorb of neptunium desorbed as the experiment progressed.

The decrease in aqueous Np and Pu 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 (Figure 1). However, the data in Figures 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).
Therefore, Np:HEDPA and Pu:HEDPA colloids may not be precipitated due to the decreased
“apparent available” concentration of HEDPA.
The partitioning of Np and Pu at low pH may also be influenced by partitioning of
Np:HEDPA and Pu:HEDPA complexes through the 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 (24) 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.

≡S-OH + An
x+ + LH
y-4 \[≡S--LH
x--An+x+y-3 + OH^-\]

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 Figure 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:

≡S-OH + An
x+ LH
y-4 \[≡SO--An-LH
x+y-5 + H^+\]

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 (25-27). 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 (28). 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 (28). 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,
formation of such a complex is speculative and must be verified through future spectroscopic
measurements.

3.3.2 pH region from 5.5 to 9.0. Across the pH range 5.5 to 9.0, a change in the behavior of
Np and Pu occurred relative to the low pH systems. 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 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, 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 colloids. Therefore,
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 Figure 5 and 6.

Since Np, Pu, and HEDPA all sorb to boehmite at circumneutral pH values, formation of ternary surface complexes as well as binary metal-surface complexes are possible in this region. As discussed above, Strathmann and Myneni (28) 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. (29) observed both binary and ternary complexes in Cu(II)-glutamate-γ-Al₂O₃ 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 Figure 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 sorption of Np and Pu either as binary surface complexes or as Np:HEDPA and Pu:HEDPA surface complexes. Again, formation of such surface complexes is speculative and must be verified with spectroscopic data.

3.3.3 pH region above 9.0. Above pH 9.0, both Np and Pu were predominantly associated with the solid phase in HEDPA free suspensions (Figures 4 and 5). This could indicate sorption or possible precipitation of insoluble hydroxides. Following addition of HEDPA, both Np and Pu slowly leached into the aqueous phase. No precipitation of any metal:HEDPA solids was observed in this pH range in this or the previous work (3). Furthermore, the presence of HEDPA appeared to prevent precipitation of Np or Pu hydrolysis products above pH 8 (Figure 1). 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 a major 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. This effect was considerably more pronounced for Np than Pu. This behavior may represent a change in the solid phase speciation from Np/Pu:HEDPA complexes to Np/Pu:hydroxide complexes or it may represent reduction of Pu(V) to Pu(IV). Unfortunately, without reliable stability constants for Np:HEDPA and Pu:HEDPA complexes, a quantitative distribution between HEDPA and hydroxide complexes cannot be calculated. However, the decrease in sorption across the pH range 8.5 to 10.0 indicates that Np:HEDPA complexes partition to the aqueous phase as the pH increases. Furthermore, as shown in Figure 3, complete sorption of Np in HEDPA-free systems occurs above pH 9.5 where the predominant species are NpO\textsubscript{2}OH(aq) and NpO\textsubscript{2}(OH)\textsubscript{2}\textsuperscript{−} (22). Therefore the increase in sorption observed above pH 10 is likely indicative of sorption of Np-hydroxide complexes rather than leaching of Np:HEDPA complexes. This effect was much more pronounced for Np relative to Pu. It is possible that the tendency of Pu(V) toward hydrolysis is weaker than that of Np(V), since the “upper” limit of the Pu(V) hydrolysis constant is estimated to be -9.7 (23) while the hydrolysis constant of Np(V) is determined to be -8.98 (22). However, more definitive explanations for the difference in the behavior of Np(V) and Pu(V) in high pH regions cannot be made until relevant data on the hydrolysis of Pu(V) become available. Stronger sorption of Np relative to Pu in alkaline pH suspensions is consistent with the general trend observed in the sorption dataset indicating that more Pu than Np is leached into the aqueous phase. As discussed above, this may be due to reduction of
Pu(V) to Pu(IV) followed by solubilization of Pu(IV):HEDPA complexes. Regardless of the primary influence, HEDPA promotes desorption of both Np and Pu from the solid phase relative to a ligand free system.

4. Conclusions

This work has shown that 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 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 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 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 that the structural rearrangement of the Pu(IV):HEDPA complex relative to Pu(V):HEPDA complexes which hinders formation of type A and type B surface complexes. Presumably this would be due to formation of a bidentate Pu(IV):HEDPA complex which will prevent 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. Furthermore, spectroscopic studies are required to verify the speculative surface complexes proposed in this manuscript.

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References


Table 1: Oxidation State Distribution of Pu in Control Solutions (1M NaCl; 1.9μM $^{242}$Pu).

<table>
<thead>
<tr>
<th></th>
<th>An(IV)</th>
<th>An(V)</th>
<th>An(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu control at pH 4$^a$</td>
<td>4% ± 3%</td>
<td>83% ± 3%</td>
<td>13% ± 4%</td>
</tr>
<tr>
<td>Pu control at pH 8$^a$</td>
<td>0% ± 4%</td>
<td>91% ± 4%</td>
<td>9% ± 5%</td>
</tr>
<tr>
<td>U(VI) stock$^b$</td>
<td>5% ± 2%</td>
<td>5% ± 1%</td>
<td>90% ± 2%</td>
</tr>
<tr>
<td>Np(V) stock$^b$</td>
<td>3% ± 1%</td>
<td>87% ± 2%</td>
<td>10% ± 3%</td>
</tr>
</tbody>
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$^a$error propagated from counting statistics
$^b$error represents standard deviation of 3 replicate measurements
**FIGURE CAPTIONS**

Figure 1: Fractions of aqueous Np (top) and Pu (bottom) in HEDPA solutions after filtration with 30k 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 2σ = 4%.

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

Figure 3: Sorption of Pu(V) (■,■) and Np(V) (▲) on boehmite after 10 days, in the absence of HEDPA. Background solution was 1M NaCl (closed symbols) or 1M NaClO4 (open symbols). 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. The bold arrow indicates the boehmite point-of-zero-salt-effect.

Figure 4: Effect of HEDPA on Pu sorption to boehmite (γ-AlOOH). For comparison, a smoothed dashed line representing data from Figure 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 2σ = 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.

Figure 5: Effect of HEDPA on Np sorption to boehmite (γ-AlOOH). For comparison, a smoothed dashed line representing data from Figure 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 2σ = 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.

Figure 6: Effect of HEDPA on Np and Pu sorption to boehmite (γ-AlOOH) versus time. Selected data at constant pH values shown in Figures 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 Figures 4 and 5).
Figure 1: Fractions of aqueous Np (top) and Pu (bottom) in HEDPA solutions after filtration with 30k MWCO filters. Symbols: pH 4 (●), pH 6 (■), pH 8 (▲), pH 9 (◇), pH 11 (□).

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Figure 3: Sorption of Pu(V) (■) and Np(V) (▲) on boehmite after 10 days, in the absence of HEDPA. Background solution was 1M NaCl (closed symbols) or 1M NaClO₄ (open symbols). 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. The bold arrow indicates the boehmite point-of-zero-salt-effect.
Figure 4: Effect of HEDPA on Pu sorption to boehmite ($\gamma$-AlOOH). For comparison, a smoothed dashed line representing data from Figure 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; $[\gamma$-AlOOH] = 600 mg L$^{-1}$; [NaCl] = 1.0 M; [Pu(V)]$_{\text{initial}}$ = 1.9 μM. Error bars removed for clarity, average 2σ = 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.
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