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

12 The effect of 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) on sorption of Np(V) and

13 Pu(V) to synthetic boehmite ($\gamma$-AlOOH) was examined a function of time and pH (between 4 to

14 11). Sorption of both elements in boehmite suspensions (1 M NaCl, 600 mg L$^{-1}$ boehmite) increased

15 with increasing pH. Sorption edges for neptunium and plutonium occurred at approximately pH 8.0

16 and 6.6, respectively. After steady state partitioning was reached, HEDPA was added to the

17 neptunium-boehmite and plutonium-boehmite suspensions. Neptunium and plutonium partitioning

18 appears to be primarily affected by the formation of soluble Np:HEDPA and Pu:HEDPA complexes,

19 the dissolution of boehmite promoted by HEDPA, and the precipitation of Np:HEDPA and

20 Pu:HEDPA colloids. The results are discussed in terms of applicability of HEDPA-promoted

21 dissolution as a waste reduction method in the treatment of sludge phases contained within high-

22 level nuclear waste storage tanks.

23

24 KEYWORDS: plutonium, neptunium, alumina, boehmite, 1-hydroxyethane-1,1-diphosphonic acid ,

25 HEDPA, nuclear waste

26

27 **1. Introduction**

28 Safe, efficient, and economical techniques are required for the treatment of high-level radioactive

29 wastes.  The nuclear wastes in the underground storage tanks at the Hanford Site in Washington

30 State, U.S.A. present an extraordinary clean-up task. Approximately 1.7 x 10$^8$ curies of radioactivity

31    are contained in 177 underground storage tanks at this site(1).  Over time the waste from spent

32    nuclear fuel reprocessing has stratified into a salt cake, a supernatant phase, and an underlying

33    sludge phase. Most of the transuranics have partitioned to the sludge phase, of which aluminum

34    oxides represent a large component. The current waste treatment strategy proposes vitrification of

35    the sludge phase followed by disposal in a geologic repository (2). However, vitrification of the

36    entire sludge phase is not economically feasible due to the large volume of the sludge and the high

37    cost of vitrification. Therefore, studies have been performed to examine the possibility of reduction

38    of the sludge volume through dissolution of the aluminum oxides with diphosphonic acids. In a

39    companion paper to this work, 1-hydroxyethane-1,1-diphosphonic acid  (HEDPA) was shown to

40    significantly enhance the solubility of Al in saturated boehmite suspensions (3).  It was also found

41    that HEDPA is capable of leaching uranium into the aqueous phase through solid phase dissolution

42    and/or the formation of U(VI):HEDPA complexes (3). Across the pH range 4 to 11, HEPDA is

43    expected to form anionic complexes based upon the stability constants reported by Reed et al. (4).

44    As the pH was increased and the boehmite surface developed a net negative charge, these anionic

45    U(VI):HEDPA complexes were repelled by the surface and remained in the aqueous phase (3). In

46    contrast to the availability of the data on the U(VI):HEDPA aqueous complexes, no studies have

47    been conducted with neptunium and plutonium, two other actinides of critical concern in nuclear

48    waste sludges.

49        Previous studies examining Np(V) leaching from simulated waste sludges with increasingly

50    aggressive solutions indicated that 25% of the Np was removed with 3M NaOH, a further 50% was

51    removed with 2.0 M $HNO_3$, and the remaining Np was removed with 0.5 M HEDPA (5). When

52    performing similar leaching experiments with a REDOX process sludge simulant (high Al content),

53    Bond et al. (6), observed 20-30% leaching of either Pu(IV) or Pu(VI) in 0.1 M $HNO_3$. However, the

54    Pu was proposed to be associated with alumina colloids based upon filtration tests (6). Significantly

55    greater leaching of Pu(IV) and Pu(VI) was observed from all simulated waste sludges using 2M

56    HNO$_3$ and 0.5 HEDPA. In that investigation, Pu was found to be a dissolved species rather than a

57    radiocolloid (6).

58         Understanding actinide partitioning to minerals in the presence of natural or synthetic

59    ligands is also necessary for the reliable prediction of hydrogeochemical behavior of the actinides.

60    Sorption to mineral surfaces is an important mechanism for retarding the subsurface migration of the

61    actinides. Aluminum oxides and oxyhydroxides are proposed to be a primary control of subsurface

62    migration. Some data are available describing Np(V) and Pu interactions with various aluminum

63    (oxyhydr)oxides (7-14). However, data describing Np and Pu sorption to mineral surfaces in the

64    presence of natural or synthetic complexing ligands are limited (8, 10, 11). In natural systems, Np

65    and Pu are typically found as hydrolyzed An(OH)$_x^{4-x}$ and AnO$_2$(OH)$_y^{1-y}$ species. The strong

66    tendency to hydrolyze and the low solubility of tetravalent actinide hydroxides may constrain the

67    aqueous phase concentrations of Np(IV) and Pu(IV). However, in oxic natural waters and in the

68    absence of strong complexants, Np and Pu are found primarily as Np(V) and Pu(V) in the aqueous

69    phase. Subsurface transport of pentavalent actinides is of particular concern because they generally

70    have a lower affinity for solid phases relative to other actinide oxidation states due to their low

71    effective charge of approximately +2.2 (15). Complexation with multidentate organic ligands, such

72    as HEDPA used in this work, may affect the partitioning of Np(V) and Pu(V) and therefore affect

73    subsurface transport rates.

74         The present study has been conducted to investigate the partitioning behavior of Np(V) and

75    Pu in HEDPA-amended synthetic boehmite suspensions. This work seeks to provide a more detailed

76    understanding of the mechanisms controlling Pu behavior than previous studies using bismuth

77    phosphate, REDOX, and PUREX waste simulants (5,6). Quantitative sorption data were obtained to

78    evaluate the applicability of HEDPA leaching as a technique to reduce the volume of the sludge

79    phases contained within the Hanford waste tanks, and examine the sorption behavior of Np(V) and

80    Pu organophosphorous complexes with regard to subsurface transport.

81

82    **2. Materials and Methods**

83    **2.1 Solid Phase Characterization**

84    The alumina used in this work was obtained from SASOL (trade name CATAPAL® B). Details

85    regarding the treatment and characterization of this material are presented elsewhere (3). The

86    alumina was found to have a predominantly amorphous character with broad XRD peaks

87    corresponding to boehmite ($\gamma$-AlOOH). The boehmite had a $N_2$(g)- BET surface area of 354 $m^2$ $g^{-1}$

88    and a point-of-zero-salt-effect of 8.1 ± 0.1.

89

90    **2.2 Chemicals and Stock Solutions of Neptunium and Plutonium**

91    HEDPA was obtained as a 70% aqueous solution (Sigma) and purified by recrystallization from

92    glacial acetic acid. Stock solutions of $^{237}$Np(V) (0.038 M) and Pu(VI) (1.8 mM) were prepared from

93    the inventory at Lawrence Berkeley National Laboratory. The oxidation states of Np(V) and Pu(VI)

94    in the stock solutions were verified using absorption spectroscopy on a Cary 5G spectrophotometer.

95    Analysis by $\alpha$-spectroscopy indicated that the alpha activity of the Pu stock was 24.6% $^{238}$Pu and

96    75.4% $^{242}$Pu.;  on a molar basis, approximately 99.9 % $^{242}$Pu.  All other chemicals were of ACS

97    reagent grade quality and used as received. All experiments were performed in either 1.0 M NaCl or

98    1.0 M NaClO$_4$. The concentrations of Np and Pu were measured by liquid scintillation counting

99    (LSC) using EcoLumeTM (MP Biomedicals Inc.) cocktail on a Wallac 1415 counter. Alpha-beta

100   discrimination was used to separate the alpha counts of $^{237}$Np from the beta activity of the $^{233}$Pa

101   daughter product. Error for all measurements was propagated using liquid scintillation counting

102   statistics.

103

104   **2.3 Preparation and Analysis of Oxidation States of Neptunium and Plutonium in Working**

105   **Solutions**

106    Working solutions of Np (94 μM) and Pu (19 μM Pu) were prepared by diluting the Np(V) and

107    Pu(VI) stock solutions mentioned above in NaCl at pH 3. The oxidation state distribution of Pu in

108    the working solution and control solutions of the sorption experiments (boehmite and HEDPA free)

109    was determined using a procedure including lanthanum fluoride coprecipitation and sorption to

110    silica gel. Details of the procedure have been described elsewhere (16, 19). The ability of this

111    procedure to separate pentavalent and hexavalent actinides was verified using Np(V) and U(VI)

112    working solutions. The oxidation state of Np in the working solution and in the subsequent sorption

113    experiments was found to remain as Np(V). Measurements of the oxidation state distribution of

114    $^{242}$Pu control solutions (no HEDPA or boehmite) in 1M NaCl are shown in Table 1 along with the

115    data from analysis of U(VI) and Np(V) solutions (as a validation test of the separation procedures).

116    The data from Np(V) and U(VI) solutions indicate the method is approximately 90% efficient under

117    the conditions used. The LaF$_3$(s) coprecipitation step was assumed to be > 99% efficient for Pu(IV)

118    removal. It was assumed that no Pu(III) was present as it would be unstable in the oxic, circum-

119    neutral pH solutions examined here. Based upon these efficiencies and assumptions, an error of

120    approximately 10% could be used to describe the Pu oxidation state distributions rather than the

121    lower error based upon counting statistics listed in Table 1.

122         The results indicate that, though all the Pu in the stock solution was initially Pu(VI), it was

123    predominantly in the pentavalent state in the control solutions, which were much more dilute and

124    less acidic than the stock solution. It appears that the Pu(VI) from the stock solution was reduced to

125    Pu(V) after dilution in 1 M NaCl. This is consistent with the observed stability of Pu(V) in dilute

126    and near neutral solutions (16-18). Therefore, the sorption experiments in this work are discussed in

127    terms of Pu(V) sorption rather than Pu(VI).

128

129    **2.4 Batch Sorption/Leaching Experiments**

130    Initially, parallel experiments in 1.0 M NaCl and 1.0 M NaClO$_4$ were conducted to evaluate the

131    effect of background electrolyte on the oxidation states of Np and Pu and their sorption/leaching

132    behavior. Experiments in the 1 M NaClO$_4$ system were later discontinued as no significant

133    difference between the two background solutions was observed. Only the results of experiments

134    with 1.0 M NaCl are described below.

135            Np and Pu were first equilibrated with boehmite suspensions in 1.0 M NaCl (pH from 4 to

136    10, roughly 0.5 pH unit increments) for 10 days. Preliminary kinetic tests (in the absence of

137    HEDPA) indicated steady state partitioning of Np and Pu was achieved between 1 to 3 days at pH 4,

138    7, and 10. To prepare the samples, 660 mg L$^{-1}$ boehmite suspensions in 15 mL high-density

139    polyethylene centrifuge tubes were adjusted to target pH values using NaOH and HCl. After the

140    boehmite suspensions reached a steady pH, an aliquot of Np(V) or Pu(V) working solution was

141    added to achieve initial Np(V) or Pu(V) aqueous concentrations of 10.6 μM and 2.1 μM,

142    respectively. After adjusting the pH of each suspension to the target pH, the suspensions were

143    placed on an orbital shaker and mixed along their longitudinal axis. After 10 days, an aliquot was

144    transferred to a centrifugal filter (30k MWCO, Nanosep, Pall Life Sciences, estimated 12 nm pore

145    size). Throughout this work, the filtrate passing through a 30k MWCO filter is operationally defined

146    as the soluble fraction.  The first 100-200 μL of filtrate were discarded to allow equilibration of the

147    solution with the filter membrane. The Np or Pu concentration in a 200 μL aliquot of the filtrate was

148    determined using LSC. Control solutions containing Np or Pu without boehmite were also prepared

149    to monitor loss of Np or Pu from the system due to precipitation or sorption to the vial walls.

150            After 10 days, the suspensions were amended with a small volume of a 50 mM HEDPA

151    stock solution (pH 7) to yield a suspension containing 5.4 mM HEDPA, 600 mg L$^{-1}$ boehmite, and

152    1M NaCl. In parallel, the control solutions without boehmite were also amended to 5 mM HEDPA.

153    The pH of the HEDPA stock solutions was adjusted to 7 to minimize the pH changes resulting from

154    the addition of HEDPA to the suspensions. The Np(V) and Pu(V) concentrations after addition of

155    the HEDPA solutions were 9.4 μM and 1.9 μM, respectively. The pH of each suspension was

156    adjusted to the target pH immediately after addition of HEDPA and re-adjusted as necessary with

157    HCl and NaOH throughout the experiment. Deviation from the initially fixed pH over the course of

158    the experiment was found to be less than 0.2 pH units for all samples. The suspensions were mixed

159    at 150 rpm on an orbital shaking platform. At specified intervals, aliquots were removed and passed

160    through 30k MWCO centrifugal filters as described above and the concentration of Np or Pu in the

161    filtrate was measured using LSC.

162         Following the experiments, the aqueous phase was removed and the vials were rinsed with

163    1.0 M NaCl. Then a 1.0 M HCl solution was added to each vial to leach any sorbed Np or Pu from

164    the vial walls. It was assumed that the amount of Np or Pu in this acid leached phase represents the

165    amount of Np or Pu sorbed to the vial walls during the experiments. In experiments with boehmite

166    present, no significant loss of Np or Pu to the vial walls was observed.

167

168    **2.5 Pu-HEDPA and Np-HEDPA solutions in the absence of boehmite**

169    Based upon observations of the boehmite-free control samples described above, more detailed

170    analysis of Np and Pu behavior in HEDPA/NaCl solutions without boehmite was required.

171    Additional boehmite-free Np and Pu solutions in 1M NaCl and 5 mM HEDPA were monitored over

172    time at pH 4, 6, 8, 9, and 11. Aliquots were removed at various times and passed through 30k

173    MWCO centrifugal filters and the concentration of Pu and Np in the aqueous phase was measured

174    using LSC. After 18 days, the size fractionation of Np and Pu was examined by measuring Np and

175    Pu in an unfiltered sample as well as filtrate passed through 100k MWCO and 30k MWCO

176    centrifugal filters (Nanosep, Pall Life Sciences). At the end of the experiments, the possibility of

177    sorption of Np and Pu to the vial walls was tested by washing the vials with NaCl and HCl as

178    discussed above.

179

180    **3. Results and Discussion**

181    **3.1 Examination of An(V)-HEDPA solutions in the absence of boehmite**

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

183    were monitored using various filtration steps. The fractions of Np or Pu that passed through 30k

184    MWCO filters are shown as a function of time over an 18-day period in Figure 1. Both Np and Pu

185    were predominantly soluble at pH 8, 9, and 11 and the data at each time interval overlap and are

186    difficult to differentiate as shown in Figure 1. Interestingly, at pH 11 the concentration of Np and Pu

187    in these systems is above the solubility limit for Np(V)-(hydr)oxide precipitates but no loss of Np or

188    Pu was observed. In control solutions without HEDPA, a loss of 51% Np and 98% Pu was observed

189    in boehmite free solutions at pH 11 and a loss of 44% Pu was observed at pH 7 (data not shown). Np

190    remained in the aqueous phase at pH 4 and 7 and Pu remained soluble at pH 4. This indicates that

191    Np and Pu were either sorbing to the vial walls or precipitating at pH 11 (and pH 7 for Pu). Sorption

192    to the vial walls was found to account for less than 2% of the Np and Pu loss using NaCl-HCl

193    washing as described above. Therefore, it appears that Np and Pu precipitates were formed at pH 11

194    in solutions containing no HEDPA. The increased solubility of Np and Pu at pH 11 in the presence

195    of HEDPA indicates that formation of Np:HEDPA and Pu:HEDPA complexes suppresses

196    precipitation of hydroxides at high pH levels.

197        At pH 4 and 6, a significant fraction of Np and Pu were removed upon passing through a

198    30k MWCO filter. Sorption of Np and Pu to the filters was ruled out as complete recovery was

199    obtained upon successive filtration of a single solution through new filters. Additionally, less than

200    2% of the total Np and Pu was sorbed to the vial walls in all systems with HEDPA present. Since

201    two common experimental artifacts indicating loss of actinides were ruled out (sorption to filtration

202    apparatus and sorption to reaction vessel walls), the loss of Np and Pu shown in Figure 1 was likely

203    due to formation of precipitates with HEDPA.  After 18 days, aliquots of each suspension were

204    passed through either 100k MWCO (estimated 200nm pore size) or 30k MWCO centrifugal filters.

205    The fraction of total Np and Pu in the filtrate is shown in Figure 2, along with an unfiltered sample.

206    As the filtration pore size decreased, the fraction of total Np and Pu in the filtrate also decreased,

207    indicating removal of a Np:HEDPA or Pu:HEDPA colloidal precipitate. Precipitation of actinide-

208  HEDPA solids at low pH was also reported in studies determining the thermodynamic parameters of

209  U:HEDPA complexes, but only at low HEDPA:U(VI) ratios (7). Furthermore, an Al:HEDPA

210  precipitate was also observed in a similar study and found to be facilitated by relatively high (> 0.1

211  M) sodium concentrations (3).

212

213  **3.2 Sorption of Np(V) and Pu(V) to boehmite in the absence of HEDPA**

214  The pH dependant sorption of Np and Pu to boehmite is shown in Figure 3. Generally,

215  sorption of both Np and Pu increased with increasing pH. Sorption edges for Pu(V) and Np(V)

216  (defined as the point at which 50% is sorbed) occurred at approximately pH 6.6 and 8.0,

217  respectively, in good agreement with previous studies examining Np(V)/Pu(V) sorption to metal

218  oxides (8, 10, 13, 14, 18, 20, 21). The sorption edge and sorption behavior in general for Pu(V) in

219  1.0 M NaCl or 1.0 M $NaClO_4$ are quite similar, suggesting that there is little effect of chloride on the

220  sorption behavior in 1.0 M ionic strength solutions and that the perchlorate medium did not prevent

221  autoreduction of Pu(VI) to Pu(V) as observed in 1.0 M NaCl.

222  At low pH values, boehmite surface hydroxyl sites are protonated resulting in an overall

223  positive surface charge. Within this pH region, $NpO_2^+$ and $PuO_2^+$ are the predominant species.

224  Repulsion between the free dioxycations and the positively charged surface limits sorption of Np

225  and Pu in low pH suspensions. As the pH increases, hydrolysis of Np(V) and Pu(V) starts to occur

226  and gradually becomes significant – about 50% of Np(V) or Pu(V) would be hydrolyzed around pH

227  9 to 10 if estimated by using the first hydrolysis constants (log $\beta^*_{11}$) of -8.98 for Np(V) (22) and -9.7

228  for Pu(V) (23), respectively. The extent of hydrolysis in the presence of mineral solids could be even

229  higher than this estimation. As shown by the study of Np(V) sorption by hematite (20), the

230  hydrolysis of $NpO_2^+$ on the mineral surface occurs approximately 2 pH units lower that in solution,

231  likely due to relatively high concentration of hydroxide sites on the mineral surface. The hydrolysis

232  of Np(V) and Pu(V) with increasing pH was coincident with the transition of the mineral surface

233  from a net positive surface charge to a net negative surface charge. This allows for greater

234    interaction between cationic $NpO_2^+/PuO_2^+$ and neutral $NpO_2OH(aq)/PuO_2OH(aq)$ species with the

235    neutral or negatively charged mineral surface as shown in Figure 3.

236

237    **3.3 Effect of HEDPA on sorption of Np and Pu on boehmite**

238         Data describing the effect of HEDPA on Pu and Np sorption to boehmite are shown in

239    Figures 4 and 5. For comparison, the data from Figure 3 describing steady-state Pu and Np sorption

240    to boehmite in the absence of HEDPA are re-plotted using a smoothed dashed line in Figures 4 and

241    5, respectively. Generally, for both Np and Pu systems, the addition of HEDPA enhances the of Np

242    and Pu partitioning to the solid phase at low pH values and reduces the sorption of Np and Pu

243    partitioning at high pH values as compared with the HEDPA-free systems.  However, notable

244    differences between the Np and Pu systems appear in the data. In the presence of HEDPA and after

245    extended equilibrating time periods, the fraction of Pu sorbed was lower than the fraction of Np

246    sorbed at similar pH values. This could suggest a higher affinity of HEDPA for Pu in the aqueous

247    phase, than is seen for Np. Assuming that the partitioning behavior of pentavalent actinides will be

248    similar and that Np remained as Np(V) throughout the experiment, the difference in behavior

249    between the Np(V) system and the Pu system (initially as Pu(V)) could indicate that Pu(V) to Pu(IV)

250    is more readily reduced under most circumstances, more so in the presence of strong chelating

251    agents

252         To aid in comparison of the Pu and Np datasets, results describing sorption at selected pH

253    values from Figures 4 and 5 were re-plotted in Figure 6 as a function of reaction time. The fraction

254    of Pu sorbed decreased at most pH values during the 100 days of the experiment. The fraction of Np

255    sorbed changes little over a longer (~200 day) time period. The increased aqueous phase

256    concentrations of Pu at pH 4.5-6.5 and above pH 8 probably suggests the formation of soluble

257    Pu(IV)-HEDPA complexes. The relative similarity of Np sorption behavior at high pH in the

258    presence and absence of the ligand indicate that Np probably remains in the pentavalent oxidation

259    state throughout these experiments. The presence or absence of Np(V) – HEDPA complexes cannot

260    be confirmed based on these results.

261        Addition of HEDPA clearly influences the partitioning of Np and Pu relative to the

262    HEDPA-free systems. The predominant factors influencing these systems are: 1) dissolution of

263    boehmite solids promoted by HEDPA, 2) sorption of Np and Pu by boehmite as free cationic,

264    hydrolyzed, or HEDPA complexed species, and 3) precipitation of Np:HEDPA or Pu:HEDPA

265    colloids as discussed in section 3.1 and shown in Figures 1 and 2. The possibility of Pu(V) reduction

266    to Pu(IV) also must be considered. However, experimental evidence verifying this reduction is not

267    included as part of this study.  Each of these factors will be discussed below as they apply to the data

268    shown in Figures 4 and 5.

269        A brief discussion of the results from previous studies examining HEDPA-promoted

270    boehmite dissolution (3) must be considered when examining the Np and Pu partitioning data

271    presented below. In a study of the partitioning of U(VI) on boehmite in the presence of HEDPA (3),

272    the ability of HEDPA to dissolve boehmite was examined under conditions similar to those used in

273    this work (5 mM HEDPA, 1 M NaCl, 600 mg L$^{-1}$ boehmite). It was found that the formation of Al-

274    HEDPA complexes and Al(OH)$_4^-$ promotes boehmite dissolution in acidic and basic pH regions,

275    with maximum boehmite dissolution occurring at pH 4 and 11 (3). As the pH increased from pH 4

276    or decreased from pH 11, the Al concentration decreased monotonically until achieving minimum at

277    pH 7.5. Complete dissolution of a 600 mg L$^{-1}$ (0.01 M as Al$^{3+}$) boehmite suspension did not occur in

278    5 mM HEDPA within 135 days (3). Additionally, a 1:1 Al:HEDPA solid phase with a molar ratio of

279    1:1 Al:HEDPA was observed across the pH range 6 to 9 (3). Therefore, the effects of the dissolution

280    of boehmite and possible coprecipitation of the actinides with Al:HEDPA precipitates must be

281    considered. The effects of HEDPA amendment on Np and Pu partitioning were defined by distinct

282    pH regions as discussed in detail below.

283        *3.3.1 pH region from 4.0 to 5.5.* Amendment of a Pu-boehmite suspension with HEDPA

284    promoted rapid sorption of Pu below the "HEDPA-free" sorption edge (pH range 4.0 to 7.5) within

285     the first 2 hours (Figures 4 and 5). This was followed by a two step desorption process where initial

286     rapid desorption was observed in the first 15 days, followed by slow desorption for the remainder of

287     the experiment. After 30 days the fraction of aqueous Pu was greater in 5 mM HEDPA than the

288     HEDPA-free system at all pH values above 5.5. Preliminary experiments also indicated the initial

289     sorption of HEDPA, Np, and Pu to boehmite was rapid relative to the rate of change observed in Np

290     and Pu partitioning shown in Figures 4 and 5. Therefore, the reaction rates within these multi-

291     component systems are likely surface controlled. When examining HEDPA promoted boehmite

292     dissolution, Powell et al., (3) proposed that detachment of the Al:HEDPA may be a rate limiting step

293     when examining boehmite dissolution. If this mechanism of surface control is important in the

294     Pu:HEDPA and Np:HEDPA systems examined here, the detachment of Al:HEDPA species could

295     also control sorption of Np and Pu through occupation of available sorption sites.

296             The effect of HEDPA on Np sorption to boehmite is similar to its effect in the Pu system,

297     consistent with the expected similar behavior of pentavalent actinides. However, the effects were

298     more subtle and the reaction rates appeared considerably slower. As shown in Figure 6, the fraction

299     of Np sorbed after addition of HEDPA shows relatively little change over time compared with the

300     Pu dataset. Additionally, the fraction of Np sorbed was much greater than that of Pu at extended

301     times. This either situation could arise from a kinetic limitation of the detachment of Np:HEDPA

302     complexes from the mineral surface, a difference in the oxidation state distribution, or in the nature

303     of the complexes formed within the two systems. Assuming Np remains in the pentavalent state, it is

304     conceivable that reduction of Pu(V) to Pu(IV) could explain these differences. Similar to the Pu

305     system, rapid sorption of Np was observed at pH values below the HEDPA-free sorption edge

306     immediately following addition of HEDPA (pH range 4 to 9, Figure 6). Following this initial uptake,

307     Np began to desorb of neptunium desorbed as the experiment progressed.

308             The decrease in aqueous Np and Pu at low pH values following the addition of HEDPA may

309     be, in part, due to precipitation of Np:HEDPA or Pu:HEDPA colloids as described above.

310     Interestingly, the aqueous concentration of Np and Pu were higher in the boehmite suspensions than

311    in the boehmite free control solutions. After 18 days at pH 4, less than 25% of the Np or Pu was

312    soluble in the control experiments (Figure 1). However, the data in Figures 4 and 5 show that after

313    15 days 48% of the Pu was soluble and after 21 days 58% of the Np was soluble. In the presence of

314    boehmite, the concentration of HEDPA available for complexation with Np or Pu is likely decreased

315    due to sorption of HEDPA to the mineral surface and complexation with dissolved Al(III).

316    Therefore, Np:HEDPA and Pu:HEDPA colloids may not be precipitated due to the decreased

317    "apparent available" concentration of HEDPA.

318           The partitioning of Np and Pu at low pH may also be influenced by partitioning of

319    Np:HEDPA and Pu:HEDPA complexes through the sorption of ternary Np:HEDPA and Pu:HEDPA

320    surface complexes. Ternary surface complexes with HEDPA could be present if one phosphonic

321    group of HEDPA binds the surface ($\equiv$S-OH) while the other binds Np or Pu. Schindler (24) has

322    characterized these complexes as type A and type B complexes as described below. A type B

323    surface complex can be envisioned as HEDPA acting as a bridging ligand between the surface and

324    Np or Pu as shown in the generalized reaction below.

325           $\equiv$S-OH + An$^{x+}$ + LH$_y^{y-4}$   $\_$   [$\equiv$S--LH$_x$--An]$^{x+y-3}$ + OH$^-$

326    It is noteworthy that type B complexes can form with polydentate ligands, such as HEDPA.

327    Therefore, if reduction of Pu(V) to Pu(IV) occurs as proposed above and a bidentate complex

328    results, type B complexes with HEDPA are less probable This would lead to an increase in the

329    aqueous Pu concentration as is seen in Figure 4. At high pH values where the cationic metal species

330    may be attracted to the negatively charged surface, a type A complex could form through metal-

331    bridging as:

332           $\equiv$S-OH + An$^{x+}$ LH$_y^{y-4}$   $\_$   [$\equiv$SO$^-$--An-LH$_y$]$^{x+y-5}$ + H$^+$

333           Formation of ternary surface complexes in which bonding with the surface occurs either

334    through the metal (metal-bridging) or ligand (ligand-bridging) have been proposed to describe the

335    partitioning of trace metals to surfaces that contain adsorbed ligands (25-27). There is a growing

336 body of spectroscopic evidence describing these two types of ternary complexes, including recent

337 spectroscopic studies on the effect of soil fulvic acid on Ni sorption to boehmite (28). The ligand-

338 bridging complex dominated at low pH conditions while under high pH conditions both metal-

339 bridging ternary complexes as well as binary metal-surface complexes are possible (28). The

340 sorption behavior of the complex is generally similar to the sorption behavior of the bridging

341 species. Therefore, in systems with low pH values where sorption of HEDPA is stronger than

342 sorption of Np or Pu, an HEDPA-bridging ternary surface complex would be expected. However,

343 formation of such a complex is speculative and must be verified through future spectroscopic

344 measurements.

345        *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

346 Np and Pu occurred relative to the low pH systems. Addition of HEDPA to the Pu-boehmite

347 suspensions at pH 5.5 to 7.5 resulted in an increase in the fraction of Pu sorbed within the first 2

348 hours. Minimal changes were observed within the first 2 hours for systems at pH 7.5 to 9.0.

349 However, during the next 97 days the fraction of sorbed Pu decreased across the entire pH range.

350 Generally, the fraction of Pu sorbed increased as the pH increased from 5 to 9. Similar results were

351 observed in the Np system. However, more Np was sorbed in 5 mM HEDPA than in HEDPA-free

352 systems at circum-neutral pH values. At all pH values lower than 8.5, addition of HEDPA enhanced

353 sorption of Np.

354        Similar to the low pH systems, the partitioning behavior in the circumneutral pH range may

355 be influenced by precipitation of Pu:HEDPA and Np:HEDPA colloids, sorption reactions, and

356 boehmite dissolution. Additionally, coprecipitation of Np and Pu with Al:HEDPA solids that form

357 across the pH range 6 to 9 must also be considered. The available data do not allow explicit

358 identification of the dominant processes. However, the observed increase in the aqueous

359 concentration of both Np and Pu are not consistent with the precipitation of colloids. Therefore,

360 sorption processes and boehmite dissolution are proposed to be the dominant processes across the

361 pH range 5.5 to 9.0. Thermodynamic data describing Np:HEDPA and Pu:HEDPA complexes are

362    unavailable at present. However, studies of U(VI):HEDPA complexation showed a series of anionic

363    species with increasingly higher charges dominating the U(VI) speciation at high pH values (7). If

364    the Np(V):HEDPA, Pu(V):HEDPA, and possibly Pu(IV):HEDPA complexes are similarly anionic,

365    desorption due to electrostatic repulsion would be expected as the pH increased and an overall

366    negative surface charge developed above pH ~8.5, as observed in Figure 5 and 6.

367          Since Np, Pu, and HEDPA all sorb to boehmite at circumneutral pH values, formation of

368    ternary surface complexes as well as binary metal-surface complexes are possible in this region. As

369    discussed above, Strathmann and Myneni (28) observed both metal-bridging boehmite-Ni-fulvic

370    acid ternary complexes as well as binary Ni-boehmite surface complexes at high pH conditions. Fitts

371    et al. (29) observed both binary and ternary complexes in Cu(II)-glutamate- $\gamma$-$Al_2O_3$ suspensions at

372    high pH conditions and concluded that the binary Cu(II)-aluminol surface complex was dominant.

373    Similarly, the increased sorption of Np and Pu with increasing pH as shown in Figure 4 and 5 is

374    indicative of complexation of Np and Pu with the surface. Within this pH range in HEDPA-free

375    solutions, both Np and Pu are predominantly sorbed. Therefore, the sorption behavior within this pH

376    range is proposed to be due to sorption of Np and Pu either as binary surface complexes or as

377    Np:HEDPA and Pu:HEDPA surface complexes. Again, formation of such surface complexes is

378    speculative and must be verified with spectroscopic data.

379          *3.3.3 pH region above 9.0.* Above pH 9.0, both Np and Pu were predominantly associated

380    with the solid phase in HEDPA free suspensions (Figures 4 and 5).This could indicate sorption or

381    possible precipitation of insoluble hydroxides. Following addition of HEDPA, both Np and Pu

382    slowly leached into the aqueous phase. No precipitation of any metal:HEDPA solids was observed

383    in this pH range in this or the previous work (3). Furthermore, the presence of HEDPA appeared to

384    prevent precipitation of Np or Pu hydrolysis products above pH 8 (Figure 1). Therefore the

385    predominant factors affecting Np and Pu partitioning in this range are sorption reactions and

386    boehmite dissolution. It is noteworthy that the change in Np and Pu partitioning in this system was

387    concurrent with significant boehmite dissolution by HEDPA (3). The rate of Np and Pu leaching

388    into the aqueous phase was consistent with the rate of boehmite dissolution observed in previous

389    work, thus suggesting boehmite dissolution was a major influencing factor across this pH range (3).

390         The fraction of Np and Pu sorbed decreased with increasing pH between pH 8.5 and 10.

391    Within this pH region, the surface transitions from a net positive surface charge to a net negative

392    surface charge. Again assuming anionic Np:HEDPA and Pu:HEDPA complexes form at these pH

393    levels, the anionic complexes will be repelled by the negative surface and partition into the aqueous

394    phase. This is consistent with a decreasing sorption of Np and Pu across this pH range. At extended

395    time periods above pH 10.0 and 10.5, for Np and Pu respectively, the partitioning trend reversed and

396    the fraction of Np and Pu sorbed increased with increasing pH.  This effect was considerably more

397    pronounced for Np than Pu. This behavior may represent a change in the solid phase speciation from

398    Np/Pu:HEDPA complexes to Np/Pu:hydroxide complexes or it may represent reduction of Pu(V) to

399    Pu(IV).  Unfortunately, without reliable stability constants for Np:HEDPA and Pu:HEDPA

400    complexes, a quantitative distribution between HEDPA and hydroxide complexes cannot be

401    calculated. However, the decrease in sorption across the pH range 8.5 to 10.0 indicates that

402    Np:HEDPA complexes partition to the aqueous phase as the pH increases. Furthermore, as shown in

403    Figure 3, complete sorption of Np in HEDPA-free systems occurs above pH 9.5 where the

404    predominant species are $NpO_2OH(aq)$ and $NpO_2(OH)_2^-$ (22).  Therefore the increase in sorption

405    observed above pH 10 is likely indicative of sorption of Np-hydroxide complexes rather than

406    leaching of Np:HEDPA complexes. This effect was much more pronounced for Np relative to Pu. It

407    is possible that the tendency of Pu(V) toward hydrolysis is weaker than that of Np(V), since the

408    "upper" limit of the Pu(V) hydrolysis constant is estimated to be  -9.7 (23) while the hydrolysis

409    constant of Np(V) is determined to be -8.98 (22). However, more definitive explanations for the

410    difference in the behavior of Np(V) and Pu(V) in high pH regions cannot be made until relevant data

411    on the hydrolysis of Pu(V) become available. Stronger sorption of Np relative to Pu in alkaline pH

412    suspensions is consistent with the general trend observed in the sorption dataset indicating that more

413    Pu than Np is leached into the aqueous phase. As discussed above, this may be due to reduction of

414    Pu(V) to Pu(IV) followed by solubilization of Pu(IV):HEDPA complexes. Regardless of the primary

415    influence, HEDPA promotes desorption of both Np and Pu from the solid phase relative to a ligand

416    free system.

417

418    **4. Conclusions**

419        This work has shown that addition of HEDPA affects the sorption of Np and Pu to boehmite

420    in a complex manner. Np and Pu partitioning appears to be primarily affected by the formation of

421    Np:HEDPA and Pu:HEDPA complexes, the dissolution of boehmite promoted by HEDPA, the

422    precipitation of Np:HEDPA and Pu:HEDPA colloids in low pH regions, and possibly reduction of

423    Pu(V) to Pu(IV). At low pH values, HEDPA initially promotes sorption of Np and Pu, relative to the

424    minimal sorption observed in ligand free systems. This effect is due to sorption of aqueous

425    Np:HEDPA and Pu:HEDPA complexes and/or precipitation of Np:HEDPA and Pu:HEDPA solids.

426    However, as the systems equilibrate for greater than 90 days, both Np and Pu leach back into the

427    aqueous phase in the pH range 5.5 to 9.0. The fraction of Np leached back into solution over time is

428    considerably lower than the fraction of Pu.

429        Generally the fraction of Np sorbed was greater in the presence of HEDPA when compared

430    with the HEDPA free system across the pH region 5.5 to 9.0 even after 135 days.  Following

431    addition of HEDPA, the fraction of Pu sorbed was less than that observed in the absence of HEDPA

432    at pH 5.5 to 9.0 after 90 days. Sorption at circumneutral pH values is proposed to be due to the

433    formation of ligand bridging and metal-bridging Np-HEDPA and Pu-HEDPA ternary surface

434    complexes. At pH greater than 9, HEDPA leaches Np and Pu from the solid phase, relative to an

435    HEDPA free system. Within this basic pH range, Np and Pu partitioning are proposed to be

436    influenced by both HEDPA and hydroxide complexes as well as boehmite dissolution.

437        The enhanced solubilization of Pu relative to Np under acidic and basic conditions observed

438    in this work could also indicate that reduction of Pu(V) to Pu(IV) may be occurring in these systems.

439    Reduction of Pu(V) to Pu(IV) facilitated by stronger Pu(IV)-HEDPA complexes and a more

440   favorable reduction potential may explain the observed differences between Np and Pu behavior.

441   However, experimental data verifying this reduction is not available.  If reduction of Pu(V) to

442   Pu(IV) were occurring, it is interesting that this effect is associated with an increase in the aqueous

443   phase concentration of Pu. This may indicate that the structural rearrangement of the

444   Pu(IV):HEDPA complex relative to Pu(V):HEPDA complexes which hinders formation of type A

445   and type B surface complexes. Presumably this would be due to formation of a bidentate

446   Pu(IV):HEDPA complex which will prevent formation of a type B surface complex.

447        These results show that the use of a strong complexing agent such as HEDPA to reduce the

448   volume of aluminum bearing sludges may cause significant leaching of Np and Pu. It is unlikely that

449   the precipitation of Np:HEDPA and Pu:HEDPA colloids at low pH levels can be exploited during

450   waste treatment processes as the increased phosphate concentration within the solids will be

451   problematic during the vitrification process. At high pH levels, HEDPA was found to significantly

452   enhance the solubility of aluminum and therefore may accomplish significant waste volume

453   reduction. However, some leaching of Np and Pu was observed. Additional experiments at high pH

454   levels are required to determine whether significant fractions of Np and Pu will remain associated

455   with the solid phase, as the trend in this work shows. Furthermore, spectroscopic studies are required

456   to verify the speculative surface complexes proposed in this manuscript.

457

464

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539

540    Table 1: Oxidation State Distribution of Pu in Control Solutions (1M NaCl; 1.9μM $^{242}$Pu).
541

|  | 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

542

FIGURE CAPTIONS
544    Figure 1: Fractions of aqueous Np (top) and Pu (bottom) in HEDPA solutions after filtration
545    with 30k MWCO filters. Symbols: pH 4 (◆), pH 6 (■), pH 8 (▲), pH 9 (◇), pH 11 (□).
546    System Parameters: [HEDPA] =5 mM; [Np(V)] = 9.4 μM; [Pu(V)] = 1.9 μM; [NaCl] = 1.0
547    M. Error bars not shown for clarity; average $2\sigma$= 4%.
548
549    Figure 2: Fractions of Pu and Np remaining in 5 mM HEDPA solutions at pH 4 and pH 6
550    after filtration with 100k MWCO (200 nm) and 30k MWCO (12 nm) filters after 18 days, in
551    comparison with those of unfiltered. System Parameters: [HEDPA] =5 mM; [$^{237}$Np(V)] =
552    9.4 μM; [$^{242}$Pu(V)] = 1.9 μM; [NaCl] = 1.0 M. $2\sigma$ error propagated from counting statistics.
553
554    Figure 3: Sorption of Pu(V) (■,□) and Np(V) (▲) on boehmite after 10 days, in the absence
555    of HEDPA. Background solution was 1M NaCl (closed symbols) or 1M NaClO$_4$ (open
556    symbols). The bold arrow indicates the boehmite point-of-zero-salt-effect. Additional
557    solution conditions: [γ-AlOOH] = 660 mg L$^{-1}$; [Pu(V)] = 2.1 μM; [Np(V)] = 10.6 μM. The
558    bold arrow indicates the boehmite point-of-zero-salt-effect.
559
560    Figure 4:  Effect of HEDPA on Pu sorption to boehmite (γ-AlOOH). For comparison, a
561    smoothed dashed line representing data from Figure 3 showing steady state distribution (10
562    day equilibrium) of Pu without HEDPA present is shown. The bold arrow indicates the
563    boehmite point-of-zero-salt-effect. Symbols: 0.1 days (■), 1 day (◇), 8 days (▲), 15 days (□),
564    30 days (◆), 60 days (△), 97 days (▫). System parameters: [HEDPA] = 5.4 mM; [γ-AlOOH]
565    = 600 mg L$^{-1}$; [NaCl] = 1.0 M; [Pu(V)]$_{initial}$ = 1.9 μM.  Error bars removed for clarity,
566    average $2\sigma$= 2% propagated from counting statistics. The bold arrow indicates the boehmite
567    point-of-zero-salt-effect. Solid lines are to aid in visualization of the data and do not
568    represent a model fit.
569
570    Figure 5:  Effect of HEDPA on Np sorption to boehmite (γ-AlOOH). For comparison, a
571    smoothed dashed line representing data from Figure 3 showing steady state distribution (10
572    day equilibrium) of Np without HEDPA present is shown.. Symbols: 0.1 days (■), 1 day (◇),
573    7 days (▲), 21 days (□), 102 days (◆), 135 days (△). System parameters: [HEDPA] = 5.4
574    mM; [γ-AlOOH] = 600 mg L$^{-1}$; [NaCl] = 1.0 M; [Np(V)]$_{initial}$ = 9.4 μM.  Error bars removed
575    for clarity, average $2\sigma$= 2% propagated from counting statistics. The bold arrow indicates
576    the boehmite point-of-zero-salt-effect. Solid lines are to aid in visualization of the data and
577    do not represent a model fit.
578
579    Figure 6: Effect of HEDPA on Np and Pu sorption to boehmite (γ-AlOOH) versus time.
580    Selected data at constant pH values shown in Figures 4 and 5 at fixed pH values has been
581    replotted- versus time for comparison (symbols representing the data at different time are
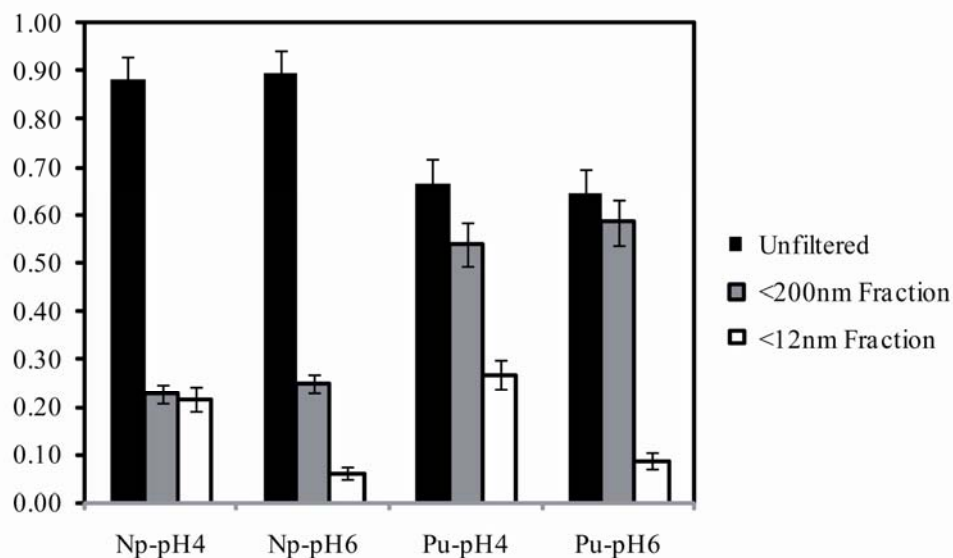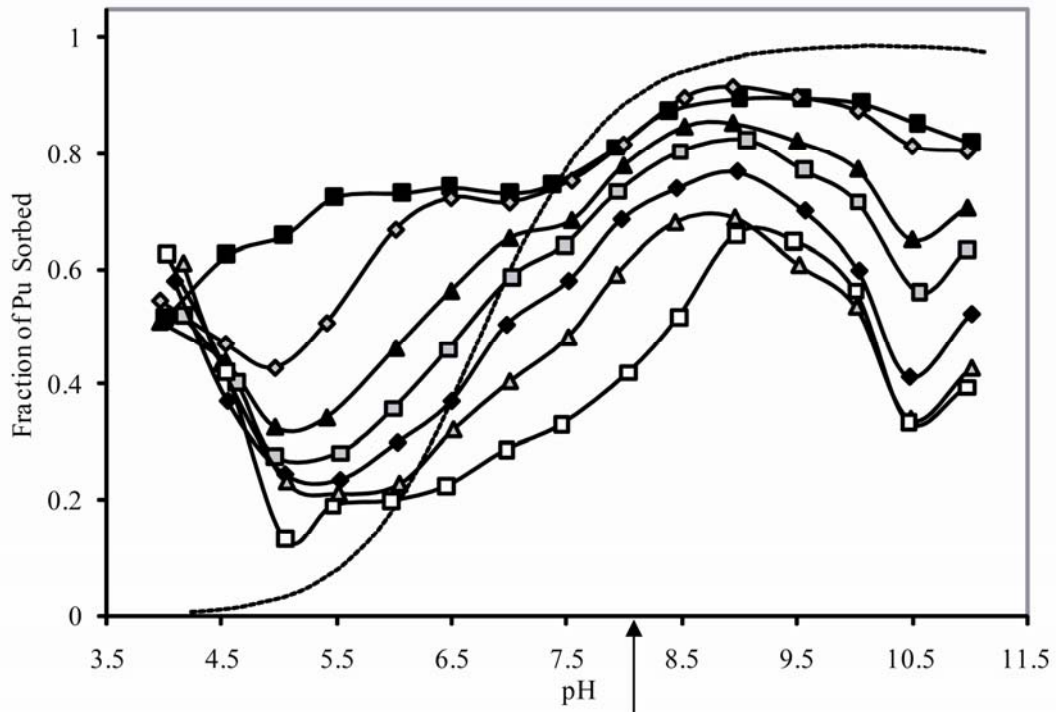582    the same as in Figures 4 and 5).
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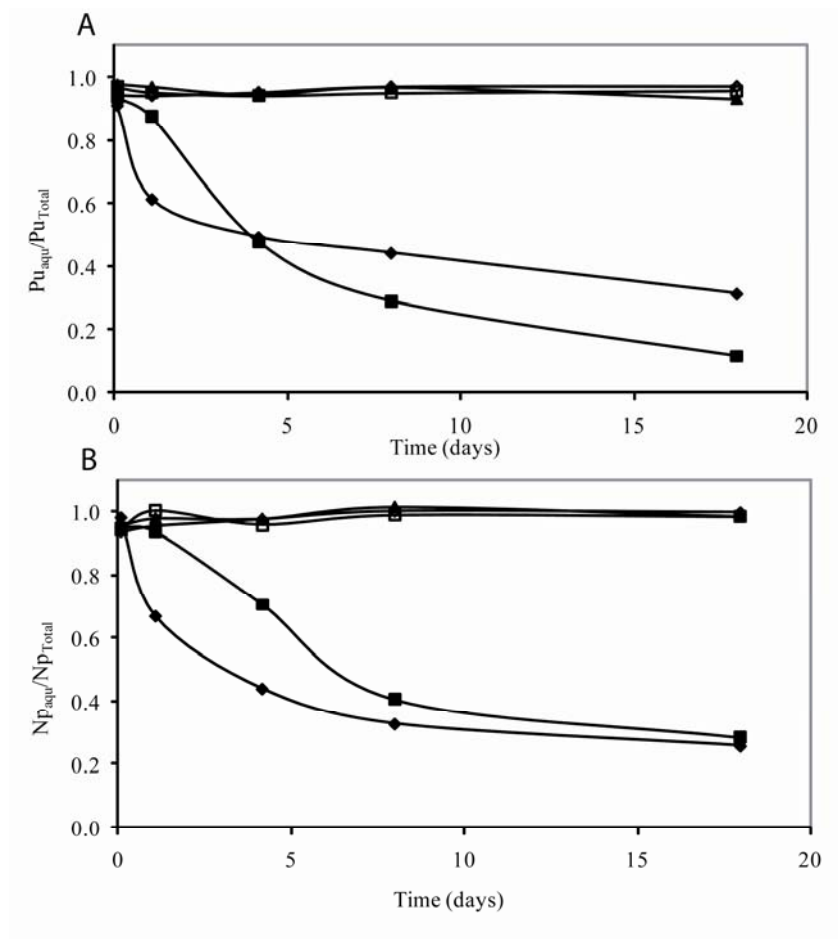
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590 M. Error bars not shown for clarity; average 2σ= 4%.
591
592

593
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597 9.4 μM; $[^{242}Pu(V)]$ = 1.9 μM; [NaCl] = 1.0 M. 2σ error propagated from counting statistics.
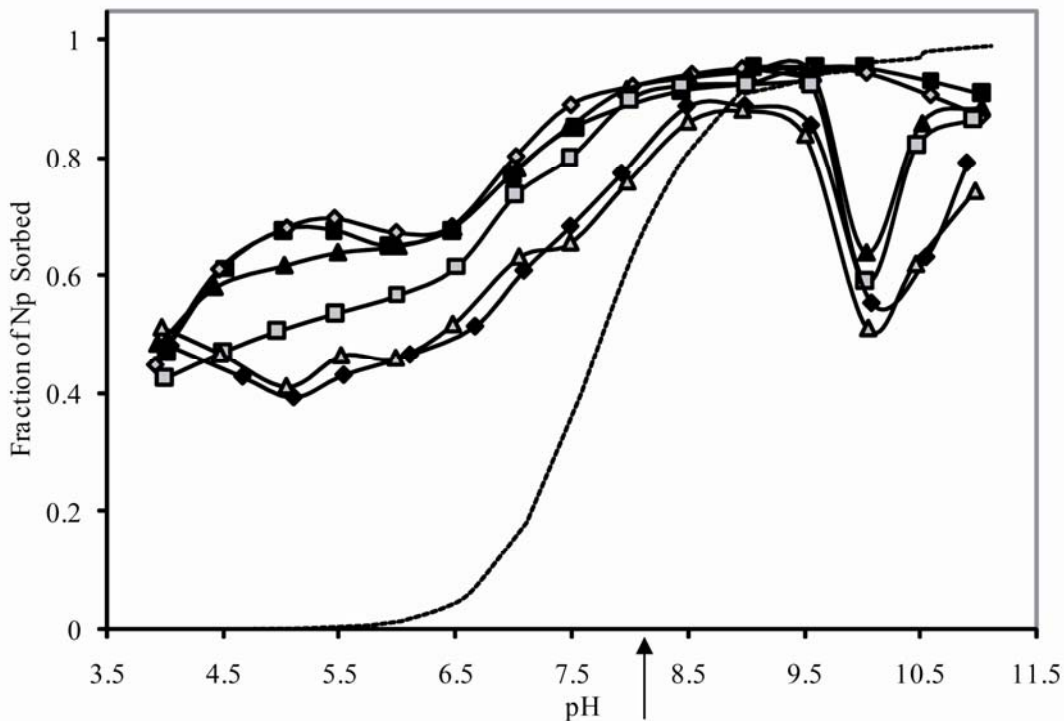598

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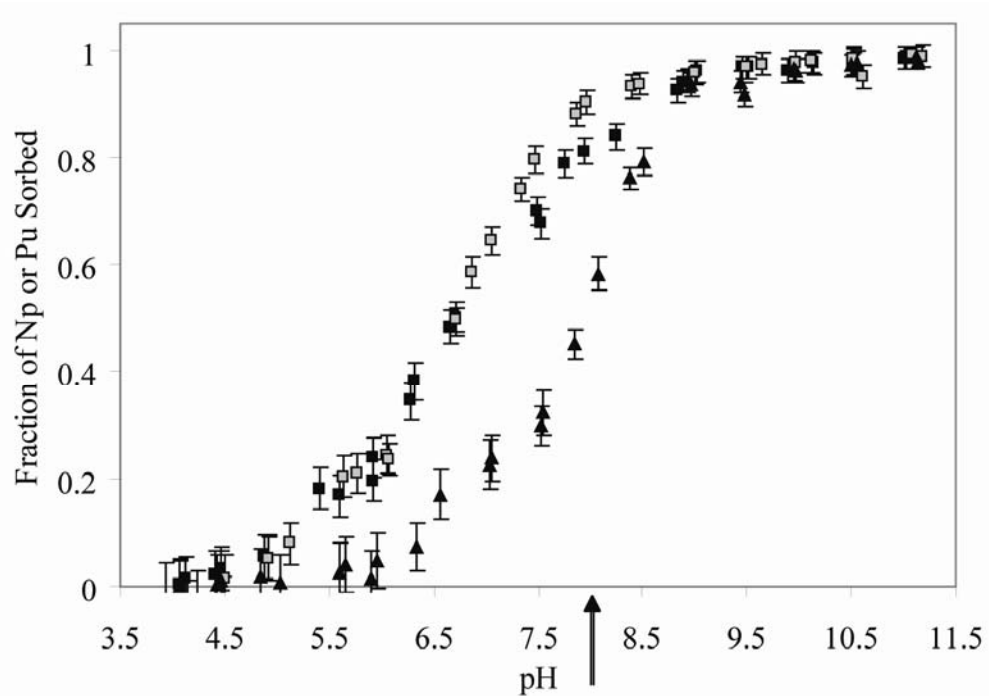


600
601 Figure 3: Sorption of Pu(V) (■,□) and Np(V) (▲) on boehmite after 10 days, in the absence
602 of HEDPA. Background solution was 1M NaCl (closed symbols) or 1M NaClO$_4$ (open
603 symbols). The bold arrow indicates the boehmite point-of-zero-salt-effect. Additional
604 solution conditions: [γ-AlOOH] = 660 mg L$^{-1}$; [Pu(V)] = 2.1 μM; [Np(V)] = 10.6 μM. The
605 bold arrow indicates the boehmite point-of-zero-salt-effect.
606

607
608    Figure 4: Effect of HEDPA on Pu sorption to boehmite (γ-AlOOH). For comparison, a
609    smoothed dashed line representing data from Figure 3 showing steady state distribution (10
610    day equilibrium) of Pu without HEDPA present is shown. The bold arrow indicates the
611    boehmite point-of-zero-salt-effect. Symbols: 0.1 days (■), 1 day (◇), 8 days (▲), 15 days (▫),
612    30 days (◆), 60 days (△), 97 days (▫). System parameters: [HEDPA] = 5.4 mM; [γ-AlOOH]
613    = 600 mg L$^{-1}$; [NaCl] = 1.0 M; [Pu(V)]$_{initial}$ = 1.9 μM.  Error bars removed for clarity,
614    average 2σ= 2% propagated from counting statistics. The bold arrow indicates the boehmite
615    point-of-zero-salt-effect. Solid lines are to aid in visualization of the data and do not
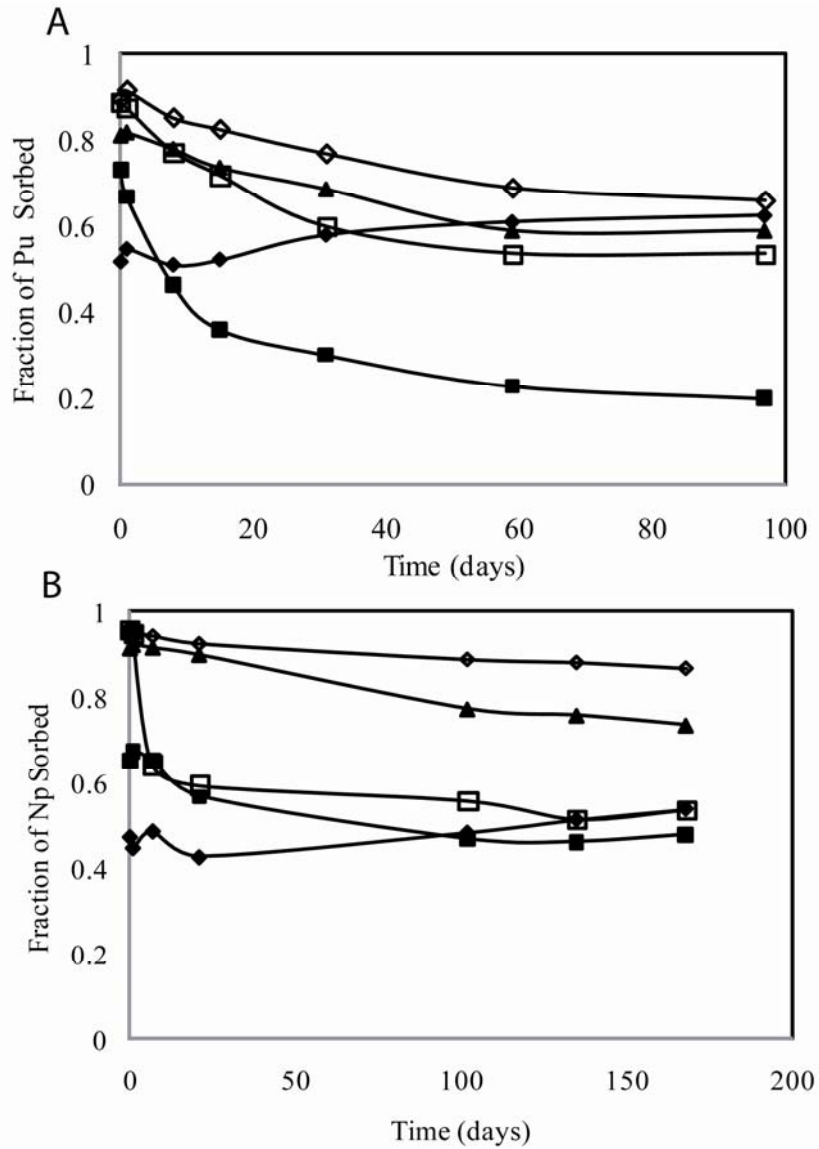616    represent a model fit.
617

618



619
620　Figure 5:  Effect of HEDPA on Np sorption to boehmite (γ-AlOOH). For comparison, a
621　smoothed dashed line representing data from Figure 3 showing steady state distribution (10
622　day equilibrium) of Np without HEDPA present is shown.. Symbols: 0.1 days (■), 1 day (◇),
623　7 days (▲), 21 days (▢), 102 days (◆), 135 days (△). System parameters: [HEDPA] = 5.4
624　mM; [γ-AlOOH] = 600 mg L$^{-1}$; [NaCl] = 1.0 M; [Np(V)]$_{initial}$ = 9.4 µM.  Error bars removed
625　for clarity, average 2σ= 2% propagated from counting statistics. The bold arrow indicates
626　the boehmite point-of-zero-salt-effect. Solid lines are to aid in visualization of the data and
627　do not represent a model fit.
628
629

630
631 Figure 6: Effect of HEDPA on Np and Pu sorption to boehmite (γ-AlOOH) versus time.
632 Selected data at constant pH values shown in Figures 4 and 5 at fixed pH values has been
633 replotted- versus time for comparison (symbols representing the data at different time are
634 the same as in Figures 4 and 5).