ACTINIDE AND LANTHANIDE INTERACTIONS WITH ALUMINUM (HYDR)OXIDE MINERALS: EQUILIBRIUM AND KINETICS ANALYSIS OF SORPTION AND DESORPTION PROCESSES

A Dissertation

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ACTINIDE AND LANTHANIDE INTERACTIONS WITH ALUMINUM (HYDR)OXIDE MINERALS: EQUILIBRIUM AND KINETICS ANALYSIS OF SORPTION AND DESORPTION PROCESSES

Abstract

by

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Nuclear energy does not generate greenhouse gas emissions during power production, but the high-level nuclear waste generated in the commercial nuclear fuel cycle remains a barrier to increased nuclear power use in the United States. This waste will eventually be disposed of in deep geologic repositories, yet the development of a nuclear repository is hindered by knowledge gaps related to how radionuclides behave and migrate in the environment. To fill these knowledge gaps, the work presented in this dissertation focuses on understanding how actinides and lanthanides interact with different aluminum (hydr)oxide minerals and how the different surface acidities of these minerals affect macroscopic sorption trends. Europium and neptunium interactions to gibbsite, bayerite, corundum, and γ-alumina were investigated through a series of batch sorption experiments at varying mineral and metal ion concentration, pH, and time.
Minerals were characterized to monitor for phase transformations and aqueous metal ion concentrations were measured using inductively-coupled plasma mass spectrometry. Kinetics analyses and equilibrium descriptions of the sorption and desorption processes of these systems are discussed in detail. Preliminary data focusing on the surface-mediated reduction of plutonium in the presence of bayerite and gibbsite are also presented.
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CHAPTER 1:
INTRODUCTION

1.1 Background

High concentrations of greenhouse gases in the atmosphere are projected to increase global temperature, acidify the oceans, and raise sea levels if emissions are not drastically reduced in the upcoming years (EPA, 2017). As the global energy demand continues to increase, the need to phase out fossil fuels in electricity production becomes even more critical. Nuclear energy does not generate greenhouse gas emissions during power production but it currently only accounts for 20% of the electricity generated in the United States (EIA, 2017). Nuclear energy has the potential to provide enough electricity while simultaneously reducing greenhouse gas emissions; however, the high-level nuclear waste generated during power production remains a barrier to increased nuclear power use.

High-level nuclear waste generated in the United States will ultimately be disposed of in deep geologic repositories (Blue Ribbon Commission, 2012). Nuclear repositories will rely on a multiple-barrier system to isolate waste from the environment for thousands of years; these containment systems will eventually fail and release radionuclides into the environment. Radionuclide contamination is of particular concern
because of the high toxicity and long half-lives \( (t_{1/2}) \) of several isotopes such as \( ^{237}\text{Np} \) \( (t_{1/2} = 2.14 \times 10^6 \text{ years}) \) and \( ^{239}\text{Pu} \) \( (t_{1/2} = 2.41 \times 10^4 \text{ years}) \). Therefore, it is necessary to understand the fate and transport of radionuclides in the environment once secondary containment barriers fail and radionuclides are released into the geosphere. As part of the certification process of future nuclear repositories, potential repository sites must undergo a performance assessment to show that the radionuclides placed in the repository will not come in contact with the aboveground ecosystems for 1 million years (NRC, 2016). Performance assessment models must show that the surface of a repository will not exceed an annual dose of 0.15 mSv for the first 10,000 years and 1.0 mSv between 10,000 and 1 million years (NRC, 2016). The reactive transport models currently used to assess radionuclide mobility in performance assessments are based on distribution coefficients \( (K_d) \). \( K_d \) models are empirically based and invalid outside of the experimental conditions under which they are determined; they are not able to accurately predict contaminant mobility under varying conditions such as ionic strength, temperature, or concentration.

In addition to eventually being placed in underground repositories, sites around the globe are currently contaminated with radionuclides from nuclear weapons testing and improper waste disposal. For example, underground testing at the Nevada Test Site generated approximately \( 1.23 \times 10^6 \text{ TBq} \) of radionuclides, including \( 1.37 \times 10^3 \text{ TBq} \) \(^{241}\text{Am}\), \( 8.88 \times 10^3 \text{ TBq} \) \(^{239,240}\text{Pu}\), and \( 1.80 \text{ TBq} \) \(^{237}\text{Np}\) (Smith et al., 2003) and an estimated \( 1.06 \times 10^3 \text{ TBq} \) \(^{241}\text{Am}\), \( 4.37 \times 10^2 \text{ TBq} \) \(^{239}\text{Pu}\), and \( 2.035 \text{ TBq} \) \(^{237}\text{Np}\) were disposed in the near-surface region of the Hanford Site as liquid waste (Cantrell et al., 2009).
Understanding how these radionuclides will migrate in the subsurface environment is important for the risk management of these contaminated sites.

Although they are still used as the industry standard to determine contaminant mobility, reactive transport models based on $K_d$ values have been unable to predict radionuclide mobility under relatively short time frames at the Nevada Test Site (Kersting et al., 1999), the Rocky Flats Technology Site (Santschi et al., 2002), and the Mayak Production Facility (Novikov et al., 2006). Plutonium at these sites was more mobile than predicted by the models, which did not take colloid formation into consideration. The failure of these models to predict mobility at these sites highlights the need for more robust transport models that hold up to varying environmental conditions and take into consideration the molecular-level interactions occurring at the mineral-water interface.

The environmental mobility of radionuclides is partially limited by sorption to geologic media via mechanisms such as specific and non-specific adsorption, ion exchange, and structural incorporation. Sorption to mobile pseudo-colloids and desorption from fixed geologic media increase the environmental availability of radionuclides. The sorption and desorption rates of radionuclides under changing conditions are also important for developing accurate reactive transport models but have been largely unaddressed in the literature. Instead, equilibrium and kinetics studies have generally focused on describing reaction rates and equilibrium sorption at one or two set solution conditions.

Studies investigating radionuclide sorption and desorption mechanisms and reaction rates have focused on various pure mineral phases, but aluminum (hydr)oxides have been largely under-investigated. Aluminum (hydr)oxides exist in the environment in
various crystalline and amorphous forms and the aluminol surface sites found on these minerals (e.g., ≡AlOH, ≡Al₂OH, ≡Al₃OH, ≡Al(OH)₂) (Franks et al., 2007; Yang et al., 2007) are also present on the bentonite clays which are proposed as backfill material for geologic repositories. These different surface morphologies and associated surface acidities are expected to influence radionuclide sorption and mobility, but the effect of these parameters has yet to be explicitly established.

This dissertation addresses these knowledge gaps by investigating the equilibrium interactions and sorption and desorption reaction rates of lanthanides and actinides to four aluminum (hydr)oxides: gibbsite (γ-Al(OH)₃), bayerite (α-Al(OH)₃), corundum (α-Al₂O₃), and γ –alumina (γ-Al₂O₃). The key findings of four projects focusing on europium, neptunium, and plutonium interactions with aluminum (hydr)oxides are summarized below and detailed discussions are provided in Chapters 2-5.

1.2 Chapter summaries

1.2.1 Comparison of europium and neptunium adsorption to aluminum (hydr)oxide minerals

Batch experiments and detailed solid-phase characterization (i.e., powder X-ray diffraction, scanning electron microscopy, and infrared spectroscopy) were used to determine the effect of secondary phase formation on the adsorption of europium and neptunium to a suite of aluminum (hydr)oxide minerals. Europium experiments were conducted in 0.01 M NaCl as a function of gibbsite, bayerite, corundum, and γ-alumina concentration (2.5 - 30 m²L⁻¹), europium concentration (10⁻⁸ - 10⁻⁵ M), and pH (3 - 12).
Neptunium experiments were conducted at constant neptunium and mineral concentrations. The composition of the mineral phase had no apparent effect on europium adsorption whereas preferential adsorption of neptunium followed the trend bayerite > corundum > γ-alumina. The data presented here suggest that there are at least two different mechanisms controlling the adsorption of europium and neptunium and highlight the need to study both aqueous-phase chemistry and the properties of mineral surfaces in order to understand the behavior of lanthanides and actinides at the mineral-water interface.

This work was accepted for publication in January 2017 (Baumer, T.; Kay, P.; Hixon, A. E. *Chem. Geol.* 2017, 464, 84-90.).

### 1.2.2 Kinetics of europium sorption to four different aluminum (hydr)oxides: Corundum, γ-alumina, bayerite, and gibbsite

Batch kinetics experiments were performed to investigate europium sorption to four aluminum (hydr)oxide minerals as a function of time (10 - 120 minutes), mineral concentration (0.5 - 50 m²·L⁻¹), pH (5 - 7), and europium concentration (10⁻⁹ - 10⁻⁷ M). Linear and non-linear pseudo-first and pseudo-second order rate equations were used to fit the data. The overall reaction rates and reaction orders with respect to proton concentration, mineral concentration, and europium concentration were determined, leading to a governing rate law for each mineral system. Europium sorption is characterized by a two-step reaction with a fast initial adsorption step followed by a slower adsorption or aging process. The pseudo-second order equations resulted in better model fits of the data. Using the non-linear pseudo-second order rate constants, it was
observed that the reaction orders for each mineral system were similar but resulted in different overall reaction rates following the trend bayerite ~ γ-alumina > corundum > gibbsite.

This work was accepted for publication in September 2018 (Baumer, T.; Hixon, A. E. J. Environ. Radioact. 2018, 195, 20-25.).

1.2.3 Kinetics of neptunium sorption and desorption in the presence of aluminum (hydr)oxide minerals: Evidence for multi-step desorption at low pH

Neptunium sorption to and desorption from the four different aluminum (hydr)oxides were investigated as a function of mineral concentration (5 – 170 m²·L⁻¹), neptunium concentration (10⁻⁹ – 10⁻⁷ M), and pH (5.5 – 10.5). Neptunium sorption was characterized by a two-step sorption reaction with an initial fast sorption step occurring within minutes followed by a slower equilibrium process, which was attributed to initial sorption of neptunium to a small number of strong sorption sites followed by sorption of neptunium to a larger number of weak sorption sites. The kinetics data were modeled using the linear and non-linear forms of the pseudo-first and pseudo-second order rate equations and the goodness of fits were compared. Non-linear pseudo-second order rate constants described neptunium sorption to aluminum (hydr)oxides most accurately and were used to determine the reaction orders with respect to mineral concentration and [H⁺]. Neptunium desorption was much slower than sorption, did not reach steady-state within the course of the study, and was not described well by either pseudo-first or second order rate equations when the pH was < 6.5. The ability of the pseudo-second
order models to accurately fit the sorption data but not the desorption data suggests that there are different forward and reverse reactions for neptunium sorption and desorption that are not captured by these relatively simple kinetics models. Additionally, the false steady-state desorption plateaus observed in this work highlight the possibility of a multi-step desorption reaction at low pH. The comparatively slow desorption kinetics observed here suggests that sorbed neptunium could be slowly released back into the aqueous phase and act as a continuous source of contamination to the environment.

A manuscript for this work was submitted in January 2019.

1.2.4 Plutonium sorption and reduction in the presence of bayerite and gibbsite

Plutonium aqueous and solid phase oxidation state distributions were monitored as a function of time in suspensions containing aluminum hydroxide suspensions and 0.01 M NaCl. Batch kinetics experiments were conducted for plutonium ($5.5 \times 10^{-10}$ M) sorption to two aluminum hydroxides – gibbsite (170 m$^2$·L$^{-1}$) and bayerite (5 m$^2$·L$^{-1}$). More plutonium sorption was observed on bayerite compared to gibbsite and resulted in distinct sorption trends for the two minerals. This observation is attributed to different ratios of singly-coordinated surface sites on the minerals and fast sorption kinetics of bayerite. Similar plutonium aqueous phase oxidation state distributions were observed in both systems. Plutonium was initially added as Pu(VI) and reduced to Pu(V) in the aqueous phase; however, reduction to Pu(IV) was only observed on the solid phase of both minerals. Reduction of plutonium on bayerite and gibbsite is attributed to surface-mediated reduction and is likely the result of Nernstian favorability of Pu(IV) complexes. Kinetics analysis shows that surface-mediated reduction is kinetically limited by sorption
and reduction for gibbsite and bayerite, respectively. This work suggests that small changes in mineral surface chemistry will influence sorption rates and, in turn, long term environmental mobility of plutonium and is the first to establish surface-mediated reduction of plutonium in the presence of aluminum hydroxide minerals.

Additional work, described in Chapter 6, is needed to make this work ready for publication.
CHAPTER 2: COMPARISON OF EUROPIUM AND NEPTUNIUM ADSORPTION TO ALUMINUM (HYDR)OXIDE MINERALS

2.1 Introduction

Anthropogenic sources of neptunium and americium have been introduced into the environment through nuclear weapons testing and improper disposal at legacy waste sites. For example, underground testing at the Nevada Test Site generated $1.23 \times 10^6$ TBq of radionuclides, including $1.80$ TBq $^{237}$Np and $1.37 \times 10^3$ TBq $^{241}$Am (Smith et. al, 2003); an estimated $1.06 \times 10^3$ TBq $^{241}$Am and $2.035$ TBq $^{237}$Np were disposed in the near-surface region of the Hanford Site as liquid waste (Cantrell, 2009). Furthermore, deep geologic disposal is generally accepted as the best long-term solution for disposing of high-level nuclear waste (Blue Ribbon Commission, 2012). The long half-lives of several radionuclides found in high-level nuclear waste [e.g., $^{237}$Np ($t_{1/2} = 2.14 \times 10^6$ years)] mean that once they are released into the environment, they will persist for millions of years. In particular, neptunium is expected to be a major radiation dose contributor in a repository after 10,000 years due to $^{241}$Am decay to $^{237}$Np. For these reasons, it is essential to predict the mobility of these radionuclides in the subsurface environment.
Metal oxides are expected to play an important role in controlling radionuclide mobility. Aluminum (hydr)oxides exist in the environment in various crystalline and amorphous forms and the aluminol surface sites found on these minerals (e.g., \(≡\text{AlOH}, \equiv\text{Al}_2\text{OH}, \equiv\text{Al}_3\text{OH}, \equiv\text{Al(OH)}_2\) (Franks and Gan, 2007; Yang et al., 2007) are also present on the bentonite clays which are proposed as backfill material for geologic repositories. These different surface morphologies and associated surface acidities are expected to influence radionuclide sorption and mobility, but the effect of these parameters has yet to be explicitly established. Yang et al. (2007) use computational studies to determine the surface acidities of gibbsite (\(\gamma\)-\text{Al(OH)}_3), corundum (\(\alpha\)-\text{Al}_2\text{O}_3), and \(\gamma\)-alumina (\(\gamma\)-\text{Al}_2\text{O}_3) and show that surface acidity follows the trend corundum > gibbsite > \(\gamma\)-alumina. These surface acidities are based on the ratios of oxygen and aluminum exposed to the mineral surface which leads to different ratios of singly-, doubly-, and triply-coordinated hydroxyl groups. Decreasing the fraction of aluminum at the surface results in a higher \(\text{pK}_a\) value (i.e., a more basic surface) and corresponds to a larger amount of singly-coordinated hydroxyl groups (Franks and Gan, 2007; Yang et al., 2007). The reported \(\text{pK}_{a1}\) and \(\text{pK}_{a2}\) values shown in Table 2.1 are derived from reactions 2.1 and 2.2, respectively, and suggest that distinct sorption behavior should be observed for corundum, gibbsite, and \(\gamma\)-alumina.

\[
\equiv\text{AlOH}_2^+ \leftrightarrow \equiv\text{AlOH} + \text{H}^+ \quad (2.1)
\]

\[
\equiv\text{AlOH} \leftrightarrow \equiv\text{AlO}^- + \text{H}^+ \quad (2.2)
\]
TABLE 2.1.

**PKA\textsubscript{1} AND PKA\textsubscript{2} VALUES\textsuperscript{1} FOR CORUNDUM, GIBBSITE, AND Γ-ALUMINA\textsuperscript{2}\n
<table>
<thead>
<tr>
<th>Mineral</th>
<th>pK\textsubscript{a1}</th>
<th>pK\textsubscript{a2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corundum (α-Al\textsubscript{2}O\textsubscript{3})</td>
<td>6.03 ± 0.25</td>
<td>7.47 ± 0.42</td>
</tr>
<tr>
<td>Gibbsite (γ-Al(OH)\textsubscript{3})</td>
<td>6.78 ± 0.4</td>
<td>10.10 ± 0.43</td>
</tr>
<tr>
<td>γ-alumina (γ-Al\textsubscript{2}O\textsubscript{3})</td>
<td>8.50 ± 0.29</td>
<td>9.20 ± 0.52</td>
</tr>
</tbody>
</table>

\textsuperscript{1} See reactions 1 and 2 in the main text
\textsuperscript{2} As supported by Yang et al. (2007)

Understanding the role of aluminum (hydr)oxide surface acidities is further complicated by the tendency of these minerals to undergo phase transformations in aqueous environments. In particular, γ-alumina slowly changes to gibbsite or bayerite under acidic and alkaline conditions, respectively (Carrier et al., 2007). These changes are hypothesized to be due to the dissolution and re-precipitation of aluminum aqueous species as a secondary mineral phase. Using transmission electron microscopy (TEM) and powder X-ray diffraction (pXRD), Carrier et al. (2007) observe the formation of bayerite (α-Al(OH)\textsubscript{3}) and gibbsite particles on the surface of γ-alumina solids after 7 days above pH 5. Lefèvre et al. (2002) show bayerite formation on the surface of γ-alumina after 4 days at circumneutral pH, which accounts for a reduction in the surface reactivity of γ-alumina.

Studies investigating americium interactions at the mineral-water interface often use non-radioactive analogs such as Eu(III) because the high radioactivity of americium...
requires specialized training and research facilities. Rabung et al. (2000) observe similar sorption behavior for Am(III) and Eu(III) in the presence of γ-alumina. As Eu(III) concentration increases over the range $9.0 \times 10^{-8}$ M – $3.1 \times 10^{-5}$ M at constant solid concentration (3.6 g·L$^{-1}$) and ionic strength (0.1 M NaClO$_4$), the sorption edge shifts to higher pH. Within experimental error, europium sorption behavior is unaffected by changes in ionic strength, which is indicative of strong inner-sphere complex formation (i.e., adsorption). Indeed, Kumar and colleagues report the formation of monodentate Baumer.t europium complexes with γ-alumina at pH 6 (Kumar et al., 2012). Kupcik et al. (2016) show that corundum and bayerite exhibit nearly identical Eu(III) adsorption trends at trace europium concentrations ($\sim 10^{-7}$ M) and suggest that the similarity in adsorption behavior is due to either the transformation of corundum into bayerite or the influence of an additional amorphous aluminum phase, although no evidence is provided to support these hypotheses.

In comparison to europium, neptunium sorption to aluminum (hydr)oxides is not as well studied and limited primarily to interactions with gibbsite. Under standard laboratory conditions, neptunium sorption to gibbsite increases with increasing pH with maximum sorption observed around pH 8. Above pH 8, sorption decreases due to the formation of negative neptunyl-carbonate (NpO$_2$CO$_3^-$) species in solution (Wu et al., 2009). In experiments containing low or no carbonate, neptunium sorption increases with increasing pH even above pH 8 due to the formation of charged neptunyl-hydroxo species (Turner et al., 1998). Regardless of the prevailing atmospheric conditions, neptunium is found to form mononuclear, inner-sphere complexes with amorphous Al(OH)$_3$ and gibbsite (Gückel et al., 2013).
The present study probes Np(V) and Eu(III) sorption to gibbsite, corundum, γ-alumina and bayerite as a function of metal concentration, mineral concentration, and pH. Secondary phase formation is monitored using pXRD, scanning electron microscopy (SEM), and Fourier transform infrared (FT-IR) spectroscopy. It is the first study to compare preferential adsorption of europium and neptunium to a suite of aluminum (hydr)oxide minerals and has two main goals: (i) to determine if the nearly identical Eu(III) sorption behavior for aluminum (hydr)oxides is due to bayerite formation and (ii) to determine if identical sorption edges are also observed for pentavalent metal ions.

2.2 Materials and Methods

2.2.1 Solid phase preparation and characterization

Aluminum oxide and hydroxide minerals were obtained from Alfa Aesar (α-Al₂O₃ and γ-Al₂O₃), Alteo (γ-Al(OH)₃), and Sasol Germany GmbH (β-Al(OH)₃). Due to their high purities and the risk of solid-phase transformation, bayerite and γ-Al₂O₃ were used as received. Gibbsite and α-Al₂O₃ powders were washed in dilute nitric acid (0.01 M) followed by dilute sodium hydroxide (0.01 M) three times before being rinsed five times with ultra-pure water. The minerals were then dried in an oven overnight at 100°C before use. The N₂(g)-BET surface area was determined at 77 K for each mineral using a Micromeritics ASAP 2020 Accelerated Surface Area and Porosity System and are presented in Table 2.2. The minerals were also characterized using a Bruker D8 Advance Davinci pXRD (2θ increments of 0.02 and a 7 second time step) to verify the purity of the mineral phases. Diffraction patterns are provided in Appendix A.
TABLE 2.2.

N<sub>2</sub>(G)-BET SURFACE AREAS OF CORUNDUM, Γ-ALUMINA, BAYERITE, AND GIBBSITE

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Surface Area (m&lt;sup&gt;2&lt;/sup&gt;g&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corundum (α-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>4.80 ± 0.06</td>
</tr>
<tr>
<td>γ-alumina (γ-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>58.10 ± 2.66</td>
</tr>
<tr>
<td>Bayerite (α-Al(OH)&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>9.49 ± 0.05</td>
</tr>
<tr>
<td>Gibbsite (γ-Al(OH)&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>64.47 ± 0.01</td>
</tr>
</tbody>
</table>

2.2.2 Batch hydration experimental conditions and methods

Phase transformations of γ-Al<sub>2</sub>O<sub>3</sub> were monitored with batch hydration experiments. Suspensions of γ-Al<sub>2</sub>O<sub>3</sub> (1170.1 ± 8.5 m<sup>2</sup>L<sup>-1</sup>) in 0.01 M NaCl were adjusted with dilute HCl and NaOH to pH 4.42, 6.84, 7.59, 8.45, and 9.93. The samples were mixed end-over-end and pH adjusted daily. At 7 and 14 days, the mineral was separated from the aqueous phase using a Buchner funnel. The samples were allowed to air dry overnight and were analyzed using pXRD, scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FT-IR). Samples analyzed with SEM were adhered to carbon tape and coated with iridium to reduce charging effects before being analyzed on a Carl Zeiss EVO 50 LEO operated at 20 kV. FT-IR analysis utilized a Bruker Tensor 27 instrument equipped with a deuterated triglycine sulfate (DTGS) detector. The resolution was 4 cm<sup>-1</sup>.
2.2.3 Neptunium and europium working solution preparation

To prepare the $1.098 \times 10^{-6}$ M neptunium working solution, a small aliquot of a $2.467 \times 10^{-5}$ M $^{237}$Np stock solution (NIST SRM 4341A) was diluted in doubly distilled nitric acid (2%). Prior to dilution, the neptunium stock was confirmed to be Np(V) using a Cary 6000i UV-vis-NIR spectrometer. Similarly, a $1.047 \pm 0.005$ M europium working solution was prepared through dilution of a $1001 \pm 4$ M europium stock solution (BDH) and was used for batch sorption experiments run at $10^{-8}$ M europium. For batch sorption experiments run at $10^{-5}$ M europium, the BDH stock solution was used without additional dilution.

2.2.4 Batch sorption experimental conditions and methods

Batch experimental conditions are summarized in Table 2.3. All suspensions were prepared in $0.01$ M NaCl and the pH was adjusted using dilute NaOH or HCl. The reactors were mixed end-over-end and samples were taken at 7 days and 14 days. During sampling, a homogenous aliquot was taken from the reactor solution and centrifuged to leave <100 nm particles in solution. The size fraction was calculated from Stokes Law, as described in Jackson (1969). The aqueous phase was diluted in doubly distilled 2% nitric acid and analyzed using inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma optical emission spectroscopy (ICP-OES). Experiments conducted at $10^{-8}$ M europium or neptunium were analyzed on a Nu Attom II ICP-MS in medium resolution to determine the aqueous metal ion concentration. An external calibration curve was used and intensities were normalized for instrumental drift using a neodymium or thorium internal standard for europium or neptunium analysis,
respectively. Experiments where the initial europium concentration was $10^{-5}$ M were analyzed with a Perkin Elmer Optima 8000 ICP-OES. All values were corrected for instrumental drift using an yttrium internal standard.

### TABLE 2.3.

**MATRIX OF EXPERIMENTAL CONDITIONS**

<table>
<thead>
<tr>
<th>Sorbant</th>
<th>Element</th>
<th>Concentration (mol·L⁻¹)</th>
<th>Solid Concentration (m²L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Al₂O₃</td>
<td>Eu</td>
<td>$(1.03 \pm 0.02) \times 10^{-8}$</td>
<td>2.40 ± 0.01</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>Eu</td>
<td>$(1.03 \pm 0.03) \times 10^{-8}$</td>
<td>4.83 ± 0.02</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>Eu</td>
<td>$(1.03 \pm 0.03) \times 10^{-8}$</td>
<td>29.5 ± 0.1</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>Eu</td>
<td>$(1.03 \pm 0.03) \times 10^{-5}$</td>
<td>5.02 ± 0.02</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>Np</td>
<td>$(9.74 \pm 0.28) \times 10^{-9}$</td>
<td>5.05 ± 0.15</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>Eu</td>
<td>$(1.04 \pm 0.05) \times 10^{-8}$</td>
<td>2.50 ± 0.01</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>Eu</td>
<td>$(1.05 \pm 0.03) \times 10^{-8}$</td>
<td>5.07 ± 0.02</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>Eu</td>
<td>$(1.03 \pm 0.02) \times 10^{-8}$</td>
<td>29.79 ± 0.21</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>Eu</td>
<td>$(1.02 \pm 0.02) \times 10^{-5}$</td>
<td>5.00 ± 0.01</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>Np</td>
<td>$(9.39 \pm 0.05) \times 10^{-9}$</td>
<td>4.91 ± 0.03</td>
</tr>
<tr>
<td>bayerite</td>
<td>Eu</td>
<td>$(1.03 \pm 0.03) \times 10^{-8}$</td>
<td>4.931 ± 0.017</td>
</tr>
<tr>
<td>bayerite</td>
<td>Eu</td>
<td>$(9.84 \pm 0.03) \times 10^{-5}$</td>
<td>4.92 ± 0.08</td>
</tr>
<tr>
<td>bayerite</td>
<td>Np</td>
<td>$(9.36 \pm 0.07) \times 10^{-9}$</td>
<td>4.88 ± 0.02</td>
</tr>
<tr>
<td>gibbsite</td>
<td>Eu</td>
<td>$(1.04 \pm 0.04) \times 10^{-8}$</td>
<td>2.54 ± 0.02</td>
</tr>
<tr>
<td>gibbsite</td>
<td>Eu</td>
<td>$(1.06 \pm 0.03) \times 10^{-8}$</td>
<td>5.15 ± 0.05</td>
</tr>
<tr>
<td>gibbsite</td>
<td>Eu</td>
<td>$(1.04 \pm 0.02) \times 10^{-8}$</td>
<td>34.93 ± 0.14</td>
</tr>
<tr>
<td>gibbsite</td>
<td>Eu</td>
<td>$(1.00 \pm 0.02) \times 10^{-5}$</td>
<td>4.99 ± 0.04</td>
</tr>
</tbody>
</table>
2.3 Results

2.3.1 Batch hydration experiments

Several previous studies have explicitly investigated the effect of hydration on \( \gamma \)-alumina surface structure and reactivity (Lefèvre et al., 2002; Carrier et al., 2007; Yang et al., 2007). Specifically, they have observed the formation of bayerite as a secondary phase after as little as ten hours when the pH of the aqueous phase is greater than five (Carrier et al., 2007). In order to determine if bayerite formation was important in our experimental systems, we conducted batch hydration experiments and determined the solid-phase composition using pXRD, SEM imaging, and FT-IR spectroscopy after 14 days.

pXRD diffraction patterns indicate that, regardless of pH, \( \gamma \)-alumina exists as the primary mineral phase even after 14 days (see Appendix A). Diffraction peaks indicative of bayerite are not observed. However, this technique has a relatively high detection limit and will not show mineral phases that represent less than 5% of the total bulk material analyzed. Therefore, based on these results it is only possible to say that at least 95% of the bulk mineral remains as \( \gamma \)-alumina after 14 days of hydration across the pH range analyzed.

SEM imaging was used to compare the surface morphology of as-received \( \gamma \)-alumina and \( \gamma \)-alumina that had been hydrated for 14 days. As shown in Figure 2.1, SEM images of the as-received material show a reasonably flat surface with parallel fractures. After hydration at pH 10, the surface remains relatively unchanged, although the parallel fractures are not as apparent as in the as-received material. While this may be indicative
of surface transformation or secondary phase formation, the results are not conclusive.

Definitive bayerite formation would have resulted in sub-micrometer platelets on the γ-alumina surface (Lefèvre et al., 2002) or independent, crystalline particles on the order of 200 nm (Carrier et al., 2007).

![SEM images](image)

Figure 2.1. SEM images of (A) as-received γ-alumina and (B) γ-alumina hydrated at pH 10 for 14 days in 0.01 M NaCl. Scale bar applies to both images.

Because of the high detection limits and inconclusive results of pXRD and SEM, respectively, FT-IR spectroscopy was used to confirm the formation of bayerite in γ-
alumina samples as a function of pH. As seen in Figure 2.2, the characteristic peaks of bayerite are observed in γ-alumina samples hydrated at pH 8.45 and 9.93, but not at lower pH values. The broad peak at approximately 3450 nm⁻¹ is attributed to O-H stretching in the hydrated samples.

![Image of FT-IR spectra](image)

Figure 2.2. FT-IR spectra of bayerite, γ-alumina, and γ-alumina hydrate at pH 4.42, 6.84, 7.59, 8.45, and 9.93 in 0.01 M NaCl for 14 days.

2.3.2 Europium batch sorption experiments

The fraction of europium associated with aluminum (hydr)oxide mineral phases was monitored as a function of pH, europium concentration, and mineral concentration. The fraction of europium removed from solution after 7 and 14 days was similar (see Appendix A). Therefore, while we assume that equilibrium was achieved within 7 days, the following discussion and data interpretation rely on the more conservative data collected at 14 days. Removal of europium from the aqueous phase is assumed to be due
to adsorption (Rabung et al., 2000; Kumar et al. 2012, 2013). The extent of europium adsorption onto gibbsite, corundum, γ-alumina, and bayerite at equilibrium is depicted as a function of pH and europium concentration in Figure 2.3. Under all experimental conditions, europium adsorption increased with increasing pH. This trend has been previously observed (Rabung et al., 2000; Naveau et al., 2005; Kupcik et al., 2016) and is partially due to electrostatic interactions between an increasingly negatively charged mineral surface and aqueous europium cations. Europium will exist primarily as Eu$^{3+}$ until pH 7 when Eu(OH)$^{2+}$ and Eu(OH)$_2^+$ species begin to form in solution. Above pH 9, Eu(OH)$_3(aq)$ is the primary europium species. While there may be slight preferential adsorption of Eu(III) to bayerite under low europium concentrations, europium behavior is similar in the presence of corundum, γ-alumina, and gibbsite.
Figure 2.3. Adsorption of (A) $(1.04 \pm 0.06) \times 10^{-8}$ M Eu(III) and (B) $(3.22 \pm 0.05) \times 10^{-5}$ M Eu(III) to bayerite (X), corundum (▲), γ-alumina (■), and gibbsite (●) as a function of pH. Experimental conditions: [mineral] = 5 m$^2$L$^{-1}$; I = 0.01 M NaCl; t = 14 days. Error bars represent the error propagated from uncertainty in ICP-MS or ICP-OES measurements.
Increasing the europium concentration from $10^{-8}$ M to $10^{-5}$ M shifts the sorption edge to higher pH values (see Figure 2.3). This decrease in adsorption with increasing europium concentration could be attributed to (i) a higher solid phase to europium ratio at $10^{-8}$ M europium than at $10^{-5}$ M europium (i.e., surface site saturation) (Dzombak and Morel, 1990), (ii) saturation of strong bonding sites at higher europium concentrations (Dzombak and Morel, 1990; Smith et al., 1999; Rabung et al., 2000; Kupcik et al., 2016), or (iii) europium precipitation (Dzombak and Morel, 1990). Although simulations using Visual MINTEQ 3.0 suggest that a $10^{-5}$ M europium solution is unstable with respect to Eu(OH)$_3$(s) above pH 7, precipitates were not observed via SEM imaging. This is similar to the results of Rabung et al. (2000), who show that even though solubility calculations predict europium precipitation, only inner-sphere complexes were observed using time resolved laser fluorescence spectroscopy (TRLFS). Furthermore, extended X-ray absorption near edge structure (EXAFS) spectroscopy results suggest the absence of Eu(III) precipitation regardless of pH despite oversaturation of Eu(III) at pH 8 (Kumar et al., 2012).

Given that Eu(III) precipitation was not observed in TRLFS and EXAFS studies, which required much higher Eu(III) concentrations than those used in the present study, we conclude that the observed decrease in adsorption with increasing europium concentration is not due to europium precipitation. Since surface site saturation would result in a sorption curve that levels off at less than 100% adsorption (Dzombak and Morel, 1990), the saturation of strong binding sites at $10^{-5}$ M europium is the most plausible explanation for this behavior. Sorption experiments as a function of mineral concentration over the range 2.5 to 30 m$^2$L$^{-1}$ resulted in very similar sorption edges (see
Figure 2.4). Assuming a total site density of 8 sites per nm$^2$, (Karamalidis and Dzombak, 2010), the calculated site concentration at the lowest mineral concentration is approximately $3 \times 10^{-5}$ sites per liter. Therefore, even at 2.5 m$^2$L$^{-1}$ gibbsite, the europium concentration is several orders of magnitude less than the surface site concentration. Thus, increasing the mineral concentration has no impact on the amount of europium removed from solution at equilibrium.

![Figure 2.4](image)

Figure 2.4. Europium adsorption to gibbsite as a function of gibbsite concentration. Experimental conditions: [Eu]$_T$ = $(1.05 \pm 0.05) \times 10^{-8}$ M; I = 0.01 M NaCl; t = 14 days. Error bars represent the error propagated from uncertainty in ICP-MS measurements.

2.3.3 Neptunium batch sorption experiments

Neptunium sorption to aluminum (hydr)oxide minerals was also monitored as a function of time and pH. As in the europium systems, the fraction of neptunium removed
from solution after 7 and 14 days was similar. Therefore, while we assume that
equilibrium was achieved within 7 days, the following discussion and data interpretations
rely on the more conservative data collected at 14 days. Figure 2.5 shows that the fraction
of neptunium associated with the solid phase increases with increasing pH. Removal
from the aqueous phase is assumed to be due to adsorption (Gückel et al., 2013). In
contrast to europium, preferential adsorption of neptunium followed the trend bayerite >
corundum > γ-alumina. In other studies of neptunium interactions with aluminum
(hydr)oxide minerals, removal of neptunium from solution is found to decrease above pH
9 due to the formation of aqueous neptunium carbonate species, such as NpO₂CO₃⁻,
NpO₂(CO₃)₂³⁻, and NpO₂(CO₃)₃⁵⁻ (Turner et al., 1998; Li and Tao, 2003; Wu et al., 2009),
which presumably undergo electrostatic repulsion by the negatively-charged surface. A
decrease in neptunium uptake is not observed in our systems and may be due to the
formation of ternary surface complexes, as described by Gückel et al. (2013) for
NpO₂CO₃⁻ sorption to gibbsite. Alternatively, our samples may not have had sufficient
contact time with air during sample preparation to reach equilibrium with CO₂, leading to
a predominance of neptunyl hydrolysis products above pH 8 (Turner et al. 1998; Rabung
et al., 2000).
2.4 Discussion and Conclusions

Previous studies have suggested that the observation of identical sorption edges for trivalent metal atoms regardless of aluminum (hydr)oxide mineral phase is due to the formation of bayerite (e.g., Kupcik et al, 2016). Our characterization using pXRD, SEM imaging, and FT-IR spectroscopy shows that bayerite is indeed forming in low concentrations on the γ-alumina surface at pH ≥ 8.45, but does not represent a significant portion of the mineral surface. Bayerite formation is due to dissolution and re-precipitation of aluminum aqueous species as a secondary mineral phase and is most important under alkaline conditions. Aluminum (hydr)oxides are less soluble at circumneutral pH than alkaline pH, so secondary phase transformation is less likely to
occur. Our results show complete adsorption of europium to all aluminum (hydr)oxide minerals at pH 7, which is lower than the pH of the onset of bayerite formation. This suggests that the transformation of the mineral surface is not solely responsible for the nearly identical edges observed to describe europium sorption to aluminum (hydr)oxides.

The difference in sorption behavior between Eu(III) and Np(V) is notable. Whereas there was no apparent correlation between Eu(III) adsorption behavior and mineral phase, preferential adsorption of neptunium followed the trend bayerite > corundum > γ-alumina. This difference in sorption behavior may be due to (i) the relative effective charges of Eu(III) and Np(V), (ii) steric constraints posed by the neptunyl dioxo cation as compared to the europium cation, or (iii) different mechanisms of complex formation between the two metal cations. Eu(III) and Np(V) have both been shown to form inner sphere complexes on aluminum (hydr)oxide surfaces (Rabung et al., 2000; Kumar et al. 2012, 2013; Gückel et al., 2013), but the effective charges of these metal ions are different. Europium exists as the hydrated cation Eu$^{3+}$, which hydrolyzes under acidic conditions and can form insoluble hydroxides. Conversely, Np(V) is found as the nearly linear dioxo cation NpO$_2^+$ and resists hydrolysis until alkaline conditions are reached. The formation of these axial oxygen bonds lowers the effective charge of neptunium to approximately 2.2 (Choppin and Rao, 1984). The effective charge of ions in solution greatly affects their environmental behavior as the strength of the ionic bond between a metal cation and anionic ligand is proportional to the effective charge of the metal ion. Generally, as the effective charge increases, the ionic bonds become shorter and stronger. Eu(III) is expected to have a higher affinity for mineral surfaces than Np(V) due to neptunium’s relatively low effective charge and, therefore, weak complex
formation. The effective charge of the metal ion has generally been considered more important than the surface charge of the mineral (Smith et al., 1999) and could explain the differences observed between Np(V) and Eu(III) sorption trends. Rabung et al. (2000) state that for metal ions with an effective charge equal to or greater than +3, the charge of the mineral surface is of minor importance. Our data support this claim. Regarding mechanisms of complex formation, there are no published studies wherein europium forms a ternary surface complex with carbonate, as has been demonstrated for neptunium (Gückel et al., 2013). In addition, a very recent study shows that Np(V) forms a bidentate, edge-sharing complex with corundum (Virtanen et al., 2016), whereas europium is known to form monodentate complexes with aluminum (hydr)oxide minerals (Kumar et al., 2012).

The data presented here suggest that there are at least two different mechanisms controlling the adsorption of europium and neptunium and highlight the need to study both aqueous-phase chemistry and the properties of mineral surfaces in order to understand the behavior of lanthanides and actinides at the mineral-water interface. It appears as if the chemical properties of Eu(III) versus Np(V) plays a larger role in determining adsorption behavior than the morphology and surface-site acidity of the aluminum (hydr)oxide minerals. Our current and future studies are focused on using advanced spectroscopic techniques such as X-ray absorption spectroscopy (XAS) to determine sorption mechanism(s), compare the surface complexes of Eu(III) and Np(V), and inform mechanistically-accurate surface complexation.
CHAPTER 3:
KINETICS OF EUROPIUM SORPTION TO FOUR DIFFERENT ALUMINUM
(HYDR)OXIDES: CORUNDUM, Γ-ALUMINA, BAYERITE, AND GIBBSITE

3.1 Introduction

Trivalent actinides, such as Am(III) and Cm(III), are present in high-level nuclear waste and will ultimately be disposed of in deep geologic repositories (Blue Ribbon Commission, 2012). As part of the mandatory certification process for U.S. nuclear repositories, a performance assessment consisting of detailed reactive transport models must show that the annual surface dose of the repository will not exceed 0.15 mSv for the first 10,000 years and will remain below 0.1 mSv for 1 million years (NRC, 2016). In addition to eventual disposal in nuclear repositories, trivalent actinides are present at legacy waste sites and at locations where nuclear weapons were tested (Smith et al, 2003; Cantrell, 2009). Sorption to minerals, soils, and sediments are partially responsible for limiting radionuclide mobility in the subsurface environment; therefore, to accurately model actinide mobility, it is necessary to develop a thorough understanding of the thermodynamics and kinetics of interactions occurring at the water-mineral interface.

Aluminum is one of the most abundant elements in the subsurface environment and exists in oxide, hydroxide, and silicate mineral forms. While pure aluminum (hydr)oxides have a low natural abundance, the aluminol sites found on these minerals
(e.g., $\equiv$AlOH, $\equiv$Al$_2$OH, $\equiv$Al$_3$OH, $\equiv$Al(OH)$_2$) (Franks and Gan, 2007; Yang et al., 2007) are also present on aluminosilicate minerals, which are abundant in nature and proposed as backfill material for future geologic repositories. Investigating how actinides interact with pure aluminum (hydr)oxide phases can provide insight into how actinides will interact with the different alumino sites. Additionally, gibbsite has been used as a model mineral for investigating metal ion interactions with aluminosilicate alteration products (Wu et al., 2009).

Yang et al. (2007) showed that the surface acidities of aluminum (hydr)oxides followed the trend corundum > gibbsite > $\gamma$-alumina (i.e., $\alpha$-Al$_2$O$_3$ > $\alpha$-Al(OH)$_3$ > $\gamma$-Al$_2$O$_3$) which are caused by different ratios of singly-, doubly-, and triply-coordinated aluminol. While these different surface acidities are expected to influence sorption, previous studies have shown that similar europium sorption trends are observed regardless of the aluminum (hydr)oxide phase (Kupcik et al., 2016; Baumer et al., 2017). Kupcik et al. (2016) hypothesize that these similar sorption trends are the result of phase transformations. For example, $\gamma$-Al$_2$O$_3$ has been previously shown to undergo phase transformations to gibbsite ($\gamma$-Al(OH)$_3$) and bayerite (a-Al(OH)$_3$) (Carrier et al., 2007; Lefèvre et al., 2002). These phase transformations are expected to lead to similar sorption sites on each mineral, which could influence the surface acidities of the aluminum (hydr)oxides and lead to similar sorption trends. However, Baumer et al. (2017) monitored for phase transformations and observed complete adsorption of Eu(III) to $\gamma$-Al$_2$O$_3$ before phase transformations were detected. This suggests that another factor is responsible for the similar sorption trends observed at equilibrium. Kinetics studies can
provide insight into how different surface acidities of the aluminum (hydr)oxides influence sorption before equilibrium is obtained.

Kinetics data are generally fit to the pseudo-first and pseudo-second order rate equations. The goodness of fit and $R^2$ values are then compared to determine which rate equation more accurately represents the data. The pseudo-first order rate equation was originally proposed by Lagergren (1898) to describe oxalic and malonic acid adsorption to charcoal and has been used extensively to describe environmental adsorption of actinide elements (Hixon and Powell, 2014; Powell et al., 2004, 2005; Begg et al., 2018). The pseudo-second order rate equation was proposed by Blanchard et al. (1984) and popularized by Ho and McKay (1999) to describe heavy metal removal from solution. Several recent publications suggest that kinetics data previously identified as fitting the pseudo-first order equations is actually better fit using pseudo-second order rate equations (Ho and McKay, 1999). These papers plot the linear forms of the rate equations and determine goodness of fit from the $R^2$ values of the lines obtained and how close the predicted equilibrium sorption is to the experimental value. Simonin (2016) suggests this method for determining whether data is better fit by pseudo-first or pseudo-second order rate equations because the linear forms favor the pseudo-second order equations. Using the non-linear forms of these rate equations provides a less biased determination of whether a reaction is fit better by pseudo-first or pseudo-second order equations (Lima et al., 2015; Simonin, 2016).

Eu(III) has been used as a non-radioactive analog for Am(III) and Cm(III) in studies investigating trivalent metal ion surface interactions because of the difficulties of working with transuranic elements (Rabung et al., 2000; Kumar et al., 2013; Kupcik et
al., 2016). Several studies have investigated equilibrium reactions of Eu(III) in the presence of aluminum (hydr)oxide minerals (Rabung et al., 2000; Kumar et al., 2012; Baumer et al., 2017; Kupcik et al., 2016), but kinetics studies are less common in the literature. Xu et al. (2017) examined the kinetics of Eu(III) sorption to γ-Al₂O₃ in the presence of phosphate as a competing ligand to show that the reaction is best described using a pseudo-second order reaction rate and Zhu et al. (2016) reported the pseudo-first and pseudo-second order reaction rates to describe europium sorption to synthetic monoclinic pyrrhotite (Fe₁₋ₓS (x = 0 to 0.2)). In both of these studies, the data was only fit to the linear forms of the rate equations and no attempt was made to fit the data to the non-linear forms. Additionally, these studies did not determine the reaction orders or overall reaction rates.

In the present study, batch sorption experiments are fit to both the linear and non-linear forms of the pseudo-first and pseudo-second order rate equations. The reaction orders with respect to mineral concentration, proton concentration, and europium concentration are determined and the overall reaction rate laws describing europium sorption to bayerite, gibbsite, corundum, and γ-alumina are derived.

3.2 Materials and Methods

3.2.1 Material preparation and characterization

Commercially obtained aluminum oxides and hydroxides were used in this study. High purity γ-Al₂O₃ (Alfa Aesar) and bayerite (α-Al(OH)₃) (Sasol) were used without further preparation. α-Al₂O₃ (Alfa Aesar) and gibbsite (γ-Al(OH)₃) (Alteo) were washed
in dilute HNO$_3$ and NaOH to remove impurities then dried overnight at 100°C in a convection oven. Before use, all minerals were characterized by N$_2$(g)-BET, Fourier transform infrared spectroscopy, and powder X-ray diffraction. A complete description of washing procedures and mineral characterization are provided in Baumer et al. (2017).

3.2.2 Europium solution preparation

A europium standard (BDH; 1001 ± 4 M) was diluted with doubly-distilled nitric acid to make three europium working solutions (1.047 ± 0.005, 10.33 ± 0.04, and 101.37 ± 0.41 ppm) for use in batch sorption experiments.

3.2.3 Batch sorption experimental conditions

Batch sorption experiments were conducted in 0.01 M NaCl. Homogenized mineral suspensions and europium working solutions were combined in 15 mL conical tubes to obtain desired concentrations before adjustment to pH 5, 6, or 7 using dilute NaOH or HCl. Appendix B summarizes the experimental conditions for batch sorption experiments. For each set of conditions, separate reactor tubes were prepared for each time point (10, 15, 30, 45, 60, and 120 minutes) and were mixed end-over-end until sampling. Each reactor vessel was only sampled once before being discarded. During sampling, a homogenous aliquot was taken from the reactor solution and centrifuged to remove particles >100 nm from solution according to Stokes law (Jackson, 1969). The aqueous phase was immediately diluted in doubly distilled 2% nitric acid and analyzed using high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). A Nu Attom II ICP-MS was used in medium resolution with an external calibration curve. All intensities were normalized for instrumental drift using a neodymium internal
standard. The fraction of europium associated with the mineral was determined by subtracting the aqueous concentration determined from ICP-MS from the added concentration. The quantity of europium associated with the surface at equilibrium \((q_e)\) and at a given time \((q_t)\) were determined using equations 3.1 and 3.2 (Tran et al., 2017)

\[
q_e = \frac{C_o - C_e}{m} V \tag{3.1}
\]

\[
q_t = \frac{C_o - C_t}{m} V \tag{3.2}
\]

where \(C_o\) (mg/L), \(C_e\) (mg/L), and \(C_t\) (mg/L) are europium concentrations in solution initially, at equilibrium, and at time \(t\), respectively, \(m\) (g) is the dried mass of the absorbent in each reactor; and \(V\) (L) is the volume of solution in each reactor.

3.2.4 Pseudo-first and pseudo-second order rate equations

The non-linear (equation 3.3) and linear (equation 3.4) forms of the pseudo-first order rate equation were used to determine the pseudo-first order rate constants, \(k_1\) (hr^{-1}). Using the linear form, plotting \(\ln(q_e - q_t)\) vs \(t\) yields a slope of \(-k_1\).

\[
q_t = q_e(1 - e^{-k_1 t}) \tag{3.3}
\]

\[
\ln(q_e - q_t) = -k_1 t + \ln(q_e) \tag{3.4}
\]

The pseudo-second order rate constants, \(k_2\) (g·mg^{-1}·hr^{-1}), were determined from the non-linear and linear pseudo-second order rate equations expressed in equations 3.5 and 3.6, respectively. Plotting \(t/q_t\) versus \(t\) allows for the determination of \(k_2\) from the intercept of linear form of the pseudo-second order rate equation.

\[
q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \tag{3.5}
\]
\[ \frac{t}{q_t} = \left( \frac{1}{q_e} \right) t + \frac{1}{k_2 q_e^2} \]  

(3.6)

To solve for \( k_1 \) and \( k_2 \) using the non-linear forms for the rate equations, the solver function in Excel was utilized. The \( R^2 \) value of each system was calculated using equation 3.7 as outlined by Simoni (2016)

\[ R^2 = 1 - \frac{\sum_{i=1}^{N}(y_i - \hat{y})^2}{\sum_{i=1}^{N}(y_i - \langle y \rangle)^2} \]  

(3.7)

where \( y_i = \ln(q_e - q_t), \hat{y} = \ln(q_e) - k_1 t, \) and \( \langle y \rangle \) equals the average of the \( y_i \) values. The solver function was used to maximize \( R^2 \) by varying \( k_1 \) and \( k_2 \) for the pseudo-first and pseudo-second order rate equations, respectively. Experimentally determined \( q_e \) values from this study and Baumer et al. (2017) were used during the optimization process.

3.2.5 Overall rate law and reaction order determination

The overall rate law describing europium sorption to each aluminum (hydr)oxide is dependent on the aqueous europium concentration \([Eu]_{aq}\), mineral concentration \([\text{mineral}]\), and hydrogen ion concentration \([H^+]\) and is described by equation 3.8

where \( a \) is the reaction order with respect to mineral concentration, \( b \) is the reaction order with respect to hydrogen ion concentration, and \( c \) is the reaction order with respect to aqueous europium concentration.

\[ \frac{d[Eu]_{aq}}{dt} = -k[\text{mineral}]^a[H^+]^b[Eu]_{aq}^c \]  

(3.8)

Plotting log \( k_1 \) or log \( k_2 \) vs log[\text{mineral}], log[H^+], and log[Eu] will yield slopes equal to the reaction orders \( a, b, \) and \( c, \) respectively. The overall reaction rate constant \( (k) \) for each
mineral system can then be determined using the reaction orders determined from the experimental data for each mineral.

3.3 Results and Discussion

The fraction of europium associated with bayerite, gibbsite, corundum, and γ-alumina was monitored as a function of time at three different mineral concentrations, europium concentrations, and pH values. Figure 3.1 shows europium sorption to gibbsite; data for the other aluminum (hydr)oxides is provided in Appendix B. For all experiments, europium removal from solution increased with time and is due to europium adsorption to the aluminum (hydr)oxides (Rabung et al., 2000; Baumer et al., 2017). Europium sorption is characterized by a two-step reaction with a fast initial adsorption step occurring within the first 10 minutes followed by a slower equilibrium sorption or aging process. The observation of a fast and slow adsorption step has been previously observed for plutonium interactions with iron (oxyhydr)oxide and manganese oxide minerals (Hixon and Powell, 2014; Shaughnessy et al., 2003). Hixon and Powell (2014) attributed the two-step reaction to an adsorption and a reduction step whereas Shaughnessy et al. (2003) attributed the two different reactions to an initial diffusion-controlled surface reaction followed by another process such as surface precipitation, micropore diffusion, or structural rearrangement of surface species. Europium is not expected to undergo surface-mediated reduction, as observed with plutonium, and aging processes, such as europium incorporation into the crystal lattice of the minerals, have not been observed in the presence of aluminum oxides in contact times under two weeks (Rabung et al., 2000). Additionally, the europium concentrations used in this study are four orders of magnitude
lower than the plutonium concentrations used by Shaughnessy et al. (2003) and surface precipitation was not observed at these concentrations (Baumer et al., 2017). The slower equilibrium sorption process is observed within 30–120 minutes of interaction, therefore fast and slow sorption steps are likely the result of europium sorption to strong and weak binding sites (Dzombak and Morel, 1990) instead of an aging process.

Figure 3.1. Fraction of europium sorbed to gibbsite as a function of time at 10⁻⁸ M Eu(III) and (▽) 50 m²·L⁻¹, (◆) 10 m²·L⁻¹, and (■) 5 m²·L⁻¹ gibbsite at pH 6; 10⁻⁸ M Eu(III), 5 m²·L⁻¹ gibbsite at (●) pH 5 and (○) pH 7; 10 m²·L⁻¹ gibbsite and (□) 10⁻⁶ M and (□) 10⁻⁷ M Eu(III) at pH 6. The exact experimental conditions are provided in Appendix B. Error bars represent the error propagated from the uncertainty in ICP-MS measurements.

Plots of the linear pseudo-first and pseudo-second order rate equations for europium sorption to gibbsite are shown in Figure 3.2 and summarized in Table 3.1. Similar plots are provided in Appendix B for corundum, γ-alumina, and bayerite and a
summary of the rate constants is provided in Table B.2. Plots of both $ln(q_e - q_t)$ versus time for pseudo-first order and $t/q_t$ versus time for pseudo-second order yield fits with high $R^2$ values. The correlation coefficients for the pseudo-second order plots appear slightly better than those of the pseudo-first order plots and did not need to be truncated to the first 30–45 minutes like the pseudo-first order.

Figure 3.2. pseudo-first (A) and pseudo-second (B) order plots of $(2.69 \pm 0.02) \times 10^{-8}$ M Eu(III) and $9.988 \pm 0.005$ m$^2$·L$^{-1}$ gibbsite at pH $6.15 \pm 0.10$ both resulted in high $R^2$ values (0.9899 and 0.9647, respectively).
### TABLE 3.1.

LINEAR AND NON-LINEAR PSEUDO-FIRST (K₁) AND SECOND ORDER (K₂) RATE CONSTANTS AND R² VALUES OF GIBBSITE (Γ-AL(OH)₃)

<table>
<thead>
<tr>
<th>System</th>
<th>Linear</th>
<th>Non-linear</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k₁</td>
<td>R²</td>
</tr>
<tr>
<td>5 m²·L⁻¹ pH 6 10⁻⁸ M Eu</td>
<td>1.633 ± 0.965</td>
<td>0.7387</td>
</tr>
<tr>
<td>10 m²·L⁻¹ pH 6 10⁻⁸ M Eu</td>
<td>1.763 ± 0.103</td>
<td>0.9899</td>
</tr>
<tr>
<td>50 m²·L⁻¹ pH 6 10⁻⁸ M Eu</td>
<td>2.608 ± 0.242</td>
<td>0.9915</td>
</tr>
<tr>
<td>10 m²·L⁻¹ pH 5 10⁻⁸ M Eu</td>
<td>0.308 ± 0.023</td>
<td>0.9850</td>
</tr>
<tr>
<td>10 m²·L⁻¹ pH 7 10⁻⁸ M Eu</td>
<td>3.847 ± 0.63</td>
<td>0.9737</td>
</tr>
<tr>
<td>10 m²·L⁻¹ pH 6 10⁻⁷ M Eu</td>
<td>4.254 ± 0.407</td>
<td>0.9909</td>
</tr>
<tr>
<td>10 m²·L⁻¹ pH 6 10⁻⁶ M Eu</td>
<td>1.642 ± 0.156</td>
<td>0.9910</td>
</tr>
</tbody>
</table>
plots. While the pseudo-second order plots appear to fit the data slightly better, Simonin (2016) argues that linear plots of the pseudo-first and pseudo-second order rate equations cannot be compared directly to determine goodness of fit because these plots do not have the same axes and are not in the same units. In order to more accurately compare $R^2$ values, plots with the same axes are needed.

Figure 3.3 shows a plot of the $q/t$ versus $q_e$ of the experimental data and the pseudo-first and -second order models for europium sorption to gibbsite. Similar plots are provided in Appendix B for the other mineral systems and the rate constants are summarized in Table B.2. Overall, the $R^2$ values of the non-linear equations are lower than the linear equations, but it also becomes apparent that the $R^2$ values of the pseudo-second order equations are generally higher than the pseudo-first order equations. For this reason, the pseudo-second order reaction rates, $k_2$, were used to determine the reaction orders with respect to europium concentration, mineral concentration, and proton concentration.

The $k_2$ values were generally observed to increase with pH and mineral concentration and decrease with increasing europium concentration. Because strong sorption sites are expected to exist on the edges of mineral surfaces, increasing the mineral concentration will increase the amount of strong sorption sites available and result in increased initial $k_2$ values. As previously observed, europium sorption to aluminum (hydr)oxides increases with increasing pH (Rabung et al., 2000; Naveau et al., 2005; Kupcik et al., 2016; Baumer et al., 2017). This is explained by the mineral surfaces becoming increasingly negatively charged as the pH increases allowing for enhanced electrostatic interactions between the mineral surface and the europium cation. The
observed decrease in $k_2$ with increasing europium concentration can also be attributed to the presence of strong and weak sorption sites. At high concentrations, the europium occupies all the strong sorption sites so europium must sorb to weaker binding sites. This shifts the sorption edge to higher pH (Baumer et al., 2017) and leads to decreased pseudo-second order reaction rates.

Figure 3.3. Non-linear pseudo-first order (PFO) and pseudo-second order (PSO) model fits to experimental data collected from systems containing $(2.69 \pm 0.02) \times 10^{-8}$ Eu(III) and $9.988 \pm 0.005$ m$^2$·L$^{-1}$ gibbsite at pH $6.15 \pm 0.10$. Error bars represent the error propagated from the uncertainty in ICP-MS measurements.

In Figure 3.4 linear regressions of $\log k_2$ vs $\log[\text{mineral}]$, $\log[H^+]$, and $\log[\text{Eu}]$ yield slopes equal to the reaction order with respect to europium concentration, mineral concentration, and $[H^+]$, respectively, for gibbsite. The reaction orders for bayerite, $\gamma$-Al$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ were determined in the same way; linear regressions are provided in Appendix B and summarized in Table 3.2. The reaction orders are consistent with those reported by Hixon and Powell (2014) and Powell et al. (2004) for plutonium interactions with hematite and goethite, respectively. Because similar values were obtained for the
reaction orders with respect to europium concentration for bayerite and gibbsite, these values were used to determine the overall reaction rates for $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$.

Figure 3.4. (a) Dependence of log $k_2$ on log [gibbsite] at pH 6.05 ± 0.03 and (2.69 ± 0.04) x 10^{-8} M Eu(III). Reaction order term $a$ provided in Table 3.2 ($R^2 = 0.96712$). (b) Dependence of log $k_2$ on log [H+] at 5.30 ± 0.02 m^2·L^{-1} gibbsite and (2.72 ± 0.04) x 10^{-8} M Eu(III). Reaction order term $b$ provided in Table 3.2 ($R^2 = 0.71867$). (c) Dependence of log $k_2$ on log [Eu] at 10.50 ± 0.05 m^2·L^{-1} gibbsite and pH 6.08 ± 0.02. Reaction order term $c$ provided in Table 3.2 ($R^2 = 0.92079$).
Large errors were associated with the reaction orders with respect to hydrogen ion concentration. These errors can be attributed to the non-linear sorption of europium as a function of pH. Baumer et al. (2017) show that europium sorption increases dramatically around pH 6, which makes it difficult to obtain kinetics data at the middle of the sorption edge. Therefore, the log-log plots used to determine the reaction order with respect to hydrogen ion concentration had low correlation coefficients and high errors.

The overall reaction rates for the different aluminum (hydr)oxides were determined using Equation 3.8 and are summarized in Table 3.4. While the reaction orders for each mineral are similar, the subtle differences lead to overall reaction rates which can vary by as much as four orders of magnitude. The overall reaction rates follow the trend bayerite \( \sim \gamma\text{-Al}_2\text{O}_3 > \alpha\text{-Al}_2\text{O}_3 > \) gibbsite. Because of the large errors associated with the reaction orders with respect to hydrogen ion concentration, the overall reaction rates were also determined with \( b \) held constant at -0.436, the reaction order with respect to \([H^+]\) for bayerite (see Table 3.5). This value was chosen arbitrarily because bayerite exhibited the fastest sorption rate. Using this assumption, the overall reaction rates follow the trend \( \gamma\text{-Al}_2\text{O}_3 > \alpha\text{-Al}_2\text{O}_3 > \) bayerite \( > \) gibbsite.

For both reaction rate determinations, europium sorption to gibbsite is 1–2 orders of magnitude slower than to the other minerals. The slower reaction rates obtained by gibbsite can be partially explained by its higher surface acidity. The pKa\(_1\) and pKa\(_2\) of \( \alpha\text{-Al}_2\text{O}_3\), gibbsite, and \( \gamma\text{-Al}_2\text{O}_3\) for reactions 3.9 and 3.10 are summarized in Appendix B.

\[
\equiv\text{AlOH}_2^+ \leftrightarrow \equiv\text{AlOH} + H^+ \quad (3.9)
\]

\[
\equiv\text{AlOH} \leftrightarrow \equiv\text{AlO}^- + H^+ \quad (3.10)
\]
The pKa$_2$ value of gibbsite is the highest of the aluminum (hydr)oxides studied here which means that the surface of the gibbsite will not be fully deprotonated until a higher pH than the other minerals. This will lead to slower overall reaction rates because the europium cations will have to sorb to less favorable (i.e., more positively charged) sorption sites.
### TABLE 3.2.

**REACTION ORDERS WITH RESPECT TO MINERAL CONCENTRATION (A), HYDROGEN ION CONCENTRATION (B) AND EUROPIUM CONCENTRATION (C) AND OVERALL REACTION RATES WITH B AND WITH B HELD CONSTANT AT -0.463**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Overall reaction rate</th>
<th>Overall reaction rate at b = -0.463</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al(OH)$_3$</td>
<td>1.05 ± 0.19</td>
<td>-0.587 ± 0.368</td>
<td>-0.457 ± 0.134</td>
<td>(7.917 ± 4.325) x 10$^{-6}$</td>
<td>(6.716 ± 4.088) x 10$^{-5}$</td>
</tr>
<tr>
<td>α-Al(OH)$_3$</td>
<td>1.36 ± 0.17</td>
<td>-0.436 ± 0.262</td>
<td>-0.547 ± 0.138</td>
<td>(3.750 ± 1.984) x 10$^{-3}$</td>
<td>(3.750 ± 1.984) x 10$^{-3}$</td>
</tr>
<tr>
<td>γ-Al$_2$O$_3$</td>
<td>1.35 ± 0.42</td>
<td>-0.805 ± 0.432</td>
<td>------</td>
<td>(3.980 ± 2.541) x 10$^{-3}$</td>
<td>(7.298 ± 5.438) x 10$^{-1}$</td>
</tr>
<tr>
<td>α-Al$_2$O$_3$</td>
<td>1.32 ± 0.03</td>
<td>-0.702 ± 0.372</td>
<td>------</td>
<td>(5.125 ± 5.863) x 10$^{-4}$</td>
<td>(3.409 ± 4.518) x 10$^{-2}$</td>
</tr>
</tbody>
</table>
When the reaction orders with respect to hydrogen ion concentration are used to determine the overall reaction rates, gibbsite and $\alpha$-$\text{Al}_2\text{O}_3$ resulted in slower rates overall. These slower reaction rates may be the result of fewer singly-coordinated aluminol sites on the gibbsite and $\alpha$-$\text{Al}_2\text{O}_3$ surfaces. Singly coordinated aluminol sites have been previously observed to be more reactive with non-crystalline alumina, such as $\gamma$-$\text{Al}_2\text{O}_3$, exhibiting a greater adsorption capacity than gibbsite (McBride, 1982). Bayerite and gibbsite have the same structure but bayerite is characterized by AB AB stacking of aluminum and hydroxyl layers instead of AB BA stacking, as observed with gibbsite. The alternating layers of aluminum and hydroxyl groups may result in bayerite exhibiting more acidic hydroxyl sites similar $\alpha$-$\text{Al}_2\text{O}_3$. Hiemstra et al. (1999) observed that bayerite absorbs more $\text{H}^+$ than gibbsite and has a higher adsorption capacitance. Minerals with higher capacitances generally exhibit a large number of defect sites which results in more a reactive surface (Hiemstra, 1999).

When the reaction orders with respect to hydrogen ion concentration are held constant, the aluminum oxides exhibit faster overall reaction rates than the aluminum (hydr)oxides. $\alpha$-$\text{Al}_2\text{O}_3$ has a lower surface acidity than gibbsite and $\gamma$-$\text{Al}_2\text{O}_3$ meaning that it will deprotonate at a lower pH and have a larger number of negatively charged sorption sites available (Yang et al., 2007). $\gamma$-$\text{Al}_2\text{O}_3$ has larger number of singly coordinated aluminol sites which makes it more reactive than the other aluminum (hydr)oxides (Hiemstra et al., 1999). Peintinger et al. (2014) used density functional theory (DFT) calculations to predict the stability of various aluminum (hydr)oxides and saw that the relative stability followed the trend gibbsite $> bayerite > \alpha$-$\text{Al}_2\text{O}_3 > \gamma$-$\text{Al}_2\text{O}_3$. This trend matches the kinetics rate observations in the present study.
3.4 Conclusions

This study showed that europium sorption to bayerite, gibbsite, corundum, and γ-alumina is characterized by an initial fast sorption reaction within the first 10 minutes followed by a slower equilibrium process. We hypothesize that the two-step process is due to the presence of at least two sorption sites (e.g., strong versus weak) on the mineral surfaces. The fraction of europium sorbed as a function time is best described by a pseudo-second order rate equation.

The reaction orders with respect to mineral concentration, hydrogen ion concentration, and europium concentration were similar for all four aluminum (hydr)oxide minerals, but overall reaction rates for the minerals varied by up to four orders of magnitude. When the reaction orders with respect to $[H^+]$ are kept constant, the overall reaction rate trend changes, but gibbsite is consistently several orders of magnitude slower than the other minerals. Overall reaction rates appear to be partially influenced by the amount of singly-coordinated aluminol and defect sites on the mineral surface. These results highlight the importance of determining the full reaction rate to understand the differences between mineral systems.
CHAPTER 4:
KINETICS OF NEPTUNIUM SORPTION AND DESORPTION IN THE PRESENCE OF ALUMINUM (HYDR)OXIDE MINERALS: EVIDENCE FOR MULTI-STEP DESORPTION AT LOW PH

4.1 Introduction

In the United States, high-level nuclear waste from the commercial nuclear fuel cycle will eventually be disposed of in deep geologic repositories (Blue Ribbon Commission, 2012). Prior to disposal, sites must be certified using detailed performance assessment models to show that the annual surface dose of a repository will not exceed 1 mSv for 1 million years (NRC, 2016). While initially a small contributor to the total activity of a nuclear repository, neptunium-237 is expected to be the major dose contributor after 10,000 years because of its long half-life (2.14 million years) and ingrowth from americium-241 decay (Kaszuba and Runde, 1999). The high toxicity and persistence of neptunium-237 highlights the importance of developing a thorough understanding of the factors controlling its environmental mobility for accurate assessment of nuclear repositories.

Neptunium exists primarily in the pentavalent oxidation state and is expected to be highly mobile because of its high solubility and low effective charge ($Z_{\text{eff}} = 2.2 \pm 0.1$ (Choppin and Rao, 1984)). The aqueous speciation of neptunium is dominated by $\text{NpO}_2^+$, but neptunyl hydroxide and carbonate species such as $\text{NpO}_2 \text{OH}$, $\text{NpO}_2 \text{CO}_3^-$,
NpO$_2$(CO$_3$)$_2^{3-}$, and NpO$_2$(CO$_3$)$_3^{5-}$ may also be present depending on the pH and the carbonate concentration of the system (Turner et al., 1998; Li and Tao, 2003; Wu et al., 2009). Neptunium sorption to mineral phases is expected to limit its environmental mobility but desorption will release it back into the environment.

The fate and transport of neptunium has been addressed in part by sorption and desorption experiments in the presence of a variety of pure mineral phases under diverse geochemical conditions (Nakayama and Sakamoto, 1991; Tochiyama et al., 1995; Kohler et al., 1999; Nakata et al., 1999, 2002, 2004; Arai et al., 2007; Jain et al., 2007; Kalmykov et al., 2007; Khasanova et al., 2007; Heberling et al., 2008; Kalmykov et al., 2008; Wu et al., 2009; Tinnacher et al., 2011; Gückel et al., 2013; Snow et al., 2013; Müller et al., 2015; Virtanen et al., 2016; Elo et al., 2017; Baumer et al., 2017). However, few studies have examined the rate at which these reactions occur (Nagasaki and Tanaka, 2000; Nakata et al., 2000; Li and Tao, 2003; Nakata et al., 2004; Tinnacher et al., 2011).

Previous research has shown that neptunium sorption is characterized by a fast sorption process, occurring within minutes, followed by a slower sorption mechanism or other aging process (Nagasaki and Tanaka, 2000; Li and Tao, 2003) and that neptunium desorption is a much slower process which occurs over days or weeks (Tinnacher et al., 2011; Elo et al., 2017). Slower desorption rates may result in a continuous source of neptunium slowly being released in the environment around contaminated sites or enhanced transport via mineral colloids (Tinnacher et al., 2011).

Detailed kinetics analyses of neptunium sorption and desorption are needed in order to determine when equilibrium has been achieved, to identify important intermediate chemical species, provide insight into sorption mechanisms, and inform
conceptual models describing the behavior of neptunium at the mineral-water interface. In general, kinetics data can be modeled using pseudo-first or pseudo-second order rate equations. However, studies investigating actinide sorption to geologic media usually make pseudo-first order assumptions (Powell et al., 2004, 2005; Zavarin et al., 2012; Begg et al., 2013; Begg et al., 2018) even though Ho and McKay (1999) demonstrate that pseudo-second order equations provide better estimations of equilibrium sorption values.

In the present study, neptunium adsorption and desorption kinetics to four different aluminum (hydr)oxides – gibbsite ($\gamma$-Al(OH)$_3$), bayerite ($\alpha$-Al(OH)$_3$), corundum ($\alpha$-Al$_2$O$_3$), and $\gamma$-alumina ($\gamma$-Al$_2$O$_3$) – are investigated over a range of solution conditions. Batch sorption and desorption data are fit to the linear and non-linear forms of the pseudo-first and pseudo-second order rate equations and the reaction orders with respect to pH and mineral concentration are determined. The kinetics modeling described in this study enhances our understanding of neptunium sorption and desorption reaction rates and can be used to predict neptunium sorption to aluminum (hydr)oxides under changing solution conditions.

4.2 Materials and Methods

4.2.1 Material preparation and characterization

High purity $\gamma$-alumina and bayerite ($\alpha$-Al(OH)$_3$) were obtained commercially from Alfa Aesar and Sasol, respectively, and used without further preparation. Impurities were removed from commercially-obtained corundum ($\alpha$-Al$_2$O$_3$) and gibbsite ($\gamma$-Al(OH)$_3$) through a washing procedure including alternating hour-long washes with 0.01 M HNO$_3$ and 0.01 M NaOH three times followed by five rinses with ultrapure water
(18.2 MΩ·cm at 25°C). The rinsed minerals were allowed to dry overnight in a convection oven (100°C) and were then characterized with N$_2$(g)-BET, Fourier transform infrared spectroscopy, and powder X-ray diffraction before use. Detailed mineral characterization is provided in Baumer et al. (2017).

4.2.2 Neptunium solution preparation

A standard neptunium stock solution ((2.467± 0.005) x 10$^{-5}$ M) was used for all experiments in this study (NIST SRM 4341A). The oxidation state of the stock solution was confirmed to be Np(V) using a Cary 6000i UV-vis-NIR spectrometer. Two neptunium working solutions were created by diluting small aliquots of the neptunium stock solution in doubly distilled nitric acid to yield concentrations of (1.098 ± 0.002) x 10$^{-6}$ M and (9.639 ± 0.049) x 10$^{-8}$ M for use in the batch experiments.

4.2.3 Batch sorption experimental conditions

Detailed descriptions of the experimental conditions are provided in Appendix C. Briefly, batch sorption experiments were conducted by combining the mineral, neptunium, and 0.01 M NaCl in 15 mL conical tubes. The samples were immediately adjusted to the desired pH using dilute NaOH or HCl and mixed end-over-end until sampling during which a 1 mL homogenous aliquot was centrifuged remove particles >100 nm from solution according to Stokes law (Jackson, 2005). The pH of each reactor was measured during sampling and each reactor was only sampled once for consistency in the sampling procedure. After centrifugation, the aqueous phase was immediately prepared for analysis with high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) by acidifying the sample in doubly distilled 2% HNO$_3$ and spiking each sample with a thorium internal standard. A Nu Attom II ICP-MS was used for all
analyses and samples were compared to an external calibration curve. Aqueous neptunium concentrations were determined directly from the ICP-MS results. The fraction of neptunium associated with the mineral was determined by subtracting the aqueous neptunium concentration from total added concentration. Equations 4.1 and 4.2 were used to determine the quantity of neptunium associated with the surface at equilibrium \( q_e \) and at a given time \( q_t \)

\[
q_e = \frac{C_o - C_e}{m} V
\]  
(4.1)

\[
q_t = \frac{C_o - C_t}{m} V
\]  
(4.2)

where \( C_o \) (mg/L), \( C_e \) (mg/L), and \( C_t \) (mg/L) are neptunium concentrations in solution at \( t = 0 \), at equilibrium, and at time \( t \), respectively, \( m \) (g) is the dried mass of the absorbent in each reactor, and \( V \) (L) is the volume of solution in each reactor (Tran et al., 2017).

Separate neptunium- and mineral-free controls were prepared and analyzed in the same manner.

4.2.4 Batch desorption experimental conditions

Set up of the batch desorption experiments was similar to the batch sorption experiments. Neptunium was combined with mineral in 0.01 M NaCl and adjusted to pH 11. Reactors were allowed to equilibrate for 6 days. This time period was previously shown to be sufficient for equilibrium to occur (Baumer et al., 2017). After 6 days, the samples were centrifuged to separate the solid and aqueous phases. The aqueous phase was prepared for analysis with ICP-MS. The solid phase was rinsed for less than 5 minutes with 0.01 M NaCl that had been pre-adjusted to pH 10.5 to remove excess neptunium from the pore space of the minerals without removing sorbed neptunium. The
samples were again centrifuged to separate the solid phase and the aqueous phase was discarded. An additional 5 mL of pH-adjusted 0.01 M NaCl was added to the reactor containing mineral with sorbed neptunium. Reactors were then capped, rotated until the desired time, and sampled in the same way as the batch sorption experiments. Neptunium desorption was measured from 5 - 60 min, after 1 week, and at an extended time frame - between one and two months - at three different pH values for each mineral. All samples were prepared for analysis with ICP-MS to determine the aqueous-phase concentration of neptunium. Equations 4.1 and 4.2 were adapted for the desorption experiments to solve for the quantity of neptunium desorbed at equilibrium, $q_{de}$, and at a given time, $q_{dt}$. This was done by substituting the concentration of neptunium on the surface initially, at a given time, and at equilibrium into equations 4.1 and 4.2.

4.2.5 Pseudo-first and pseudo-second order rate equations

Pseudo-first and pseudo-second order rate constants, $k_1$ and $k_2$ (hr$^{-1}$), respectively, were determined using the non-linear (equation 4.3) and linear (equation 4.4) forms of the pseudo-first order rate equation and non-linear (equation 4.5) and linear (equation 4.6) forms of the pseudo-second order rate equation as described by Baumer and Hixon (2018).

\begin{align*}
q_t &= q_e (1 - e^{-k_1 t}) \\
\ln(q_e - q_t) &= -k_1 t + \ln(q_e) \\
q_t &= \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \\
\frac{t}{q_t} &= \left(\frac{1}{q_e}\right) t + \frac{1}{k_2 q_e^2}
\end{align*}
For the non-linear forms of the rate equations, we used the solver tool in Excel to optimize the $R^2$ value as a function of $k_1$ and $k_2$. The $R^2$ value of each system was calculated using equation 4.7 to determine the correlation between the experimental and modeled data

$$R^2 = 1 - \frac{\sum_{i=1}^{N} (y_i - \hat{y}_i)^2}{\sum_{i=1}^{N} (y_i - \langle y \rangle)^2} \quad (4.7)$$

where $y_i = \ln(q_e - q_t)$, $\hat{y}_i = \ln(q_e) - k_1 t$, and $\langle y \rangle$ equals the average of the $y_i$ values (Simonin, 2016). The sorption and desorption $q_e$ values used during the optimization process were determined experimentally in this study. Desorption data from the 1-week time point was used as “equilibrium” desorption values for each system for consistency across the mineral systems. A summary of the rate constants, degrees of freedom, and p-values is provided in Appendix C.

### 4.2.6 Reaction order determination

Equation 4.8 describes the overall rate law used to describe neptunium sorption to each aluminum (hydr)oxide where $a$, $b$, and $c$ are the reaction orders with respect to mineral concentration ($[\text{mineral}]$), hydrogen ion concentration ($[H^+]$), and aqueous neptunium concentration ($[Np]_{aq}$), respectively.

$$\frac{d[Np]_{aq}}{dt} = -k[\text{mineral}]^a[H^+]^b[Np]^c \quad (4.8)$$

The overall reaction rates ($k$) were determined by holding the neptunium concentration constant to obtain equation 4.9

$$\frac{d[Np]_{aq}}{dt} = -k_2[Np]^c_{aq} \quad (4.9)$$

where $k_2 = k[\text{mineral}]^a[H^+]^b$. $k$ can be solved through rearrangement such that
\[ k = \frac{k_2}{[\text{mineral}]^a[H^+]^b} \]  

(4.10)

4.3 Results and Discussion

4.3.1 Neptunium sorption kinetics

Aqueous neptunium concentrations were measured as a function of time for suspensions containing bayerite (\(\alpha\)-Al(OH)\(_3\)), gibbsite (\(\gamma\)-Al(OH)\(_3\)), corundum (\(\alpha\)-Al\(_2\)O\(_3\)), and \(\gamma\)-alumina (\(\gamma\)-Al\(_2\)O\(_3\)). Figure 4.1 shows neptunium sorption to corundum at three different mineral concentrations, neptunium concentrations, and pH values. Data for bayerite, gibbsite, and \(\gamma\)-alumina are provided in Appendix C. Neptunium sorption increased with time for all minerals and was characterized by a rapid sorption step occurring within the first 10 minutes followed by a slower equilibrium sorption process. This two-step sorption process has been observed previously for the sorption of transition metals (Davis et al., 1987; Haung et al.; 2007; Liu et al., 2018) and \(f\)-block elements (Tochiyama et al., 1996; Shaughnessy et al., 2003; Hixon and Powell, 2014; Baumer and Hixon, 2018; Smith et al., 2018) to metal oxide minerals. In general, the two-step process is attributed to a fast, diffusion-controlled surface reaction followed by a rate-limiting step that can be explained by a variety of processes, including surface precipitation, diffusion into micropores, structural arrangement, or surface-mediated reduction. In the present study, neptunium is not expected to undergo-surface mediated reduction or precipitate from solution (Baumer et al., 2017). Furthermore, steady-state is observed in these systems within hours whereas aging processes, such as incorporation, generally occur over weeks (Rabung et al., 2000). An alternative explanation for the two-step sorption process leverages the concept of strong (or high-affinity) and weak (or low-
affinity) sorption sites (Dzombak and Morel, 1990). Strong sites, such as singly-coordinated aluminol sites, are generally located on mineral edges and at defect sites while weak sites are located on the faces of mineral surfaces (McBride et al., 1982). Thus, the concentration of weak sites is typically much larger than the concentration of strong sites and a two-step sorption process can be explained by initially fast sorption of neptunium to strong sites followed by a slower association of neptunium with weak sites.

Model fits to the sorption data were derived from the linear pseudo-first and -second order rate equations (Equations 4.4 and 4.6, respectively). Graphical results and tabular summaries are provided in Appendix C. High correlation coefficients ($R^2 > 0.95$) were obtained for the linear plots of the pseudo-first and pseudo-second order rate equations for all minerals in this study. Several of the pseudo-first order plots were truncated to the first 30 minutes to obtain better $R^2$ values, but the pseudo-second order plots were linear without truncation. Kinetics data favors the linear form of the pseudo-second order rate equations close to equilibrium (Simonin, 2016), so the high $R^2$ values obtained without truncation of the data do not necessarily indicate that the data is better fit by the pseudo-second order model. To remove this bias, the data was also compared to the non-linear forms of the pseudo-first and -second order rate equations. Both non-linear forms have the same axes and allow for a more accurate comparison of $R^2$ values (Simonin, 2016). Figure 4.2 shows the $q_t/q_e$ versus time plots of the experimental neptunium sorption to corundum data and the pseudo-first and-second order models. Plots for the other aluminum (hydr)oxides can be found in Appendix C. As previously observed by Baumer and Hixon (2018), the $R^2$ values of the non-linear equations were lower than the linear equations, but the pseudo-second order models resulted in better
correlations overall compared to the non-linear pseudo-first order models. The non-linear pseudo-first order models generally over-predicted neptunium sorption to aluminum (hydr)oxides for all minerals. In the context of environmental modeling, this could result in neptunium being more mobile than expected. Therefore, reaction orders were determined using the non-linear $k_2$ values of each system.

Figure 4.1 Fraction of Np(V) sorbed to corundum as a function of time and (A) neptunium concentration, (B) pH, and (C) mineral concentration. Specific experimental conditions are provided in Appendix C. Error bars represent the error propagated from the uncertainty in ICP-MS measurements and gravimetric sample preparation.
The non-linear pseudo-second order rate constants increased with increasing mineral concentration and pH for all of the aluminum (hydr)oxides. The observed increase with mineral concentration is presumably due to an increased number of total sorption sites, including strong sorption sites. Neptunium sorption also increased with increasing pH (Figure 4.1B) and is attributed to the mineral surface becoming increasingly negatively charged and attracting the neptunium cation based on electrostatic interactions (Zavarin et al., 2012; Baumer et al. 2017, Elo et al., 2017). At higher pH, stronger ternary neptunium carbonate complexes are also expected to form compared to those formed at lower pH (Arai et al., 2007; Gückel et al., 2013).

Neptunium sorption is expected to increase with decreasing neptunium concentration because there is a larger fraction of binding sites available relative to the neptunium concentration (Fendorf and Sparks, 1994; Li and Tao, 2003; Hixon and Powell, 2014; Bedemo et al, 2016; Baumer and Hixon, 2018). However, Figure 4.1A shows that there is no correlation between sorption and neptunium concentration in this study. In these experiments, the aqueous carbonate concentration was limited because the suspensions were only open to the atmosphere during preparation and sampling; otherwise, vials were capped and sealed with plastic paraffin film. At higher neptunium concentrations, neptunium sorption in a capped vial resembles neptunium sorption in an anerobic environment (Turner et al., 1998; Baumer et al., 2017), presumably because neptunium carbonate complexes represent a lower fraction of the total neptunium concentration. At $10^{-9}$ M Np, less sorption was observed, which could be the result of a larger fraction of the total neptunium existing as negatively-charged aqueous carbonate complexes. These complexes are not expected to be attracted to the negatively-charged
mineral surfaces at high pH and would lead to lower than expected sorption at these pH values compared to carbonate-free systems. The non-linear sorption trend with varying neptunium concentration results in non-linear pseudo-second order rate constants (see Appendix C). Therefore, the reaction order with respect to neptunium concentration could not be determined.

Figure 4.2. Non-linear pseudo-first order (PFO) and pseudo-second order (PSO) model fits to experimental data collected from systems containing (9.98 ± 0.05) x 10^{-9} M Np(V) and 5.111 ± 0.005 m^2·L^{-1} corundum at pH 10.78 ± 0.05. Error bars represent the error propagated from the uncertainty in ICP-MS measurements and gravimetric sample preparation and are contained within the data points.

Log-log plots of \( k_2 \) vs [corundum] and \([H^+]\) yielded linear regressions with slopes equal to the reaction order with respect to mineral concentration and proton concentration, respectively (see Appendix C). The results are summarized in Table 4.1. The reaction orders with respect to proton concentration were nearly identical, indicating a similar dependence on pH regardless of the mineral that is present. Each aluminum (hydr)oxide has been shown to exhibit a different point of zero charge and different equilibrium constants (Yang et al., 2007), so the surface charge is expected to be different
for each mineral over the pH range of this study. Furthermore, Baumer et al. (2017) also show that neptunium sorption edges for bayerite, corundum, and \( \gamma \)-alumina are different at equilibrium. Therefore, similar reaction orders with respect to pH are not expected and do not appear to be related to the acid-base chemistry of the minerals. The reaction orders with respect to bayerite and gibbsite concentrations are higher than those of the aluminum oxides, which is likely due to the similar crystal structures within each mineral grouping.

### TABLE 4.1.

**REACTION ORDERS WITH RESPECT TO MINERAL CONCENTRATION (A), HYDROGEN ION CONCENTRATION (B) AND OVERALL REACTION RATES**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>( a )</th>
<th>( b )</th>
<th>Overall reaction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bayerite (( \alpha )-Al(OH)(_3))</td>
<td>2.17 ± 0.40</td>
<td>-0.296 ± 0.067</td>
<td>(1.40 ± 0.28) ( \times 10^{-4} )</td>
</tr>
<tr>
<td>Gibbsite (( \gamma )-Al(OH)(_3))</td>
<td>1.64 ± 0.40</td>
<td>-0.181 ± 0.071</td>
<td>(5.00 ± 1.27) ( \times 10^{-4} )</td>
</tr>
<tr>
<td>Corundum (( \alpha )-Al(_2)O(_3))</td>
<td>0.92 ± 0.49</td>
<td>-0.155 ± 0.015</td>
<td>(7.92 ± 0.04) ( \times 10^{-2} )</td>
</tr>
<tr>
<td>( \gamma )-Alumina (( \gamma )-Al(_2)O(_3))</td>
<td>1.40 ± 0.43</td>
<td>-0.119 ± 0.055</td>
<td>(8.14 ± 0.14) ( \times 10^{-3} )</td>
</tr>
</tbody>
</table>

The overall reaction rates were determined for each mineral system using equation 4.10 and followed the trend corundum > \( \gamma \)-alumina > gibbsite > bayerite. This trend is similar to the europium sorption trend reported by Baumer and Hixon (2018) with the aluminum hydroxides resulting in slower overall reaction rates compared to the aluminum oxides. The rate constants also appear to be highly dependent on the reaction order with respect to mineral concentration and follow an inverse trend (e.g., corundum has the lowest reaction order with respect to mineral concentration but the fastest overall
reaction rate). Aluminum deficiency in the gibbsite and bayerite crystal structures (Franks and Gan, 2007) and a large number of edge and defect sites on the $\gamma$-alumina surface (McBride et al., 1982) lead to higher concentrations of singly-coordinated surface sites, which have higher deprotonation pK$_a$ values than doubly-coordinated surface sites (Hiemstra et al., 1999; Yang et al., 2007; Baumer and Hixon, 2018). Singly-coordinated aluminol sites are harder to deprotonate, presumably because the charge of the oxygen cannot be distributed over multiple aluminum ions. The pK$_a$ values determined by Yang et al. (2007) suggest that the corundum aluminol sites will deprotonate around pH 7 while $\gamma$-alumina and gibbsite aluminol sites will not deprotonate until pH 9 and 10, respectively. Given that the reaction orders with respect to mineral concentration were determined at approximately pH 9.5, we expect that the corundum surface will have more negatively-charged surface sites available than gibbsite or $\gamma$-alumina, even though our experiments were normalized to surface area measurements. The availability of more negatively-charged surface sites leads to a faster reaction rate for corundum. Adversely, higher pK$_a$ values for $\gamma$-alumina, gibbsite, and bayerite lead to slower reaction rates because fewer negatively-charged sites, which are the most favorable for neptunium sorption, are present on the mineral surfaces. Thus, the reaction rate constants appear to be directly connected to the concentration of singly-coordinated aluminol sites at the mineral surface.

4.3.2 Neptunium Desorption Kinetics

Neptunium desorption from bayerite, gibbsite, corundum, and $\gamma$-alumina was measured as a function of time and pH (see Figure 4.3). Neptunium desorption increased with decreasing pH, which is consistent with previous literature findings (Elo et al., 2017).
and is attributed to the mineral surfaces having more positive charge at low pH than at high pH. Neptunium desorption also increased with time. As with the sorption experiments, there appears to be a two-step desorption reaction. However, while steady-state sorption in these systems was observed within an hour, steady-state desorption was not obtained even after several months. Approximately 10-30% of the neptunium remained sorbed to the mineral surface after one week, which can be explained by either irreversible sorption or extremely slow desorption kinetics (Nakata et al., 2000; Tinnacher et al., 2011). In the present study, steady-state desorption was not obtained, which suggests that the 1-week timeframe was not sufficient for complete desorption to occur. Therefore, the 10-30% of neptunium that was not desorbed is likely the result of extremely slow desorption kinetics rather than the presence of irreversibly-sorbed surface complexes. This observation is further supported by longer desorption time points (> 1 week), which show that neptunium continued to be removed from the mineral surfaces (see Appendix C).

The non-linear pseudo-second order reaction rates describing neptunium desorption from corundum are shown in Table 4.2. Data for bayerite, gibbsite, and γ-alumina are provided in Appendix C. The pseudo-second order rate equations were able to accurately model the neptunium desorption data at pH > 7, however, neither the pseudo-first or -second order rate equations accurately predicted neptunium desorption at pH < 6.5 (see Figure 4.4). Figure 4.3 shows that desorption at these lower pH values appeared to plateau after 30 minutes, but 1-week desorption data suggests that these plateaus are far from equilibrium; only half of the neptunium that desorbed at 1 week was desorbed within the first hour. The relatively large equilibrium desorption value at low
pH (~89%) lead to an overprediction of neptunium desorption at short times and low $R^2$ values. The solver function used to optimize the pseudo-first and -second order rate constants drove the model towards equilibrium and was not able to account for the plateau observed at low pH. This highlights a deficiency in the simple model used in this study, which cannot accurately represent the complex, possibly multi-step, desorption reactions occurring at low pH.

Figure 4.3. (A) Fraction of neptunium desorbed from corundum as a function of time and pH. (B) Fraction of neptunium desorbed after one week as a function of pH and mineral phase. Specific experimental conditions are provided in Appendix C. Error bars represent the error propagated from the uncertainty in ICP-MS measurements and gravimetric sample preparation.

Two pieces of evidence suggest that there are different forward and reverse reactions for the sorption and desorption of neptunium in the presence of aluminum.
(hydr)oxide minerals: (1) the ability of the pseudo-second order models to accurately fit the sorption data, but not the desorption data, at low pH and (2) the observation that steady-state sorption in these systems was observed within an hour whereas steady-state desorption was not obtained. The desorption plateau that occurs within the first hour at pH < 6.5 suggests the possibility of a multi-step desorption reaction at low pH with initial desorption of a weakly sorbed surface complex followed by desorption of a more strongly sorbed complex. These results provide indirect evidence of different reaction pathways for sorption and desorption and highlight the importance of kinetics analyses in refining the conceptual models which describe neptunium behavior at the mineral-water interface.

TABLE 4.2.

PSEUDO-SECOND ORDER REACTION RATE CONSTANTS ($K_2$) OF NEPTUNIUM DESORPTION FROM CORUNDUM DETERMINED USING THE NON-LINEAR FORM OF THE PSEUDO-SECOND ORDER RATE EQUATION

<table>
<thead>
<tr>
<th>Corundum ($m^2\cdot L^{-1}$)</th>
<th>Neptunium (M)</th>
<th>pH</th>
<th>$k_2$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.14 ± 0.01</td>
<td>($8.11 \pm 0.48 \times 10^{-9}$)</td>
<td>5.28 ± 0.10</td>
<td>3.11</td>
<td>-6.96</td>
</tr>
<tr>
<td>5.140 ± 0.004</td>
<td>($8.06 \pm 0.10 \times 10^{-9}$)</td>
<td>7.58 ± 0.28</td>
<td>26.5</td>
<td>0.973</td>
</tr>
<tr>
<td>5.146 ± 0.010</td>
<td>($8.03 \pm 0.05 \times 10^{-9}$)</td>
<td>9.81 ± 0.06</td>
<td>96.3</td>
<td>0.701</td>
</tr>
</tbody>
</table>
Figure 4.4. Non-linear pseudo-first order (PFO) and pseudo-second order (PSO) model fits to experimental desorption data at (A) \( (6.75 \pm 0.57) \times 10^{-9} \) M Np, \( 5.20 \pm 0.01 \) m\(^2\)·L\(^{-1}\) corundum, and pH \( 5.28 \pm 0.10 \) (\( R^2 = -7.45 \)) and (B) \( (6.60 \pm 0.92) \times 10^{-9} \) M Np, \( 5.25 \pm 0.01 \) m\(^2\)·L\(^{-1}\) corundum, and pH \( 7.60 \pm 0.24 \) (\( R^2 = 0.97 \)). Error bars represent the error propagated from the uncertainty in ICP-MS measurements and gravimetric sample preparation and are contained within the data points.

4.4 Environmental Relevance

Neptunium will be a major dose contributor of nuclear repositories after 10,000 years, therefore, understanding the interactions controlling its mobility are of extreme importance. Kinetics analyses of the neptunium sorption and desorption rates in this study provide important information about how neptunium will interact with aluminum (hydr)oxides in the environment. Neptunium sorption is rapid and steady-state is obtained within an hour, but desorption is much slower and occurs over several months. These
observations are important because they suggest that sorbed neptunium could be slowly released back into the aqueous phase and act as a continuous source of contamination to the environment. This study also shows that neptunium sorption to aluminum (hydr)oxides is well described by pseudo-second order rate equations, but desorption from the aluminum (hydr)oxides was not well described by the either the pseudo-first or pseudo-second order reaction equations at pH < 6.5. This suggests a multi-step desorption process may be occurring. The inability of the rate equations to represent the desorption data further supports the possibility of different sorption and desorption reaction mechanisms and deserves further study.
CHAPTER 5:
PLUTONIUM SORPTION AND REDUCTION IN THE PRESENCE OF BAYERITE
AND GIBBSITE

5.1 Introduction

Plutonium has been introduced into the environment through nuclear weapons testing and improper disposal at legacy waste sites. At the Nevada National Security Site, an estimated $8.88 \times 10^3$ TBq of plutonium was released into the environment though weapons testing and approximately $4.37 \times 10^2$ TBq of plutonium was disposed of in the near surface region of the Hanford Site (Smith et al., 2003; Cantrell et al., 2009). Understanding the environmental mobility of plutonium is important because of the high toxicity and long half-lives of several isotopes, yet current models have been unable to predict plutonium mobility in both the U.S. and Russia (Kersting et al., 1999; Santschi et al., 2002; Novikov et al., 2006). The inability of current reactive transport models to predict plutonium mobility over relatively short time periods highlights the need to develop a better understanding of the molecular-level interactions of plutonium with mineral surfaces as well as a more thorough understanding of the rate of sorption and reduction as a function of solution conditions.

Aluminum minerals are abundant in nature and several aluminum (hydr)oxides exist in the environment, including corundum ($\alpha$-Al$_2$O$_3$) and gibbsite ($\gamma$-Al(OH)$_3$). Additionally, the gibbsite structure is present between alternating silicon layers in
important clay minerals, including the illite, kaolinite, and montmorillonite/smectite groups. These clays are abundant in nature and are components of the bentonite material that will be used as backfill at future nuclear repositories (Sellin and Leupin, 2013). While expected to play an important role in controlling plutonium mobility in the environment, no studies have focused on understanding plutonium interactions with aluminum (hydr)oxides.

Plutonium interactions with a wide variety of minerals including iron (oxyhydr)oxides (Keeney-Kennicutt and Morse, 1985; Sanchez et al., 1985; Powell et al., 2004, 2005; Kirsch et al., 2011; Romanchuk et al., 2011, 2013; Hixon and Powell, 2014; Emerson and Powell, 2015; Zhao et al., 2016), manganese oxides (Keeney-Kennicutt and Morse, 1985; Duff et al., 1999; Morgenstern and Choppin, 2002; Shaughnessy et al., 2003; Powell et al., 2006), quartz (Hixon et al., 2013), and clays (Zavarin et al., 2012; Marsac et al., 2015; Banik et al., 2016; Begg et al., 2018) have been investigated. These studies have shown that sorption is highly dependent on the initial plutonium oxidation state. Environmentally-relevant plutonium oxidation states include Pu(III), Pu(IV), Pu(V), and Pu(VI). Plutonium sorption is directly related to effective charge and follows the trend Pu(V) < Pu(III) < Pu(VI) < Pu(IV). Pu(III) and Pu(IV) retain their overall charge whereas Pu(V) and Pu(VI) have lowered effective charges due to the formation of the nearly linear dioxo cations, PuO$_2^+$ and PuO$_2^{2+}$, respectively. Plutonium sorption behavior is complicated by the tendency of Pu(V/VI) to reduce to Pu(IV) at the mineral surface, a process called surface-mediated reduction. Initial observations of surface-mediated reduction stemmed from the shifting of Pu(V) sorption edges to lower pH
values over time and the similarities between Pu(IV) and Pu(V) sorption edges at steady-state (Keeney-Kennicutt and Morse, 1985; Sanchez et al., 1985).

The exact mechanism(s) supporting the observation of surface-mediated reduction have yet to be determined. A recent review on plutonium surface-mediated reduction highlighted seven possible reaction mechanisms (Hixon and Powell, 2018), but the most probable explanations include electron transfer via redox active elements at the mineral surface (Powell et al., 2004; 2005; Hixon et al., 2010; Hixon and Powell, 2014), electron shuttling due to semiconductor properties of the mineral (Powell et al., 2004; 2005), and a Nernstian favorability of Pu(IV) complexes or colloids (Powell et al., 2004; 2005; 2006; Hixon et al., 2010; 2013; Hixon and Powell, 2014). Nernstian favorability has generally been used to explain surface-mediated reduction on minerals without semiconductor properties or redox sensitivity (Hixon et al., 2013), such as aluminum (hydr)oxides. The occurrence of surface-mediated reduction on aluminum (hydr)oxide surfaces, and by what mechanism, has not been documented in the peer-reviewed literature.

The reaction rates describing plutonium sorption (and reduction) to aluminum (hydr)oxides are also missing from the peer-reviewed literature. Several studies have modeled plutonium sorption data using the linear pseudo-first order reaction equations to determine reaction rate constants for plutonium sorption and reduction in the presence of iron (oxyhydr)oxides (Powell et al., 2004; 2005; Hixon and Powell, 2014) and clay minerals (Begg et al., 2014; 2018). These studies show that pseudo-first order reaction rates increase with decreasing plutonium concentration and increasing mineral concentrations.
This current study describes plutonium sorption to two aluminum hydroxides – bayerite ($\alpha$-Al(OH)$_3$) and gibbsite ($\gamma$-Al(OH)$_3$) – between pH 6 - 10 and fits the experimental sorption data to pseudo-first order rate equations. The aqueous- and solid-phase oxidation state distributions were measured throughout the experiments to determine the rate and extent of reduction as well as to monitor for evidence of surface-mediated reduction.

5.2 Materials and Methods

CAUTION: Plutonium is radioactive and should only be handled by trained workers in approved radiation facilities! The work described below was conducted in laboratories licensed by the U.S. Nuclear Regulatory Commission and the University of Notre Dame Radiation Control Committee. These laboratories are dedicated to transuranic work and equipped with HEPA-filtered hoods.

5.2.1 Mineral Preparation and Characterization

Bayerite and gibbsite were obtained commercially from Sasol Germany GmbH and Alteo, respectively. The bayerite was high purity and used without any further treatment. Gibbsite was washed with alternating solutions of 0.01 M NaOH and 0.01 M HNO$_3$ three times and then rinsed five times in ultrapure water (18.2 MΩ·cm at 25°C). The gibbsite was dried at 100°C to remove excess water. Powder X-ray diffraction was used to confirm the identity of the mineral phases and N$_2$(g)-BET was used to determine surfaces areas of 9.84 ± 0.05 and 64.4 ± 0.01 m$^2$ g$^{-1}$ for bayerite and gibbsite, respectively.
5.2.2 Plutonium working solution preparation

A plutonium working solution was prepared by oxidizing a $^{238}$Pu standard (NIST SRM 4323B) using an excess of KBrO$_3$(s). The oxidation state distribution of plutonium was tracked as a function of time using the solvent extraction and coprecipitation methods established in the literature (Powell et al., 2004; 2005; Hixon et al., 2013; Hixon and Powell, 2014). A complete summary of the oxidation analysis procedure is provided in Appendix D. Generally, 0.5 M bis-(ethylhexyl)-phosphoric acid (HDEHP) in cyclohexane and 0.025 M 4-benzyol-3-methyl-1-phenyl-2-pyrazolin-5-one (PMBP) in cyclohexane were used to isolate Pu(IV/VI) and Pu(IV) in the organic phases, respectively. Additionally, a lanthanide fluoride coprecipitation removed Pu(IV) from the aqueous phase as a solid precipitant. All plutonium aliquots from the solvent extraction and coprecipitation procedures were analyzed with liquid scintillation counting to determine the plutonium concentration in each phase; the oxidation state distribution was calculated from these values. The final working solution contained $(2.45 \pm 0.82) \times 10^{-7}$ M total plutonium with an oxidation state distribution of 19% Pu(V) and 81% Pu(VI).

5.2.3 Batch sorption experimental conditions

Batch sorption experiments were prepared in 50 mL conical tubes by combining approximately 45 mL of 0.01 M NaCl with a homogenized mineral solution to obtain a mineral concentration of 5 g·L$^{-1}$. The solutions were then spiked with the plutonium stock solution to give a final concentration of approximately $5.5 \times 10^{-10}$ M Pu and $5.8 \text{ m}^2\cdot\text{L}^{-1}$ bayerite or $37 \text{ m}^2\cdot\text{L}^{-1}$ gibbsite. The oxidation distribution of the plutonium stock solution was analyzed prior to spiking each set of samples. The separate reactors were then adjusted to pH 6, 7, 8, 9, and 10 using dilute NaOH and HCl, sealed with paraffin film,
and placed on an end-over-end rotator until sampling. Summaries of exact experimental conditions are provided in Appendix D. The reactors were sampled multiple times over two months. During each sampling, homogeneous 3-mL aliquots were divided into three 1.5 mL microcentrifuge tubes and centrifuged at 5500 rpm for 30 minutes to remove particles > 100 nm (Jackson, 2005). An aliquot of the aqueous phase was measured with a liquid scintillation counter to determine the plutonium concentration and three additional aliquots were used in the oxidation state analysis procedure described in Appendix D. The remaining aqueous phase was separated from the solid phase and the solid phase was leached in 0.3 M HCl for 15 minutes to remove sorbed Pu(V) and Pu(VI). The samples were centrifuged for an additional 30 minutes to remove particles > 100 nm and the oxidation state analysis procedure was repeated with the aqueous leachate. Plutonium not removed by the leachate was assumed to be Pu(IV) (Powell et al., 2004).

5.2.4 Kinetics modeling

The reduction and sorption rates must both be considered when determining the overall reaction rates describing plutonium interactions with the aluminum hydroxides. Reaction rates that consist of a slow and a fast rate step are kinetically controlled by the slow step. In this study, the sorption and reduction rate constants were determined independently and compared to determine the rate-controlling step. The overall rate law describing plutonium sorption to each aluminum hydroxide when reduction of Pu(V/VI) is the rate limiting step has been adapted from Powell et al. (2004) and is shown in equation 5.1. Equation 5.2 shows the overall reaction rate law when sorption is the rate limiting step.
\[
\frac{df_{\text{Pu}(V/VI)}^{\text{total}}}{dt} = -k_{\text{rxn}} df_{\text{total}}^{\text{Pu}(V/VI)} [\text{mineral}]^b [H^+]^c \tag{5.1}
\]
\[
\frac{d[\text{Pu}]_{\text{aq}}}{dt} = -k_{\text{rxn}} [\text{Pu}]_{\text{aq}}^a [\text{mineral}]^b [H^+]^c \tag{5.2}
\]

In equations 5.1 and 5.2, \( k_{\text{rxn}} \) is the overall reaction rate, \( df_{\text{total}}^{\text{Pu}(V/VI)} \) is the total fraction of Pu(V) and Pu(VI) in the system (i.e., solid + aqueous), \([\text{Pu}]_{\text{aq}}\) is the aqueous plutonium concentration, \([\text{mineral}]\) is the mineral concentration, \([H^+]\) is the hydrogen ion concentration, \(a\) is the reaction order with respect to plutonium concentration, \(b\) is the reaction order with respect to mineral concentration, and \(c\) is the reaction order with respect to \([H^+]\).

By holding two variables constant and assuming pseudo-first order reaction kinetics, it is possible to determine the sorption rate constants \(k_{\text{sorp}}\) and reduction rate \(k_{\text{red}}\) constants for each system. The pseudo-first order rate expression for sorption and reduction are shown in equations 5.3 and 5.4, respectively,

\[
\frac{d[\text{Pu}]_{\text{aq}}}{dt} = -k'_{\text{sorp}} [\text{Pu}]_{\text{aq}}^a \tag{5.3}
\]
\[
\frac{df_{\text{Pu}(V/VI)}^{\text{total}}}{dt} = -k'_{\text{red}} df_{\text{total}}^{\text{Pu}(V/VI)} \tag{5.4}
\]

where \(k'_{\text{sorp}} = k_{\text{rxn}} [\text{mineral}]^a [H^+]^b\) and \(k'_{\text{red}} = k_{\text{rxn}} [\text{mineral}]^a [H^+]^b\). Integrating both pseudo-first order rate equations and plotting \(\ln([\text{Pu}]_{\text{aq}}/[\text{Pu}]_{\text{aq},i})\) versus time and \(\ln(df_{\text{total}}^{\text{Pu}(V/VI)}/df_{\text{total}}^{\text{Pu}(V/VI),i})\) versus time yields \(k'_{\text{sorp}}\) and \(k'_{\text{red}}\) for each system. When \(k'_{\text{sorp}} > k'_{\text{red}}\), equation 5.1 was used to determine the overall reaction rate; otherwise equation 5.2 was used.
5.3 Results and Discussion

5.3.1 Batch Sorption Experiments

Plutonium sorption to bayerite (α-Al(OH)$_3$) was monitored as a function of pH and time; the results are shown in Figure 5.1A-B. The fraction of plutonium associated with the solid phase increased with increasing pH, which is attributed to the plutonium cations having a higher affinity for the increasingly negatively-charged mineral surface as the pH is raised. At pH ≥ 9.42, more that 90% of the plutonium was removed from solution within five days. Sorption at these pH values remained constant for the entire timeframe of the study, indicating either steady-state sorption or extremely slow reaction kinetics. At lower pH values, sorption increased with time and steady-state was not observed within 30 days. Slow plutonium reaction kinetics have been previously observed for plutonium sorption to quartz (Hixon et al., 2013) and clays (Zavarin et al., 2012; Begg et al., 2018).
Figure 5.1. (A-B) Plutonium sorption to bayerite as a function of time and pH. Experimental conditions: \([\text{Pu}]_T = (5.50 \pm 0.18) \times 10^{-10} \text{ M}; [\alpha-\text{Al(OH)}_3] = 5.801 \pm 0.002 \text{ m}^2\cdot\text{L}^{-1}; I = 0.01 \text{ M NaCl}. \)  
(C-D) Plutonium sorption to gibbsite as a function of time and pH. Experimental conditions: \([\text{Pu}]_T = ((5.45 \pm 0.10) \times 10^{-10} \text{ M}; [\gamma-\text{Al(OH)}_3] = 37.57 \pm 0.1 \text{ m}^2\cdot\text{L}^{-1}; I = 0.01 \text{ M NaCl}. \)

Plutonium sorption to gibbsite (\(\gamma-\text{Al(OH)}_3\)) was also monitored as a function of time; the results are shown in Figure 5.1C-D. Similar to bayerite, plutonium sorption to gibbsite increased with pH but an S-shaped sorption curve was not observed. Overall, less plutonium sorption was observed at all pH values with only 30% sorption occurring at pH 10 within the first 5 days. Sorption increased with time and steady-state was not obtained during the timeframe of this study. After 30 days at pH 10, only 40% of the plutonium was associated with the gibbsite. The steady increase in sorption was similar to
plutonium sorption to bayerite at pH ≤ 7.20 and is likely the result of extremely slow reaction kinetics.

Distinct sorption trends for gibbsite and bayerite can be attributed to subtle differences in their crystal structures. Both gibbsite and bayerite have pillared structures consisting of a double layer of oxygen and aluminum with aluminum ions filling two-thirds of the octahedral sites. The structural differences between gibbsite and bayerite are caused by different stacking patterns of the double layers. Gibbsite and bayerite are characterized as having AB BA and AB AB stacking sequences, respectively (Franks et al., 2007). Bayerite is well-defined in the Z direction, which leads to long, thin bayerite fibers with high proportions of singly-coordinated aluminol sites (Hiemstra et al., 1999). Singly-coordinated aluminols generally only exist on the edges of gibbsite. Bayerite also has a higher proton sorption capacity than gibbsite, presumably because of the large number of singly-coordinated aluminols (Hiemstra et al., 1999). The greater plutonium sorption we observe for bayerite as opposed to gibbsite above pH 8 is likely the result of these highly reactive sorption sites. The bayerite surface is also less thermodynamically stable than gibbsite (Peintinger et al., 2014) and will slowly transition to gibbsite over time. How these stability differences effect sorption has not yet been determined.

5.3.2 Plutonium Oxidation State Distribution

The aqueous-phase oxidation state distributions of plutonium in the presence of bayerite and gibbsite were monitored as a function of time (see Appendix D). Pu(VI) was observed to reduce to Pu(V) in the aqueous phase, but no reduction to Pu(IV) was observed. This observation was consistent for both aluminum hydroxides and is consistent with the literature (Powell et al., 2004; 2005; 2006; Hixon et al., 2010; 2013,
Hixon and Powell, 2014). Parson-Moss et al. (2014) attribute the reduction of Pu(VI) to Pu(V) in the aqueous phase to alpha radiolysis, but changes in redox potential can also explain the observed reduction. In this study, Pu(VI) reduction to Pu(V) is relatively slow and an oxidation state distribution of approximately 50% Pu(V) and 50% Pu(VI) is obtained after 30 days.

The solid-phase plutonium oxidation state distributions for gibbsite and bayerite at pH 9 are provided in Figure 5.2. For both minerals, the fraction of Pu(VI) decreased as the fractions of Pu(V) and Pu(IV) increased. Pu(IV) was only observed on the solid phase of both minerals, and not in the aqueous phase, so reduction was mediated by the mineral surfaces. For the bayerite system, Pu(V) appeared to be relatively stable on the surface and was the primary oxidation state for the entire timeframe of this study. This suggests that above pH 8, plutonium sorbs to the bayerite surface as either Pu(V) or Pu(VI) and resists reduction to Pu(IV) for at least 30 days. In contrast, the primary solid-phase oxidation state of the gibbsite system was Pu(IV) after 30 days. Therefore, sorption appears to be the rate-limiting step for plutonium surface-mediated reduction on gibbsite and reduction is the rate-limiting step for plutonium surface-mediated reduction on bayerite. Aluminum hydroxides are not redox active and other proposed mechanisms of surface-mediated reduction, including plutonium disproportionation and alpha radiolysis, have been disproven (Hixon and Powell, 2014; Hixon and Powell, 2018). This suggests that Nernstian favorability is the most probable mechanism of surface-mediated reduction on these aluminum hydroxide surfaces.
5.3.3 Kinetics Modeling

The pseudo-first order sorption and reduction rate constants were determined for plutonium interactions with gibbsite and bayerite. Figure 5.3 shows plots of the
\[
\ln ([Pu_{aq,t}/Pu_{aq,i}]) \quad \text{and} \quad \ln (f_{total,t}^{Pu(VI)} / df_{total,t}^{Pu(VI)})
\]
versus time for bayerite and gibbsite at pH 9; the sorption and reduction rate constants are summarized in Table 5.1. The \(k'_{\text{sor}}\) and \(k'_{\text{red}}\) values were determined from the slope of the line between the first sampling point and the origin. The kinetics modeling was forced through the origin because, without doing so, the rate equations were not able to capture the large jump in sorption
between the initial start time and the 5-day sampling point. The sorption and reduction rate equations were also determined from the slope of the line connecting all the sampling points. Generally, the $k'_{\text{sorp}}$ and $k'_{\text{red}}$ values increased with increasing pH, which means that sorption and reduction occurred faster at higher pH. This is likely due to the increased availability of negatively-charged surface sites resulting in more sorption (Powell et al., 2005), and increased sorption, in turn, allowing for more surface-mediated reduction. The $k'_{\text{sorp}}$ values for bayerite were consistently larger than the bayerite $k'_{\text{red}}$ values, except at pH 6.8, which suggests that surface-mediated reduction in the system was kinetically limited by the reduction of Pu(V/VI) to Pu(IV) above pH 6.8. For gibbsite, the $k'_{\text{sorp}}$ values were smaller than the $k'_{\text{red}}$ values, indicating that surface-mediated reduction on the gibbsite surface was limited by plutonium sorption.

**TABLE 5.1.**

THE PSEUDO-FIRST ORDER SORPTION AND REDUCTION RATE CONSTANTS OF PLUTONIUM ($5.5 \times 10^{-10}$ M) ON GIBBSITE ($37 \text{ M}^2\cdot\text{L}^{-1}$) AND BAYERITE ($5.8 \text{ M}^2\cdot\text{L}^{-1}$)

<table>
<thead>
<tr>
<th></th>
<th>Gibbsite</th>
<th>Bayerite</th>
<th>Bayerite</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 10</td>
<td>0.0022</td>
<td>0.0038</td>
<td>0.0001</td>
</tr>
<tr>
<td>pH 9</td>
<td>0.0008</td>
<td>0.0028</td>
<td>0.0001</td>
</tr>
<tr>
<td>pH 7.3</td>
<td>0.0005</td>
<td>0.0032</td>
<td>0.0004</td>
</tr>
<tr>
<td>pH 6.8</td>
<td>0.0005</td>
<td>0.0009</td>
<td>0.0002</td>
</tr>
</tbody>
</table>

$^1$The specific experimental conditions are provided in APPENDIX D.
Figure 5.3. The pseudo-first order $k'_{\text{so}}$ for plutonium sorption to bayerite (A) and gibbsite (C) and $k'_{\text{red}}$ for plutonium reduction on bayerite (B) and gibbsite (D). Experimental conditions: (A-B) $(5.51 \pm 0.10) \times 10^{-10}$ M Pu, $5.801 \pm 0.002$ m$^2$·L$^{-1}$ bayerite, pH $9.43 \pm 0.18$; (C-D) $(5.45 \pm 0.18) \times 10^{-10}$ M Pu, $37.57 \pm 0.1$ m$^2$·L$^{-1}$ gibbsite, pH $8.98 \pm 0.43$.

5.4 Conclusions

This study presents the first peer-reviewed evidence for plutonium surface-mediated reduction on the aluminum hydroxide minerals bayerite and gibbsite. Careful monitoring of the aqueous- and solid-phase oxidation state distributions shows that reduction to Pu(IV) only occurs on the solid phase. The exact method of plutonium reduction is not known, but is likely the result of Nernstian favorability of Pu(IV) surface
complexes or colloids. This study also showed that plutonium sorption/reduction to bayerite and gibbsite are controlled by different kinetics factors. Plutonium sorbs quickly to bayerite at high pH and surface-mediated reduction is limited by reduction of Pu(V) to Pu(IV) on the mineral surface. Plutonium surface-mediated reduction on gibbsite and on bayerite at pH < 6.8 is limited kinetically by sorption. Gibbsite and bayerite have identical chemical compositions but differences in AB BA versus AB AB stacking leads bayerite having more singly-coordinated aluminol sites and a higher reactivity than gibbsite. The slight differences in chemical structure lead to different sorption trends and surface-mediated reduction rates. The differences in kinetics caused by bayerite and gibbsite need to be taken into consideration to accurately model the environmental mobility of plutonium.
CHAPTER 6:
CONCLUSIONS AND FUTURE WORK

This dissertation has focused on filling important knowledge gaps related to how actinides and lanthanides interact with different aluminum (hydr)oxides and how the surface sites of these minerals effect macroscopic sorption trends. Baumer et al. (2017) provided a detailed discussion of equilibrium europium and neptunium sorption trends to gibbsite, bayerite, corundum, and γ-alumina. Nearly identical europium sorption trends have previously been attributed to aluminum oxide phase transformations, but Baumer et al. (2017) show, through careful monitoring of the solid phases, that phase transformations alone cannot explain this observation. These observations were further supported by different macroscopic sorption trends being obtained for neptunium sorption to aluminum (hydr)oxides for the same minerals.

Baumer et al. (2018) investigated the kinetics of europium sorption and observed that, even though nearly identical equilibrium sorption trends are obtained, sorption reaction rates vary by orders of magnitude. Europium sorption to gibbsite is consistently several orders of magnitude slower than europium sorption to bayerite, corundum, and γ-alumina. Neptunium sorption rates to these minerals exhibited the same general trend with neptunium sorbing faster to the aluminum oxides and slower to the aluminum hydroxides. The different sorption rates for the minerals was attributed to the availability of singly-coordinated aluminol sites on the aluminum hydroxides. Neptunium desorption
rates were also monitored and were observed to be slower than neptunium sorption reaction rates. This suggests that different neptunium sorption and desorption reaction pathways and mechanisms may exist for aluminum (hydr)oxides.

Singly-coordinated aluminol sites were attributed to different plutonium sorption trends for gibbsite and bayerite. This work showed for the first time in the peer-reviewed literature that plutonium-surface mediated reduction occurs on the surfaces of aluminum hydroxides. While surface-mediated reduction occurs for both gibbsite and bayerite, Pu(V) surface complexes are able to persist on the bayerite surface for at least 30 days. On gibbsite, Pu(V) complexes are less stable and reduce to Pu(IV) complexes within weeks. Kinetics analysis of these systems shows that surface-mediated reduction on bayerite is controlled kinetically by the Pu(VI/V) reduction rate while surface-mediated reduction on gibbsite is kinetically controlled by plutonium sorption to the mineral. For this work to be ready for publication, more data needs to be collected at long and short timeframes to develop a more thorough understanding of the sorption and reduction behavior on plutonium in these systems. The point of zero charge of both minerals should also be determined to enhance the discussion of why differences in sorption behavior exist for each mineral.

The work presented in this dissertation has raised several more questions related to europium, neptunium, and plutonium sorption complexes on the aluminum (hydr)oxide surfaces. Spectroscopic data, such as EXAFS and XANES, could be used to determine the identity of sorbed surface complexes. This would allow for a direct comparison between the minerals and well as be useful for surface-complexation modeling. Surface-complexation modeling would give more insight into the different sorption reactions for
each system at equilibrium. Because different neptunium sorption trends were obtained at equilibrium, it is likely that different sorption reactions occur for each mineral. It is possible that these differences will become more evident with detailed surface-complexation modeling. Desorption data should also be collected for europium and plutonium to allow for the development of a full reaction rate, taking both forward and reverse reactions into consideration. More focus should be given to identifying why different forward and reverse reactions appear to exist for neptunium sorption and desorption and determine if these differences are consistent for other metal ions. Understanding the distinct sorption and desorption reactions, as well as the rates at which they occur, will allow for a more thorough understanding of the sorption behavior of different actinides and lanthanides and allow for the development of more accurate reactive transport models.
Figure A.1. Plot of pXRD spectra showing (A) gibbsite, (B) bayerite, (C), γ-alumina, (D) corundum phases as they were received.
Figure A.2. Europium adsorption to corundum as a function of pH and time. Experimental conditions: \([\text{Eu}]_T = (1.03 \pm 0.03) \times 10^{-8} \text{ M}; \) [corundum] = 4.83 ± 0.02; \(I = 0.01 \text{ M NaCl}.\) Error bars represent the error propagated from uncertainty in ICP-MS measurements.

### TABLE A.1

MATRIX OF EXPERIMENTAL CONDITIONS

<table>
<thead>
<tr>
<th>Sorbant</th>
<th>Element</th>
<th>Ionic Strength (mol·L⁻¹)</th>
<th>Concentration (mol·L⁻¹)</th>
<th>Solid Concentration (m²·L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha\text{-Al}_2\text{O}_3)</td>
<td>Eu</td>
<td>0.01 NaCl</td>
<td>((1.03 \pm 0.03) \times 10^{-8})</td>
<td>4.83 ± 0.02</td>
</tr>
<tr>
<td>(\alpha\text{-Al}_2\text{O}_3)</td>
<td>Eu</td>
<td>0.05 NaCl</td>
<td>((1.04 \pm 0.03) \times 10^{-8})</td>
<td>4.80 ± 0.02</td>
</tr>
<tr>
<td>(\alpha\text{-Al}_2\text{O}_3)</td>
<td>Eu</td>
<td>0.10 NaCl</td>
<td>((1.03 \pm 0.04) \times 10^{-8})</td>
<td>4.80 ± 0.01</td>
</tr>
<tr>
<td>(\alpha\text{-Al}_2\text{O}_3)</td>
<td>Np</td>
<td>0.01 NaCl</td>
<td>((9.74 \pm 0.28) \times 10^{-9})</td>
<td>5.05 ± 0.15</td>
</tr>
<tr>
<td>(\alpha\text{-Al}_2\text{O}_3)</td>
<td>Np</td>
<td>0.05 NaCl</td>
<td>((9.04 \pm 0.06) \times 10^{-9})</td>
<td>4.75 ± 0.02</td>
</tr>
<tr>
<td>(\alpha\text{-Al}_2\text{O}_3)</td>
<td>Np</td>
<td>0.10 NaCl</td>
<td>((9.13 \pm 0.09) \times 10^{-9})</td>
<td>4.81 ± 0.02</td>
</tr>
</tbody>
</table>
Figure A.3 Diffraction patterns showing $\gamma$-alumina that has been hydrated for 14 days at pH 4, 7, 8, 9, and 10.

Figure A.4. Neptunium adsorption to corundum as a function of pH and time under varying ionic strengths. Error bars represent the error propagated from uncertainty in ICP-MS measurements.
Figure A.5. Europium adsorption to corundum as a function of pH and time under varying ionic strengths. Error bars represent the error propagated from uncertainty in ICP-MS measurements.
APPENDIX B:
SUPPORTING INFORMATION FOR CHAPTER 3

Figure B.1. Fraction of europium sorbed as a function of time to $\gamma$-Al$_2$O$_3$ (A), $\alpha$-Al$_2$O$_3$ (B), and bayerite (C)
<table>
<thead>
<tr>
<th>Sorbant</th>
<th>Eu Concentration (mol·L⁻¹)</th>
<th>Sorbant Concentration</th>
<th>Average pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Al₂O₃</td>
<td>(2.70 ± 0.05) x 10⁻⁸</td>
<td>0.506 ± 0.002</td>
<td>7.01 ± 0.04</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>(2.76 ± 0.05) x 10⁻⁸</td>
<td>0.969 ± 0.004</td>
<td>6.95 ± 0.11</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>(2.72 ± 0.01) x 10⁻⁸</td>
<td>5.059 ± 0.002</td>
<td>7.16 ± 0.06</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>(2.69 ± 0.04) x 10⁻⁸</td>
<td>5.10 ± 0.01</td>
<td>6.06 ± 0.06</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>(2.68 ± 0.03) x 10⁻⁸</td>
<td>5.11 ± 0.01</td>
<td>5.15 ± 0.18</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>(2.68 ± 0.06) x 10⁻⁸</td>
<td>5.16 ± 0.01</td>
<td>5.17 ± 0.03</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>(2.69 ± 0.06) x 10⁻⁸</td>
<td>5.116 ± 0.005</td>
<td>6.12 ± 0.01</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>(2.70 ± 0.03) x 10⁻⁸</td>
<td>5.162 ± 0.001</td>
<td>6.95 ± 0.01</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>(2.70 ± 0.02) x 10⁻⁸</td>
<td>10.91 ± 0.02</td>
<td>6.02 ± 0.01</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>(2.681 ± 0.003) x 10⁻⁸</td>
<td>49.94 ± 0.37</td>
<td>6.02 ± 0.02</td>
</tr>
<tr>
<td>α-Al(OH)₃</td>
<td>(2.75 ± 0.04) x 10⁻⁸</td>
<td>5.10 ± 0.04</td>
<td>5.07 ± 0.01</td>
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<tr>
<td>α-Al(OH)₃</td>
<td>(2.63 ± 0.03) x 10⁻⁸</td>
<td>5.127 ± 0.008</td>
<td>6.02 ± 0.01</td>
</tr>
<tr>
<td>α-Al(OH)₃</td>
<td>(2.77 ± 0.07) x 10⁻⁸</td>
<td>5.142 ± 0.009</td>
<td>6.98 ± 0.04</td>
</tr>
<tr>
<td>α-Al(OH)₃</td>
<td>(2.69 ± 0.02) x 10⁻⁸</td>
<td>9.988 ± 0.005</td>
<td>6.15 ± 0.01</td>
</tr>
<tr>
<td>α-Al(OH)₃</td>
<td>(2.71 ± 0.02) x 10⁻⁸</td>
<td>52.30 ± 0.10</td>
<td>6.18 ± 0.01</td>
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<tr>
<td>α-Al(OH)₃</td>
<td>(2.22 ± 0.08) x 10⁻⁷</td>
<td>5.12 ± 0.01</td>
<td>6.15 ± 0.16</td>
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<tr>
<td>α-Al(OH)₃</td>
<td>(2.180 ± 0.002) x 10⁻⁶</td>
<td>5.12 ± 0.01</td>
<td>6.10 ± 0.06</td>
</tr>
<tr>
<td>γ-Al(OH)₃</td>
<td>(2.68 ± 0.07) x 10⁻⁸</td>
<td>5.28 ± 0.02</td>
<td>6.12 ± 0.10</td>
</tr>
<tr>
<td>γ-Al(OH)₃</td>
<td>(2.72 ± 0.05) x 10⁻⁸</td>
<td>10.46 ± 0.05</td>
<td>6.06 ± 0.04</td>
</tr>
<tr>
<td>γ-Al(OH)₃</td>
<td>(2.71 ± 0.02) x 10⁻⁸</td>
<td>52.65 ± 0.04</td>
<td>6.06 ± 0.01</td>
</tr>
<tr>
<td>γ-Al(OH)₃</td>
<td>(2.63 ± 0.02) x 10⁻⁸</td>
<td>5.32 ± 0.02</td>
<td>5.26 ± 0.01</td>
</tr>
<tr>
<td>γ-Al(OH)₃</td>
<td>(2.73 ± 0.05) x 10⁻⁸</td>
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<td>6.94 ± 0.06</td>
</tr>
<tr>
<td>γ-Al(OH)₃</td>
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<td>6.14 ± 0.03</td>
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<tr>
<td>γ-Al(OH)₃</td>
<td>(2.252 ± 0.002) x 10⁻⁶</td>
<td>10.50 ± 0.09</td>
<td>6.12 ± 0.04</td>
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</table>
Figure B.1. Pseudo-first (left) and -second (right) order linear rate equations for $10^{-8}$ M Eu(III) sorption to $10 \text{ m}^2 \cdot \text{L}^{-1} \gamma$-Al$_2$O$_3$ at pH 6 (■), $0.5 \text{ m}^2 \cdot \text{L}^{-1} \alpha$-Al$_2$O$_3$ at pH 7 (▲), and $10 \text{ m}^2 \cdot \text{L}^{-1}$ bayerite at pH 6 (●).
Figure B.2. Non-linear pseudo-first order (PFO) and pseudo-second order (PSO) model fits to experimental data collected from systems containing $10^{-8}$ Eu(III) and $10\text{ m2} \cdot \text{L}^{-1}$ $\gamma$-Al2O3 at pH 6 ( ■), $0.5\text{ m2} \cdot \text{L}^{-1}$ $\alpha$-Al2O3 at pH 7 ( ▲), and $10\text{ m2} \cdot \text{L}^{-1}$ bayerite at pH 6 ( ●).
TABLE B.2.
LINEAR AND NON-LINEAR PSEUDO-FIRST ($K_1$) AND -SECOND ORDER ($K_2$) RATE CONSTANTS AND $R^2$ VALUES OF CORUNDUM ($\alpha$-Al$_2$O$_3$), Γ-AL$_2$O$_3$, AND BAYERITE ($\alpha$-Al(OH)$_3$)

<table>
<thead>
<tr>
<th>System</th>
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<th>Non-linear</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>$\alpha$-Al$_2$O$_3$ – 0.5 m$^2$/L pH 7 10$^{-8}$M Eu</td>
<td>$2.63 \pm 0.52$</td>
<td>0.93</td>
</tr>
<tr>
<td>$\alpha$-Al$_2$O$_3$ – 1.0 m$^2$/L pH 7 10$^{-8}$M Eu</td>
<td>$6.21 \pm 1.32$</td>
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</tr>
<tr>
<td>$\alpha$-Al$_2$O$_3$ – 5 m$^2$/L pH 7 10$^{-8}$M Eu</td>
<td>$1.391 \pm 0.007$</td>
<td>1.00</td>
</tr>
<tr>
<td>$\alpha$-Al$_2$O$_3$ – 5 m$^2$/L pH 6 10$^{-8}$M Eu</td>
<td>$0.49 \pm 0.24$</td>
<td>0.78</td>
</tr>
<tr>
<td>$\alpha$-Al$_2$O$_3$ – 5 m$^2$/L pH 5 10$^{-8}$M Eu</td>
<td>$0.48 \pm 0.180$</td>
<td>0.83</td>
</tr>
<tr>
<td>$\gamma$-Al$_2$O$_3$ – 5 m$^2$/L pH 5 10$^{-8}$M Eu</td>
<td>$0.614 \pm 0.085$</td>
<td>0.9685</td>
</tr>
<tr>
<td>$\gamma$-Al$_2$O$_3$ – 5 m$^2$/L pH 6 10$^{-8}$M Eu</td>
<td>$1.631 \pm 0.072$</td>
<td>0.9962</td>
</tr>
<tr>
<td>$\gamma$-Al$_2$O$_3$ – 5 m$^2$/L pH 7 10$^{-8}$M Eu</td>
<td>$4.583 \pm 0.325$</td>
<td>0.9852</td>
</tr>
<tr>
<td>$\gamma$-Al$_2$O$_3$ – 10 m$^2$/L pH 6 10$^{-8}$M Eu</td>
<td>$0.371 \pm 0.039$</td>
<td>0.9888</td>
</tr>
<tr>
<td>$\gamma$-Al$_2$O$_3$ – 50 m$^2$/L pH 6 10$^{-8}$M Eu</td>
<td>$1.805 \pm 0.090$</td>
<td>0.9925</td>
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<tr>
<td>$\alpha$-Al(OH)$_3$ – 5 m$^2$/L pH 5 10$^{-8}$M Eu</td>
<td>$1.076 \pm 0.099$</td>
<td>0.9916</td>
</tr>
<tr>
<td>$\alpha$-Al(OH)$_3$ – 5 m$^2$/L pH 6 10$^{-8}$M Eu</td>
<td>$1.017 \pm 0.639$</td>
<td>0.7169</td>
</tr>
<tr>
<td>System</td>
<td>Linear</td>
<td>Non-linear</td>
</tr>
<tr>
<td>------------------------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td></td>
<td>k₁</td>
<td>R²</td>
</tr>
<tr>
<td>α-Al(OH)₃ – 5 m²/L pH 7 10⁻⁸M Eu</td>
<td>1.775 ± 0.185</td>
<td>0.9684</td>
</tr>
<tr>
<td>α-Al(OH)₃ – 10 m²/L pH 6 10⁻⁸M Eu</td>
<td>3.540 ± 0.101</td>
<td>0.9992</td>
</tr>
<tr>
<td>α-Al(OH)₃ – 50 m²/L pH 6 10⁻⁸M Eu</td>
<td>1.390 ± 0.196</td>
<td>0.9618</td>
</tr>
<tr>
<td>α-Al(OH)₃ – 5 m²/L pH 6 10⁻⁷M Eu</td>
<td>1.576 ± 0.103</td>
<td>0.9915</td>
</tr>
<tr>
<td>α-Al(OH)₃ – 5 m²/L pH 6 10⁻⁶M Eu</td>
<td>1.362 ± 0.764</td>
<td>0.7609</td>
</tr>
</tbody>
</table>
APPENDIX C:
SUPPORTING INFORMATION FOR CHAPTER 4
### TABLE C.1.

MATRIX OF EXPERIMENTAL CONDITIONS

<table>
<thead>
<tr>
<th>Sorbant</th>
<th>Np Concentration (mol·L⁻¹)</th>
<th>Sorbant Concentration (m²L⁻¹)</th>
<th>Average pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Al₂O₃</td>
<td>(8.98 ± 0.03) x 10⁻⁹</td>
<td>0.5090 ± 0.0007</td>
<td>9.64 ± 0.04</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>(8.96 ± 0.08) x 10⁻⁹</td>
<td>1.029 ± 0.003</td>
<td>9.58 ± 0.09</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>(8.99 ± 0.04) x 10⁻⁹</td>
<td>5.11 ± 0.01</td>
<td>9.72 ± 0.08</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>(8.98 ± 0.05) x 10⁻⁹</td>
<td>5.111 ± 0.005</td>
<td>10.78 ± 0.05</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>(8.98 ± 0.04) x 10⁻⁹</td>
<td>5.094 ± 0.009</td>
<td>7.76 ± 0.06</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>(9.49 ± 0.04) x 10⁻¹₀</td>
<td>5.108 ± 0.009</td>
<td>9.66 ± 0.06</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>(9.96 ± 0.03) x 10⁻⁸</td>
<td>5.136 ± 0.009</td>
<td>9.55 ± 0.02</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>(8.99 ± 0.08) x 10⁻⁹</td>
<td>51.57 ± 0.17</td>
<td>9.49 ± 0.07</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>(8.98 ± 0.06) x 10⁻⁹</td>
<td>4.984 ± 0.010</td>
<td>9.52 ± 0.01</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>(9.00 ± 0.09) x 10⁻⁹</td>
<td>0.980 ± 0.008</td>
<td>9.53 ± 0.05</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>(8.92 ± 0.11) x 10⁻⁹</td>
<td>4.97 ± 0.02</td>
<td>10.650 ± 0.008</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>(8.99 ± 0.07) x 10⁻⁹</td>
<td>4.970 ± 0.006</td>
<td>7.74 ± 0.09</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>(9.53 ± 0.09) x 10⁻¹₀</td>
<td>4.981 ± 0.003</td>
<td>9.60 ± 0.04</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>(9.71 ± 0.09) x 10⁻⁸</td>
<td>5.06 ± 0.01</td>
<td>9.56 ± 0.03</td>
</tr>
<tr>
<td>α-Al(OH)₃</td>
<td>(9.572 ± 0.005) x 10⁻⁹</td>
<td>5.13 ± 0.02</td>
<td>9.12 ± 0.05</td>
</tr>
<tr>
<td>α-Al(OH)₃</td>
<td>(9.967 ± 0.004) x 10⁻⁹</td>
<td>10.21 ± 0.04</td>
<td>8.90 ± 0.10</td>
</tr>
<tr>
<td>α-Al(OH)₃</td>
<td>(9.787 ± 0.008) x 10⁻⁹</td>
<td>10.29 ± 0.07</td>
<td>10.70 ± 0.04</td>
</tr>
<tr>
<td>α-Al(OH)₃</td>
<td>(9.909 ± 0.004) x 10⁻⁹</td>
<td>10.20 ± 0.04</td>
<td>7.69 ± 0.12</td>
</tr>
<tr>
<td>α-Al(OH)₃</td>
<td>(9.782 ± 0.006) x 10⁻⁹</td>
<td>29.66 ± 0.16</td>
<td>9.17 ± 0.10</td>
</tr>
<tr>
<td>α-Al(OH)₃</td>
<td>(9.96 ± 0.18) x 10⁻⁸</td>
<td>5.60 ± 0.01</td>
<td>9.54 ± 0.04</td>
</tr>
<tr>
<td>α-Al(OH)₃</td>
<td>(9.42 ± 0.07) x 10⁻¹₀</td>
<td>5.149 ± 0.009</td>
<td>9.66 ± 0.06</td>
</tr>
<tr>
<td>γ-Al(OH)₃</td>
<td>(8.98 ± 0.04) x 10⁻⁹</td>
<td>66.26 ± 0.22</td>
<td>10.67 ± 0.04</td>
</tr>
<tr>
<td>γ-Al(OH)₃</td>
<td>(9.02 ± 0.05) x 10⁻⁹</td>
<td>34.14 ± 0.32</td>
<td>9.59 ± 0.05</td>
</tr>
<tr>
<td>γ-Al(OH)₃</td>
<td>(9.00 ± 0.02) x 10⁻⁹</td>
<td>169.7 ± 1.5</td>
<td>9.59 ± 0.06</td>
</tr>
<tr>
<td>γ-Al(OH)₃</td>
<td>(8.93 ± 0.07) x 10⁻⁹</td>
<td>66.11 ± 0.24</td>
<td>9.59 ± 0.03</td>
</tr>
<tr>
<td>γ-Al(OH)₃</td>
<td>(8.87 ± 0.06) x 10⁻⁹</td>
<td>66.17 ± 0.14</td>
<td>7.67 ± 0.24</td>
</tr>
<tr>
<td>γ-Al(OH)₃</td>
<td>(9.11 ± 0.08) x 10⁻¹⁰</td>
<td>169.8 ± 0.5</td>
<td>9.67 ± 0.09</td>
</tr>
<tr>
<td>γ-Al(OH)₃</td>
<td>(1.01 ± 0.02) x 10⁻⁷</td>
<td>169.2 ± 0.5</td>
<td>9.58 ± 0.02</td>
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</tbody>
</table>
Figure C.1. The fraction of neptunium sorbed over time for bayerite (A-C), γ-Al₂O₃ (E-G), and gibbsite (H-J). The specific experimental conditions are in Table C.1.
TABLE C.2.
LINEAR AND NON-LINEAR PSEUDO-FIRST ($k_1$) AND SECOND ORDER ($k_2$) RATE CONSTANTS, $R^2$, DEGREES OF FREEDOM, AND P-VALUES OF CORUNDUM ($\alpha$-Al$_2$O$_3$), $\Gamma$-Al$_2$O$_3$, BAYERITE ($\alpha$-Al(OH)$_3$), AND GIBBSITE ($\Gamma$-Al(OH)$_3$)

<table>
<thead>
<tr>
<th>System</th>
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<th></th>
<th></th>
<th></th>
<th></th>
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<tr>
<td></td>
<td>$k_1$</td>
<td>$R^2$</td>
<td>df</td>
<td>$p$</td>
<td>$k_2$</td>
<td>$R^2$</td>
<td>df</td>
<td>$p$</td>
</tr>
<tr>
<td>$\alpha$-Al$_2$O$_3$ - 0.5 m$^2$/L pH 9.5 10$^{-8}$ M Np</td>
<td>2.89 ± 0.63</td>
<td>0.913</td>
<td>3</td>
<td>1.78E-01</td>
<td>3.08 ± 0.23</td>
<td>0.989</td>
<td>3</td>
<td>1.06E-01</td>
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<tr>
<td>$\alpha$-Al$_2$O$_3$ - 1 m$^2$/L pH 9.5 10$^{-8}$ M Np</td>
<td>2.57 ± 0.91</td>
<td>0.799</td>
<td>3</td>
<td>6.83E-01</td>
<td>5.85 ± 0.31</td>
<td>0.995</td>
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<td>1.56E-01</td>
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<tr>
<td>$\alpha$-Al$_2$O$_3$ - 5 m$^2$/L pH 9.5 10$^{-8}$ M Np</td>
<td>0.75 ± 0.16</td>
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<td>$\alpha$-Al$_2$O$_3$ - 5 m$^2$/L pH 10.5 10$^{-8}$ M Eu</td>
<td>0.93 ± 0.14</td>
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<td>$\alpha$-Al$_2$O$_3$ - 5 m$^2$/L pH 7.5 10$^{-8}$ M Eu</td>
<td>2.69 ± 0.92</td>
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<td>5.46 ± 1.06</td>
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<td>$\alpha$-Al$_2$O$_3$ - 5 m$^2$/L pH 9.5 10$^{-8}$ M Eu</td>
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<td>0.976</td>
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<td>6.23E-02</td>
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<td>$\alpha$-Al$_2$O$_3$ - 5 m$^2$/L pH 9.5 10$^{-8}$ M Eu</td>
<td>0.48 ± 0.18</td>
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<td>2</td>
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<td>9.79 ± 1.47</td>
<td>0.999</td>
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<td>5.33E-02</td>
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<td>$\gamma$-Al$_2$O$_3$ - 50 m$^2$/L pH 9.5 10$^{-8}$ M Np</td>
<td>2.64 ± 0.23</td>
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<td>2.69 ± 1.19</td>
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<td>$\gamma$-Al$_2$O$_3$ - 5 m$^2$/L pH 10.5 10$^{-8}$ M Np</td>
<td>1.29 ± 0.06</td>
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<td>1.76 ± 0.57</td>
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<td>$\gamma$-Al$_2$O$_3$ - 5 m$^2$/L pH 7.5 10$^{-8}$ M Np</td>
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<td>7.34 ± 0.18</td>
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<td>1.11± 0.21</td>
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<td>1.49 ± 0.32</td>
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<td>9.65 ± 2.23</td>
<td>1</td>
<td>3</td>
<td>4.91E-02</td>
</tr>
<tr>
<td>System</td>
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<td>R^2</td>
<td>df</td>
<td>p</td>
<td>k_2</td>
<td>R^2</td>
<td>df</td>
<td>p</td>
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</tr>
<tr>
<td>α-Al(OH)_3 – 10 m^2/L pH 9 10^{-8}M Np</td>
<td>0.64 ± 0.05</td>
<td>0.975</td>
<td>5</td>
<td>1.19E-04</td>
<td>8.81 ± 2.04</td>
<td>1</td>
<td>5</td>
<td>1.24E-02</td>
</tr>
<tr>
<td>α-Al(OH)_3 – 10 m^2/L pH 10.5 10^{-8}M Np</td>
<td>2.28 ± 0.26</td>
<td>0.987</td>
<td>3</td>
<td>4.10E-02</td>
<td>41.9 ± 11.4</td>
<td>1</td>
<td>3</td>
<td>6.69E-02</td>
</tr>
<tr>
<td>α-Al(OH)_3 – 10 m^2/L pH 7.5 10^{-8}M Np</td>
<td>0.48 ± 0.11</td>
<td>0.908</td>
<td>3</td>
<td>6.91E-02</td>
<td>7.05 ± 6.78</td>
<td>0.989</td>
<td>4</td>
<td>3.14E-01</td>
</tr>
<tr>
<td>α-Al(OH)_3 – 30 m^2/L pH 9 10^{-8}M Np</td>
<td>14.62 ± 0.02</td>
<td>0.996</td>
<td>4</td>
<td>1.65E-06</td>
<td>55.99 ± 0.44</td>
<td>0.996</td>
<td>5</td>
<td>6.52E-01</td>
</tr>
<tr>
<td>α-Al(OH)_3 – 5 m^2/L pH 9 10^{-9}M Np</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Al(OH)_3 – 5 m^2/L pH 9 10^{-8}M Np</td>
<td>0.50 ± 0.09</td>
<td>0.937</td>
<td>3</td>
<td>1.40E-02</td>
<td>-4.30 ± 0.11</td>
<td>0.997</td>
<td>3</td>
<td>3.90E-01</td>
</tr>
<tr>
<td>γ-Al(OH)_3 – 66 m^2/L pH 10.5 10^{-8}M Np</td>
<td>5.89 ± 0.29</td>
<td>0.995</td>
<td>3</td>
<td>6.13E-02</td>
<td>27.63 ± 0.12</td>
<td>0.998</td>
<td>4</td>
<td>3.87E-04</td>
</tr>
<tr>
<td>γ-Al(OH)_3 – 34 m^2/L pH 9.5 10^{-8}M Np</td>
<td>2.85 ± 0.38</td>
<td>0.983</td>
<td>2</td>
<td>8.67E-01</td>
<td>3.81 ± 0.02</td>
<td>0.994</td>
<td>3</td>
<td>9.65E-03</td>
</tr>
<tr>
<td>γ-Al(OH)_3 – 170 m^2/L pH 9.5 10^{-8}M Np</td>
<td>4.325 ± 0.309</td>
<td>0.985</td>
<td>4</td>
<td>9.26E-03</td>
<td>88.06 ± 1.52</td>
<td>1</td>
<td>4</td>
<td>7.21E-03</td>
</tr>
<tr>
<td>γ-Al(OH)_3 – 66 m^2/L pH 9.5 10^{-8}M Np</td>
<td>4.77 ± 1.30</td>
<td>0.931</td>
<td>2</td>
<td>4.73E-01</td>
<td>22.55 ± 0.23</td>
<td>0.998</td>
<td>3</td>
<td>8.07E-02</td>
</tr>
<tr>
<td>γ-Al(OH)_3 – 66 m^2/L pH 7.5 10^{-8}M Np</td>
<td>2.40 ± 0.23</td>
<td>0.991</td>
<td>2</td>
<td>1.04E-01</td>
<td>6.95 ± 0.80</td>
<td>0.987</td>
<td>2</td>
<td>1.28E-01</td>
</tr>
<tr>
<td>γ-Al(OH)_3 – 170 m^2/L pH 9.5 10^{-8}M Np</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Al(OH)_3 – 170 m^2/L pH 9.5 10^{-7}M Np</td>
<td>0.681 ± 0.050</td>
<td>0.995</td>
<td>2</td>
<td>6.73E-02</td>
<td>2.76 ± .076</td>
<td>0.998</td>
<td>3</td>
<td>9.19E-02</td>
</tr>
</tbody>
</table>
Figure C.2. Pseudo-first (left) and second (right) order linear rate equations for $10^{-8}$ M Np(V) sorption to $5 \text{ m}^2\text{L}^{-1} \gamma$-Al$_2$O$_3$ at pH 9.5 (■), 170 m$^2$·L$^{-1}$ gibbsite at pH 9.5 (▲), and 10 m$^2$·L$^{-1}$ bayerite at pH 6 (●).
Figure C.3. Non-linear pseudo-first order (PFO) and pseudo-second order (PSO) model fits to experimental data collected from systems containing $10^{-8}$ Np(V) and 5 m$^2$·L$^{-1}$ $\gamma$-Al$_2$O$_3$ at pH 9.5 (■), 170 m$^2$·L$^{-1}$ gibbsite at pH 9.5 (▲), and 10 m$^2$·L$^{-1}$ bayerite at pH 9 (●).
Figure C.4. (A) Dependence of log $k_2$ on log [gibbsite] at pH 9.5 and $10^{-9}$ M Np(V). (B) Dependence of log $k_2$ on log [H$^+$] at 67 m$^2$L$^{-1}$ gibbsite and $10^{-9}$ M Np(V).
TABLE C.3.

PSUEDO-SECOND ORDER REACTION RATES ($k_2$) OF NEPTUNIUM

DESORPTION FROM GIBBSITE, BAYERITE, AND $\gamma$-ALUMINA DETERMINED

USING THE NON-LINEAR FORM OF THE PSEUDO-SECOND ORDER RATE EQUATION

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mineral (m$^2$·L$^{-1}$)</th>
<th>Neptunium (M)</th>
<th>pH</th>
<th>$k_2$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gibbsite</td>
<td>333.0 ± 0.7</td>
<td>(4.67 ± 0.12) x 10$^{-9}$</td>
<td>9.20 ± 0.07</td>
<td>309.15</td>
<td>0.979</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>330.0 ± 1.0</td>
<td>(3.83 ± 0.91) x 10$^{-9}$</td>
<td>6.51 ± 0.19</td>
<td>60.95</td>
<td>0.275</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>331.0 ± 1.2</td>
<td>(4.63 ± 0.14) x 10$^{-9}$</td>
<td>4.88 ± 0.24</td>
<td>7.99</td>
<td>-11.14</td>
</tr>
<tr>
<td>Bayerite</td>
<td>32.83± 0.09</td>
<td>(7.78 ± 0.15) x 10$^{-9}$</td>
<td>6.41 ± 0.05</td>
<td>25.23</td>
<td>-0.027</td>
</tr>
<tr>
<td>Bayerite</td>
<td>32.90 ± 0.04</td>
<td>(7.78 ± 0.12) x 10$^{-9}$</td>
<td>7.38 ± 0.09</td>
<td>64.32</td>
<td>0.738</td>
</tr>
<tr>
<td>Bayerite</td>
<td>32.90 ± 0.04</td>
<td>(7.75 ± 0.13) x 10$^{-9}$</td>
<td>9.59 ± 0.12</td>
<td>267.85</td>
<td>0.867</td>
</tr>
<tr>
<td>$\gamma$-alumina</td>
<td>50.64 ± 0.08</td>
<td>(7.48 ± 0.07) x 10$^{-9}$</td>
<td>6.40 ± 0.08</td>
<td>1.886</td>
<td>-1.07</td>
</tr>
<tr>
<td>$\gamma$-alumina</td>
<td>50.54 ± 0.15</td>
<td>(7.35 ± 0.08) x 10$^{-9}$</td>
<td>7.83 ± 0.28</td>
<td>6.317</td>
<td>0.863</td>
</tr>
<tr>
<td>$\gamma$-alumina</td>
<td>50.70 ± 0.06</td>
<td>(8.03 ± 0.05) x 10$^{-9}$</td>
<td>9.81 ± 0.06</td>
<td>996.62</td>
<td>0.394</td>
</tr>
</tbody>
</table>
Figure C.5. Neptunium desorption from bayerite at one week and two months. Error bars represent the error propagated from the uncertainty in ICP-MS and gravimetric measurements.
APPENDIX D:
SUPPORTING INFORMATION FOR CHAPTER 5

TABLE D.1.
EXPERIMENTAL PARAMETERS OF PLUTONIUM SORPTION TO GIBBSITE
AND BAYERITE EXPERIMENTS

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Plutonium Concentration (M)</th>
<th>Mineral Concentration (m2/L)</th>
<th>pH at 5 days</th>
<th>pH at 10 days</th>
<th>pH at 17 days</th>
<th>pH at 28 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bayerite</td>
<td>(5.31 ± 0.18) x 10^-10</td>
<td>5.827 ± 0.002</td>
<td>4.90</td>
<td>4.99</td>
<td></td>
<td>5.03</td>
</tr>
<tr>
<td></td>
<td>(5.48 ± 0.18) x 10^-10</td>
<td>5.852 ± 0.002</td>
<td>6.32</td>
<td>5.97</td>
<td>5.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(5.38 ± 0.18) x 10^-10</td>
<td>5.760 ± 0.002</td>
<td>7.15</td>
<td>6.92</td>
<td>6.83</td>
<td>6.89</td>
</tr>
<tr>
<td></td>
<td>(5.46 ± 0.18) x 10^-10</td>
<td>5.806 ± 0.002</td>
<td>8.37</td>
<td>7.23</td>
<td>7.20</td>
<td>7.33</td>
</tr>
<tr>
<td></td>
<td>(5.50 ± 0.18) x 10^-10</td>
<td>5.801 ± 0.002</td>
<td>9.67</td>
<td>9.48</td>
<td>9.48</td>
<td>9.17</td>
</tr>
<tr>
<td></td>
<td>(5.33 ± 0.18) x 10^-10</td>
<td>5.805 ± 0.002</td>
<td>10.43</td>
<td>10.25</td>
<td>10.31</td>
<td>10.18</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>(5.46 ± 0.18) x 10^-10</td>
<td>37.28 ± 0.01</td>
<td>5.53</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(5.45 ± 0.18) x 10^-10</td>
<td>37.52 ± 0.01</td>
<td>6.23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(5.46 ± 0.18) x 10^-10</td>
<td>37.40 ± 0.01</td>
<td>6.80</td>
<td>6.85</td>
<td>6.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(5.49 ± 0.18) x 10^-10</td>
<td>37.20 ± 0.01</td>
<td>7.81</td>
<td>7.26</td>
<td>7.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(5.44 ± 0.18) x 10^-10</td>
<td>37.57 ± 0.01</td>
<td>9.22</td>
<td>9.23</td>
<td>8.48</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(5.46 ± 0.18) x 10^-10</td>
<td>37.34 ± 0.01</td>
<td>10.22</td>
<td>10.25</td>
<td>10.25</td>
<td></td>
</tr>
</tbody>
</table>
Figure D.1. Flow chart showing the sampling procedure for the determination of the reaction order with respect to plutonium(V) concentration in the presence of aluminum (hydr)oxides.
Figure D.2. Aqueous oxidation state distribution of plutonium in the presence of bayerite at pH 10, pH 9, pH 8, and pH 7.
Figure D.3. Aqueous oxidation state distribution of plutonium in the presence of gibbsite at pH 10, pH 9, and pH 8.


Cantrell, K.J. Transuranic Contamination in Sediment and Groundwater at the U.S. DOE Hanford Site; PNNL-18640, **2009**.


Dzombak, D.A.; Morel, F.M.M. Surface Complexation Modeling: Hydrous Ferric Oxide; Wiley & Sons: New York, **1990**.


Hixon, A.E.; Arai, Y.; Powell, B.A.; Examination of the effect of alpha radiolysis on plutonium(V) sorption to quartz using multiple plutonium isotopes. *J. Colloid Interface Sci.*, 2013, 403, 105-112.


Karamalidis, A.K.; Dzombak, D.A. Surface Complexation Modeling: Gibbsite; Wiley & Sons: Hoboken, New Jersey, **2010**.


Kupcik, T.; Rabung, T.; Lützenkirchen, J.; Finck, N.; Geckeis, H. Macroscopic and spectroscopic investigations on Eu(III) and Cm(III) sorption onto bayerite (β-Al(OH)3) and corundum (α-Al2O3). *Colloid Interface Sci.* **2016**, *461*, 215-224.


