Examination of Uranium(VI) Leaching During Ligand Promoted Dissolution of Waste Tank Sludge Surrogates

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Summary. The dissolution of synthetic boehmite (γ-AlOOH) by 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) was examined in a series of batch adsorption/dissolution experiments. Additionally, the leaching behavior of [233]U(VI) from boehmite was examined as a function of pH and HEDPA concentration. The results are discussed in terms of sludge washing procedures that may be utilized during underground tank waste remediation. In the pH range 4 to 10, complexation of Al(III) by HEDPA significantly enhanced dissolution of boehmite. This phenomenon was especially pronounced in the neutral pH region where the solubility of aluminum, in the absence of complexants, is limited by the formation of sparsely soluble aluminum hydroxides. At pH higher than 10, dissolution of synthetic boehmite was inhibited by HEDPA, likely due to sorption of Al(III):HEDPA complexes. Addition of HEDPA to equilibrated U(VI)-synthetic boehmite suspensions yielded an increase in the aqueous phase uranium concentration. Partitioning of uranium between the solid and aqueous phase is described in terms of U(VI):HEDPA speciation and dissolution of the boehmite solid phase.

1. Introduction

The underground storage tanks at the Hanford Site in Washington State, U.S.A. contain the byproducts from a number of spent nuclear fuel reprocessing processes including the bismuth phosphate ($BiPO_4$), Redox and PUREX processes (1). Over time the waste has stratified into a salt cake, a supernatant phase, and an underlying sludge phase. Insoluble aluminum oxides make up a significant fraction of the sludge phase (1). Most of the transuranics have partitioned into the sludge phase, making vitrification of the sludge phase for geologic disposal a plausible treatment process (1). However, vitrification will be

31   prohibitively expensive due to the large volume of the sludge phase. Therefore, reduction of the volume

32   of the sludge through dissolution of the aluminum oxides presents a favorable alternative.

33   Various strategies of sludge leaching have been proposed and tested with sludge stimulants,

34   including leaching with increasingly aggressive procedures (0.01M $NaNO_2$ + 0.01M NaOH, 3M NaOH,

35   0.05M glycolic acid + 0.10M NaOH, 0.10M HNO_3, 2.0M HNO_3, 0.5M HEDPA (1-hydroxyethane-1,1-

36   diphosphonic acid)) (1-3). It was found that the aluminosilicates cannot be removed using the baseline

37   washing procedure (0.01 M $NaNO_2$ + 0.01 M NaOH) and no single treatment achieved complete

38   dissolution (1-3). Data from these experiments suggest that HEDPA could be an effective leachant to

39   reduce the volume of waste sludge. In order to develop an efficient waste treatment process, further

40   studies are needed to understand the extent of sludge phase dissolution and the partitioning of actinides

41   (U, Np and Pu) during the leaching process.

42   As a diphosphonic acid, HEDPA is known to form strong complexes with metal ions including

43   actinides and aluminum across a wide pH range (4-6). In the absence of complexing ligands, aluminum

44   (hydro)oxides are only sparingly soluble. Therefore, formation of Al(III):HEDPA complexes will

45   promote sludge dissolution. However, partitioning of the actinides between the sludge and aqueous phase

46   must also be understood in order to evaluate the viability of HEDPA for sludge washing. Formation of

47   U(VI):HEDPA complexes affects the partitioning of uranium during the leaching of waste sludge with

48   HEDPA. Previous experiments demonstrated that greater than 95% of the total uranium was leached from

49    $BiPO_4$, Redox, and PUREX sludge waste simulants by washing the sludge with 0.5 M HEDPA (3).

50   Recently, a number of $(UO_2)_mH_hL_l$ (where L stands for the fully deprotonated HEDPA anion) complexes,

51   ranging from cationic to anionic, were identified in the pH region from 2 to 12 using potentiometry,

52   calorimetry, and spectroscopic techniques (4). The thermodynamic data provided by Reed et al. (4) are

53   used below to describe observed behavior of uranium in synthetic boehmite suspensions amended with

54   HEDPA.

55   The objective of this study was to investigate the ability of HEDPA to accomplish dissolution of

56   synthetic boehmite and to examine the leaching of uranium during dissolution. A companion study was

57 also performed to examine the leaching of neptunium and plutonium under similar conditions (7). The

58 data are expected to assist in the development of remediation strategies to be used during waste tank

59 sludge washing.

60

61 **2. Materials and Methods**

62 **2.1 Solid Phase Characterization**

63 The alumina used in this work was obtained from SASOL (trade name CATAPAL® B). Powder X-ray

64 diffraction data, determined using a Seimens D-500 Diffractometer, indicate that the material has the

65 crystal structure of boehmite (γ-AlOOH) although a significant amorphous character was indicated

66 through broad peaks in the XRD spectra. A surface area of 354 m^2 g^{-1} was measured by $N_2(g)$ adsorption

67 using a Micrometrics BET Surface Area Analyzer. Potentiometric tirations were conducted with 100 g L^{-1}

68 boehmite suspensions in 0.01, 0.1, and 1.0 M NaCl to determine the point-of-zero-salt-effect (pzse). The

69 titration results are shown in Figure 1. The boehmite surface has a net positive or negative charge due to

70 protonation or deprotonation of surface hydroxyl groups with changing pH. The intersection of the

71 curves for the three NaCl concentrations at pH 8.1 represents the point at which changes in the

72 concentration of the background electrolyte have no effect on the net surface charge density (8). This

73 value is consistent with the zero-point-of-charge measured for several synthetic aluminas (9-11). The

74 apparent proton surface charge density was calculated assuming a surface site density of 1.7 sites per nm^2.

75

76 **2.2 Preparation of Uranium Working Solution**

77 A stock solution of ^{233}U(VI) tracer was obtained from the inventory at Lawrence Berkeley National

78 Laboratory and purified by ion exchange. Analysis by α-spectroscopy indicated that the purified uranium

79 contains 96.6% ^{233}U and 3.3% ^{232}U. A 1.1 x 10^{-4} M U(VI) working solution in 1M NaCl at pH 3 was

80 prepared from the stock solution and used for sorption experiments. The concentration of uranium was

81   determined by liquid scintillation counting (LSC) using EcoLumeTM (MP Biomedicals Inc.) cocktail on

82   a Wallac 1415 liquid scintillation counter.

83

84   **2.3 Dissolution of boehmite using HEDPA**

85   Working suspensions spanning the pH range 4 to 11 were prepared by equilibrating boehmite with 1.0 M

86   NaCl then using these suspensions to prepare samples for batch experiments. The batch experiments were

87   performed in polypropylene centrifuge tubes shaken along their longitudinal axis on an orbital shaker at

88   150 rpm. Batch dissolution experiments to examine the dissolution of boehmite by HEDPA were

89   conducted in suspensions with a constant boehmite concentration of 600 mg L^{-1} (10 mM as Al) containing

90   5 mM, 10 mM, and 50 mM HEDPA. At specified intervals, aliquots were removed and passed through

91   200 nm nylon filters (Gelman Acrodisc). The aluminum concentration in the filtrate was measured using

92   ICP-OES (Perkin Elmer, Optima 5300 DV). The pH of each suspension was adjusted towards an initial

93   pH during sampling intervals using 0.1 and 0.01 M HCl and NaOH. At a few intervals, the HEDPA

94   concentration in the filtrate was measured using a standard spectrophotometric method (12) employing a

95   Cary 5G Spectrophotometer.

96   A series of potentiometric titrations were attempted to examine Al(III):HEDPA complex

97   formation in 1 M NaCl. However the titrations were unsuccessful as a white precipitate was observed

98   across the pH range 4 to 9. To identify the precipitate, a series of solutions were prepared in 1 M NaCl

99   with total Al(III):HEDPA ratios varying from 1:1 to 1:5. The precipitates were isolated via centrifugation

100   and re-dissolved in ultra pure H_2O. The aluminum and HEDPA concentrations in the resulting solution

101   were used to calculate the Al(III):HEDPA molar ratio in the solids. Additionally, to examine the effect of

102   the background electrolyte and electrolyte concentrations, Al(III):HEPDA precipitates were formed in 0.1

103   and 1.0 M NaCl, KCl, $NaNO_3$, and $(CH_3)_4NCl$ as well as ultra pure water. Aliquots of each solution were

104   passed through filters with nominal pore sizes ranging from 450 nm to 12 nm to determine the particle

105   size range of the precipitates.

106

107 **2.4 Sorption of uranium to boehmite**

108 The effect of HEDPA on uranium partitioning to synthetic boehmite was examined by amending

109 equilibrated U(VI)-boehmite suspensions with HEDPA as described below. The uranium-boehmite

110 suspensions were prepared by adding an aliquot of the U(VI) working solution to a boehmite suspension

111 previously adjusted to a desired pH. The initial solution conditions were 6.1 μM U(VI), 660 mg L^{-1}

112 boehmite, and 1.0 M NaCl. The samples were mixed at 150 rpm for 10 days. Preliminary kinetic tests (in

113 the absence of HEDPA) indicated steady state uranium partitioning was achieved after 7 days. At

114 specified intervals, the soluble uranium concentration was determined in the filtrate obtained by passing a

115 subsample through a centrifugal filter (30k molecular-weight-cut-off, Nanosep, Pall Life Sciences,

116 estimated 12 nm pore size). The U concentration was measured by LSC as described above.

117 After 10 days, half of the uranium-boehmite suspensions were amended with a small volume of a

118 0.05 M HEDPA stock solution (pH 7) to yield a suspension containing 5.4 mM HEDPA, 600 mg L^{-1}

119 boehmite, and 1M NaCl. The other half of the suspensions were amended with a 0.5 M HEDPA solution

120 (pH 7) to yield a 50 mM, 600 mg L^{-1}, 1 M NaCl suspension. The final U(VI) concentration was 5.8 μM in

121 all suspensions. Boehmite-free control solutions were also amended to 5.4 mM HEDPA as described

122 above. The soluble uranium concentration was determined via filtration followed by LSC as described

123 above.

124

125 **3. Results and Discussion**

126 **3.1 HEDPA Interactions with Boehmite: Sorption and Dissolution**

127 In the absence of complexants, the aqueous phase concentration of aluminum is limited by the formation

128 of sparsely soluble Al (hydr)oxide solids, especially at circum-neutral pH values. As shown in Figure 2,

129 addition of HEDPA clearly enhances the dissolution of boehmite. Across the pH range 5 to 9, samples

130 amended with HEDPA have aluminum concentrations significantly higher than the HEDPA-free control

131 system. The enhanced dissolution of boehmite in the presence of HEDPA is likely the results of formation

132   of $Al_mH_hL_l$ complexes (where L represents completely deprotonated HEDPA and m, h, and l are

133   stoichiometric coefficients). The exact identity of specific complexes is uncertain at this point as the data

134   available in the current literature are not in agreement (5,6) and our potentiometric experiments to obtain

135   such data were unsuccessful due to the formation of a white precipitate across the neutral pH range (see

136   Section 2.3). The nature and composition of the white precipitate was not fully determined, but analysis

137   of the precipitate isolated from 1.0 M NaCl solutions with various Al(III):HEDPA molar ratios (from 1:1

138   to 1:2.5) indicated that it always had a 1:1 Al(III):HEDPA molar ratio. The observation of a 1:1

139   Al(III):HEDPA precipitate suggests that the low aluminum concentration across the neutral pH range

140   (Figure 2) may be controlled by the solubility of an Al(III):HEDPA solid phase. It was worth noting that

141   the constitution and concentration of the background electrolyte significantly affected the physical

142   characteristics of the precipitate. Precipitates prepared in 1.0 M NaCl and 1.0 M $NaNO_3$ tended to form

143   clearly distinct particles while precipitates from 1.0 M $(CH_3)_4NCl$ and 1.0 M KCl tended to have a gel-

144   like character, suggesting that sodium may cause significant aggregation of the Al(III):HEDPA particles.

145   In addition, the concentration of NaCl was also found to have a significant effect on the precipitate.

146   Solutions containing aluminum and HEDPA in a 2:5 molar ratio in ultra pure H_2O, 0.1 M NaCl, or 1.0 M

147   NaCl were passed through filters with pore sizes ranging from 450 nm to 12 nm. The fraction of soluble

148   aluminum was found to be inversely related to the ionic strength of the solution.

149   The concentrations of aluminum in more acidic (pH 4 to 5) and basic (pH > 10) regions were

150   higher than those in the neutral pH region (Figure 2). After 2 days at pH 4 to 5, the concentrations of

151   aluminum were comparable in systems with or without HEDPA. This is due to the formation of $Al(OH)^{2+}$

152   and $Al(OH)_2^+$ species yielding macromolar concentrations of aluminum in the absence of HEDPA. At pH

153   > 10, the dominant aqueous species is $Al(OH)_4^-$, yielding high aluminum concentrations in systems

154   without HEDPA. At pH 11, the presence of HEDPA resulted in a lower aluminum concentration than that

155   in the control system up to 16 days (Figure 2). This difference may be due to precipitation of an

156   Al(III):HEDPA solid as described above or slow kinetics of dissociation of Al(III):HEDPA complexes

157   from the mineral surface. Data in the literature indicate that phosphate may form multi-nuclear surface

158   complexes which could inhibit detachment of the metal-ligand complex from the surface or even inhibit

159   dissolution (13). Therefore, as HEDPA surface complexation would be expected to occur through the

160   phosphate group, the inhibition of boehmite dissolution may be due to formation of a multi-dentate

161   surface complex.

162

163   **3.2 Sorption of U(VI) to synthetic boehmite in the absence of HEDPA**

164   Data describing the sorption of uranium in the absence of HEDPA are shown in Figure 3. In the absence

165   of HEDPA, approximately 15% of the uranium was sorbed at pH 4. As the pH increased, the fraction of

166   uranium sorbed increased until relatively steady partitioning was reached at pH > 5. Above pH 5,

167   approximately 90% of the total uranium was sorbed. The sorption edge occurring between pH 4 and 5 has

168   been preciously observed by a number of researchers examining uranium sorption to aluminum

169   (hydr)oxides (10, 14-15) This behavior is consistent with electrostatic attraction/repulsion between

170   uranium and the boehmite surface. As shown in Figure 1, the boehmite surface charge transitions from a

171   net positive to a net negative charge as the pH increases. This is due to the protonation and deprotonation

172   of aluminol surface sites. At low pH values the positively charged uranyl dioxycation is repelled by the

173   positively charged boehmite surface. As the pH was increased, both the net positive surface charge and

174   the positive charge on the U(VI) species decreased (the latter due to hydrolysis), resulting in stronger

175   sorption of U(VI) onto boehmite. The slight decrease in the fraction of uranium sorbed observed at higher

176   pH values is presumed to be due to formation of soluble uranyl-carbonates. Although experiments were

177   run in sealed centrifuge tubes, no effort was made to exclude carbonate from these experiments.

178

179   **3.3 Effect of HEDPA Concentration on U(VI) sorption to Boehmite**

180   Significant leaching of uranium from boehmite occurred rapidly following the amendment of the

181   equilibrated uranium-boehmite suspensions to either 5 mM HEDPA or 50 mM HEDPA (Figure 4a and

182   4b). At all pH values above 4.5, the addition of HEDPA resulted in rapid leaching of uranium from

183   boehmite. Four hours after amendment of the uranyl-boehmite suspensions with 5 mM HEDPA, the

184   fraction of uranium sorbed within the neutral pH region dropped from approximately 90% to

185   approximately 50% (Figure 4a). Over the next 181 days, the concentration of uranium in the aqueous

186   phase continued to increase. This slow step could be due to a rate limitation of the dissociation of a

187   U(VI):HEDPA complex from the boehmite surface or due to continued dissolution of the boehmite phase.

188   A similar effect was observed for the 50 mM HEDPA system although a larger fraction of the total

189   uranium was leached into the aqueous phase within the first 4 hours (Figure 4b). Furthermore, the

190   concentration of uranium in the aqueous phase after 181 days was significantly greater in the 50 mM

191   HEDPA suspension relative to the 5 mM HEDPA suspension. The increased partitioning of uranium to

192   the aqueous phase in the 50 mM HEDPA system is presumably due to enhanced dissolution of the

193   boehmite solid phase, saturation of the remaining boehmite surface sites with HEDPA, and/or formation

194   of U(VI):HEDPA complexes. As shown in Figure 2, after 135 days, at least 10% of the aluminum in

195   boehmite suspensions with 50 mM HEDPA is soluble at all pH values examined (Al concentration greater

196   than 1.0×10^{-3} M). At pH values less than 5, the boehmite was almost completely dissolved. Therefore the

197   total boehmite surface available for sorption of uranium or U(VI):HEDPA complexes was significantly

198   diminished in the 50 mM HEDPA system.

199   Data in Figure 4a (for the 5 mM HEDPA system) indicate a loss of uranium from the aqueous

200   phase at low pH values following the addition of HEDPA. Such loss appears to be consistent with the

201   precipitation of U(VI):HEDPA complexes that was observed at low pH and low HEDPA:U(VI) ratios

202   (<2) by Reed et al. (4). However, precipitation of a U(VI):HEDPA complex in these sorption experiments

203   is not expected, because the HEDPA concentration is between 3 and 4 orders of magnitude higher than

204   the uranium concentration and uranium was found to remain in the aqueous phase in all control (with

205   HEDPA but without boehmite) solutions spanning the pH range 4 to 11 for the duration of these

206   experiments. Possible reasons for the observed loss of U(VI) in the low pH regions of the 5 mM HEDPA

207   system are discussed in Section 3.4.

208

209   **3.4 Effect of pH and HEDPA on U(VI) sorption to Boehmite**

210   *3.4.1 Uranium partitioning in the acidic pH region:* Unless specified, the effects of pH on uranium

211   partitioning will be discussed below in terms of the 5.4 mM HEDPA system (Figure 4a). At pH 4, the

212   addition of HEDPA increased the fraction of uranium sorbed from 15% to 47% within 4 hours (the

213   fraction remained unchanged for the remainder of the experiment up to 181 days). This is the only sample

214   in which the addition of HEDPA caused an increase in the sorption of uranium. The uranium partitioning

215   at low pH observed in this system is similar to the observations of Cheng et al. (16) who found that

216   phosphate caused increased uranium sorption to goethite-coated sands at low pH values, relative to

217   phosphate free suspensions. A similar pH effect was also observed by Guo et al. (17) and Guo et al., (18)

218   when examining thorium and uranium sorption in alumina suspensions amended with phosphate. Guo et

219   al., (18) proposed that the enhanced sorption of uranium was due to formation of ternary surface

220   complexes with U(VI) and phosphate.

221   Assuming that the behavior of the phosphate groups of HEDPA may be similar to that of

222   phosphate, the increased uranium sorption observed in this work was also likely caused by the formation

223   of a ternary U-HEDPA-AlOH surface complex. As the speciation plot of U(VI) in a 5.4 mM HEDPA

224   solution shows, a number of anionic U(VI):HEDPA species exist in low pH regions (Figure 5). On the

225   other hand, the boehmite surface carries a net positive charge at low pH values. Therefore the observed

226   increase in sorption could be due to sorption of anionic species such as $UO_2L_2H_4^{2-}$ or $UO_2L_2H_3^{3-}$. Similar

227   ternary surface complexes have been proposed to explain increased metal sorption at low pH values in the

228   presence of anionic metal-ligand complexes (19-21). In this case, sorption of the metal is proposed to be

229   due to the formation of a ternary complex where the ligand bridges the mineral surface and the metal.

230   Such a geometry could be conceptualized utilizing the two phosphate groups of HEDPA. Within this pH

231   region (pH ~4), HEDPA will be present as H_2L^{2-} (based upon the pK_a values reported by Reed et al., (4))

232   and will be attracted to the positively charged boehmite surface. Nowack and Stone (22) examined

233   HEDPA sorption to goethite and found that at low pH values, deprotonated anionic HEDPA species were

234   attracted to the positively charged goethite surface. As the pH increased, and the surface developed a net

235   negative charge, the sorption of HEDPA decreased (22). He et al., (23) observed similar pH effects when

236   examining phosphate sorption to alumina.

237   *3.4.2 Uranium partitioning at circumneutral pH :* Across the pH region from 5 to 8, the fraction

238   of sorbed uranium decreased significantly following the addition of HEDPA (Figure 4a). After 1 and 6

239   days, the fraction of uranium sorbed increased as the pH was increased from approximately 5 to 6.5.

240   Across the pH range 6.5 to 9, a relatively steady partitioning of uranium was observed for the sampling

241   intervals at 0.2, 1, and 6 days. After 6 days, a more general trend appeared in the data where the fraction

242   of uranium sorbed was found to increase as the pH increased from pH 5. It is noteworthy that

243   coprecipitation of uranium with an Al(III):HEDPA complex as discussed above is also a possibility.

244   However, the increase in uranium sorption with increasing pH is not consistent with coprecipitation as the

245   primary mechanism for loss of uranium from the aqueous phase. Across this circumneutral pH region (5

246   to 9), the anionic U(VI):HEDPA species $UO_2L_2H_2^{4-}$, $UO_2L_2H^{5-}$, and $UO_2L_2^{6-}$ are predominant (Figure 5)

247   and the boehmite surface maintains a net positive surface charge (Figure 1). This will allow for an

248   attractive force between the anionic U(VI):HEDPA complexes and the positively charged sites on the

249   boehmite surface. Since both free HEDPA and free U(VI) are known to sorb within this pH region, a

250   ternary surface complex could form through either uranium or HEDPA.

251   *3.4.3 Uranium partitioning above pH 9:* Above pH 9, the fraction of sorbed uranium decreased

252   significantly following the addition of HEDPA (Figure 4a). There was a slight decrease in the fraction of

253   uranium sorbed over the first 59 days followed by a significant decrease after 180 days. The rate at which

254   uranium was leached into the aqueous phase was similar to the rate of boehmite dissolution (Figure 2),

255   indicating that dissolution was a primary factor controlling uranium partitioning within this pH region. At

256   earlier time intervals, the fraction of uranium sorbed across the pH region 9 to 11 was higher relative to

257   the circumneutral pH region. This difference is proposed to be due to a change in the partitioning of

258   HEDPA within this pH region. Nowack and Stone (22) observed a significant decrease in the fraction of

259   HEDPA sorbed to goethite above pH 9. This is consistent with the full deprotonation of HEDPA in 1.0 M

260   NaCl (pK_{a4} = 9.5, measured in this work, data not shown). Therefore, boehmite sorption sites which are

261 occupied by HEDPA at neutral and acidic pH regions may be available for sorption of uranyl either as a

262 uranyl hydroxide or as a U(VI):HEDPA complex. In the absence of a complexing ligand, uranium

263 strongly sorbs to aluminum (oxy)hydroxides at high pH values (Figure 3 and references 10, 14, 15).

264 Therefore formation of a U(VI):hydroxide or U(VI):HEDPA (whereby surface complexation would occur

265 through uranium rather than through the phosphate groups of HEDPA) surface complex is feasible.

266 However, verification of such complexes through spectroscopy would be desirable, if not necessary, prior

267 to incorporation of such species into modeling efforts.

268

269 **4. Conclusions**

270 Results from this work show that HEDPA is capable of significantly enhancing the solubility of

271 aluminum hydroxides. The degree of enhancement is dependent upon the bulk solution pH and the

272 concentration of HEDPA. HEDPA is capable of leaching uranium from synthetic boehmite through solid

273 phase dissolution and/or the formation of U(VI):HEDPA complexes. Across the pH range examined, the

274 speciation of U(VI):HEDPA complexes affects the partitioning of uranium between the solid and aqueous

275 phase. Partitioning of uranium was observed to vary with pH and correlated with the partitioning of

276 HEDPA and HEDPA-promoted boehmite dissolution. The sorption of uranium to boehmite in the

277 presence of HEDPA is proposed to be through ternary U(VI):HEDPA surface complexes. However, no

278 spectroscopic evidence is provided to indicate formation of such complexes. These results indicate that

279 HEDPA could be used to reduce the volume of the aluminum component of sludge within the Hanford

280 waste tanks. However, because a significant fraction of uranium (and presumably other actinides) could

281 also be leached from boehmite by the addition of HEDPA, careful consideration of the partitioning of the

282 actinides must be made if a strong complexant such as HEDPA is selected for sludge washing.

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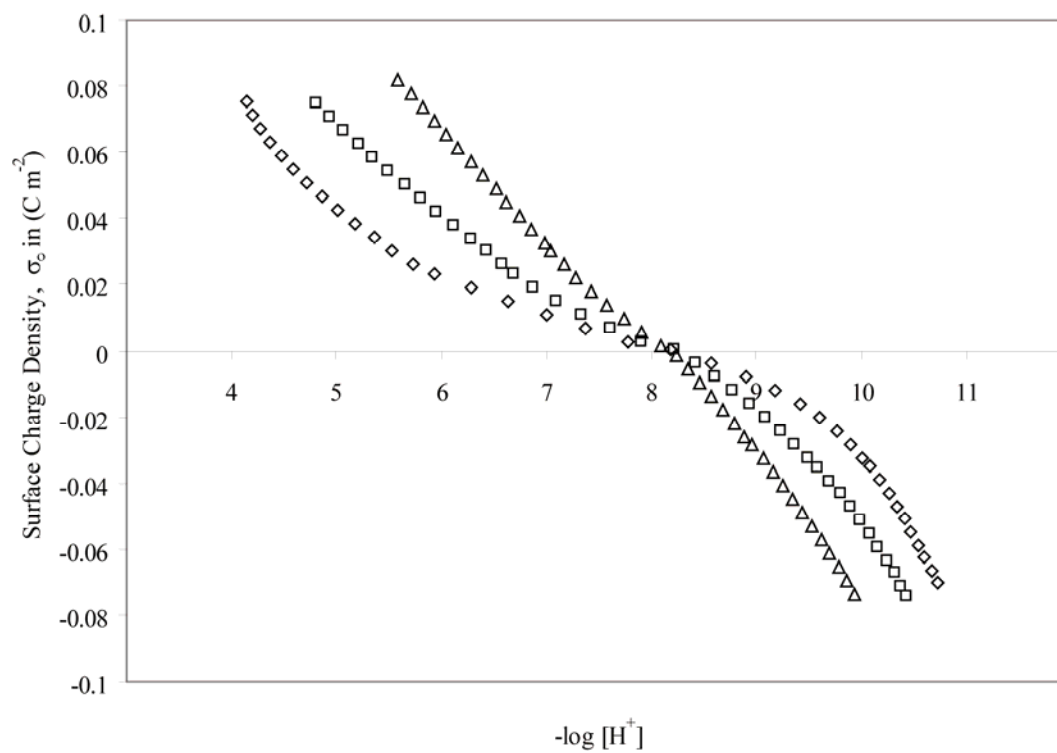
348
349 Figure 1: Potentiometric titrations of 100 g L^{-1} boehmite suspensions in 0.01 M NaCl ($\diamond$), 0.10
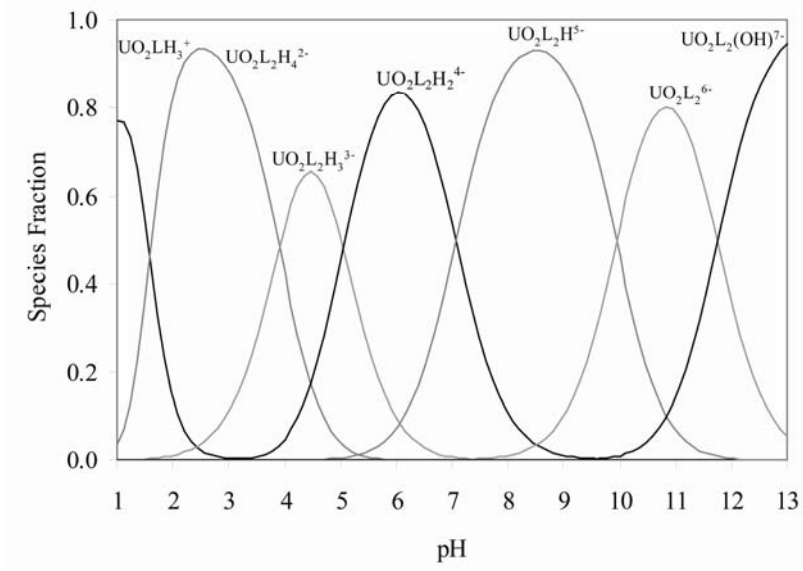350 M NaCl ($\square$), and 1.0 M NaCl ($\triangle$).
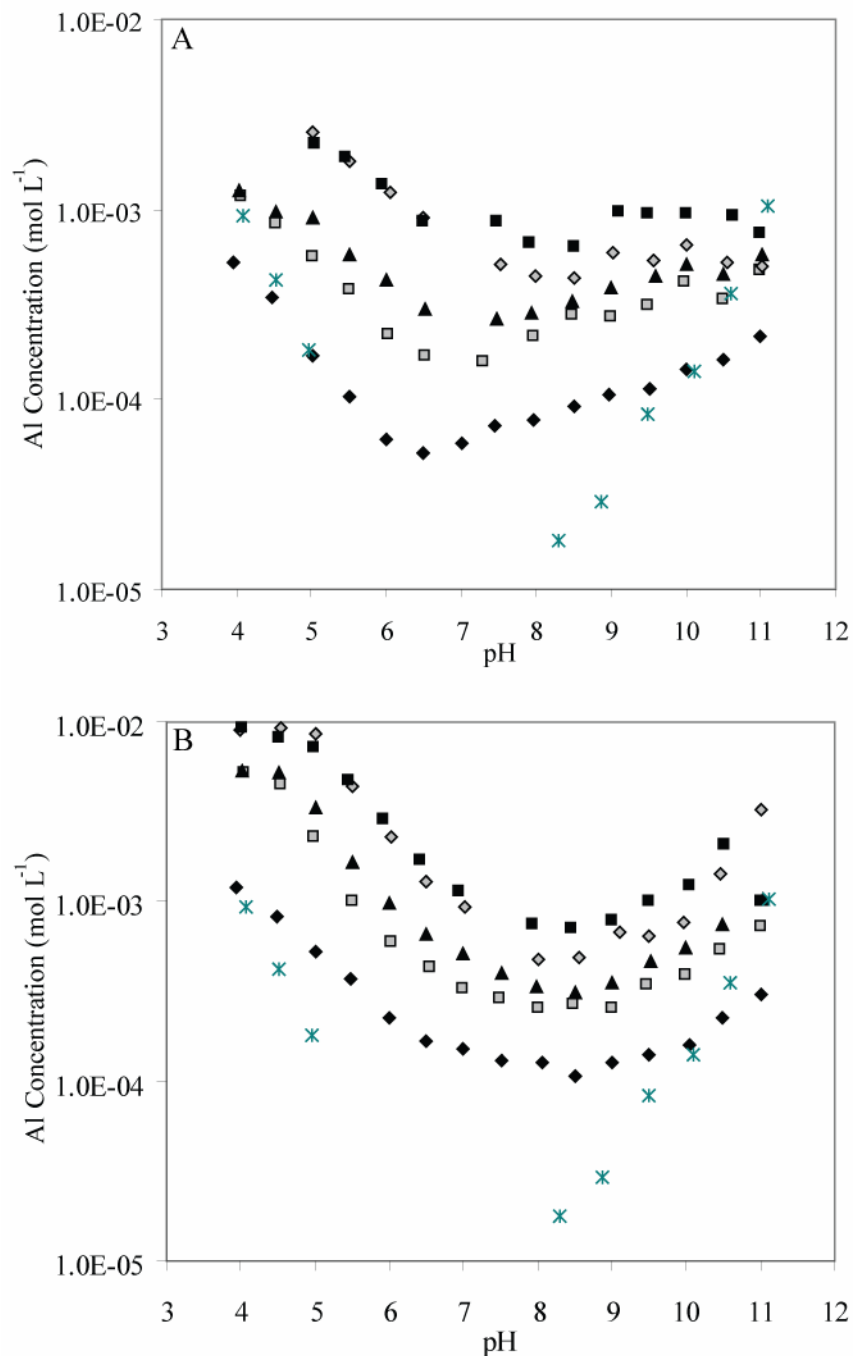
351
352
353 Figure 2: Effect of HEDPA on synthetic boehmite (γ-AlOOH) dissolution, [γ-AlOOH] = 600 mg
354 L^{-1} (10 mM as Al^{3+}), [NaCl] = 1.0 M. (A) [HEDPA] = 5.4 mM; (B) [HEDPA] = 50 mM.
355 Symbols: (◆) 2 days, (▫) 16 days, (▲) 36 days, (◇) 86 days, and (■) 135 days. (✳) Control system
356 contains no HEDPA and was measured after 135 days. Error bars, typically contained within
357 area of symbol at 95% certainty, have been removed for clarity.
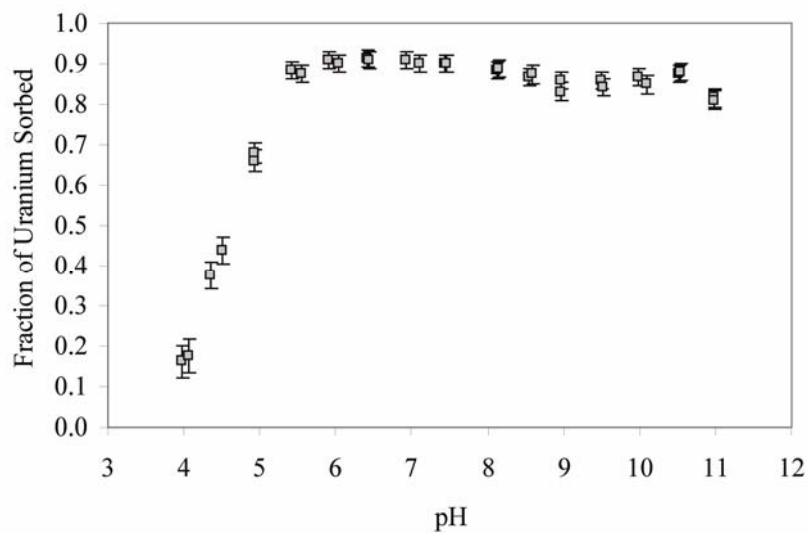
358
359 Figure 3: Fraction of uranium sorbed to boehmite versus pH after 10 day equilibration. System
360 parameters: [γ-AlOOH] = 0.66 g L^{-1}; [U(VI)] = 6.1 μM; [NaCl] = 1.0 M.
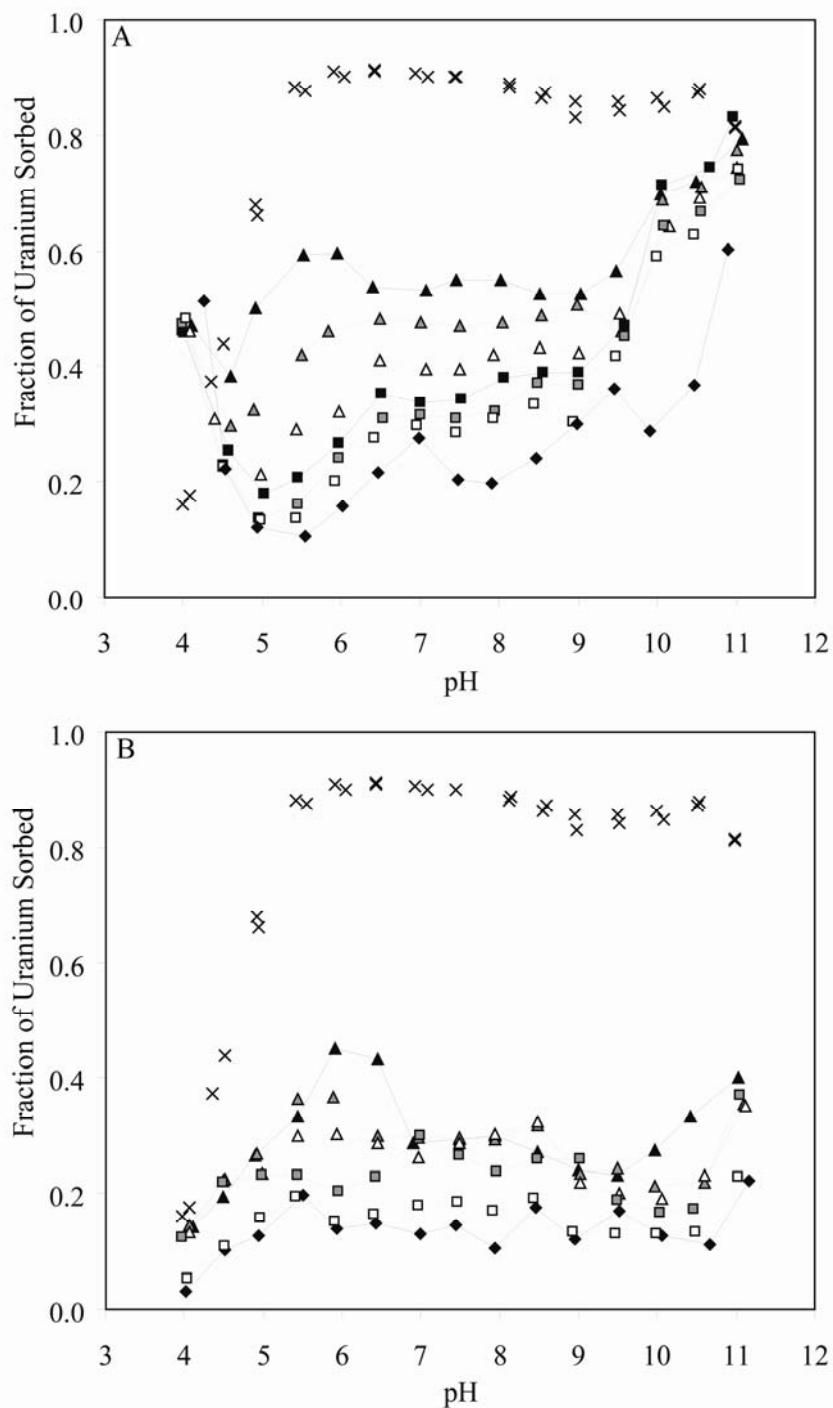
361
362 Figure 4: Effect of 5 mM (A) or 50 mM HEDPA (B) on Uranium Sorption to Boehmite:
363 Symbols (▲) 0.2 days, (△) 1 day, (△) 6 days, (■) 14 days, (▣) 30 days, (□) 59 days, and (◆) 180
364 days. For comparison, data from Figure 3 showing steady state distribution (10 day equilibrium)
365 of U(VI) without HEDPA present is shown (✕). System parameters: [γ-AlOOH] = 600 mg L^{-1};
366 [NaCl] = 1.0 M; [U(VI)] = 5.8 μM. Error bars removed for clarity, average 2σ = 3% propagated
367 from counting statistics.

18

368
369 Figure 5: Speciation of U(VI) in 5.4 mM HEDPA and 1.0 M NaCl, calculated with the
370 thermodynamic constants reported by Reed et al., (4). L stands for the fully deprotonated
371 HEDPA anion.
372