



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



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ABSTRACT

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 as a function of gibbsite (γ -Al(OH)₃), bayerite (α -Al(OH)₃), corundum (α -Al₂O₃), and γ -alumina (γ -Al₂O₃) concentration (2.5–30 m² L⁻¹), europium concentration (10⁻⁸–10⁻⁵ M), pH (3–12), and ionic strength (0.01–0.1 M NaCl). 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.

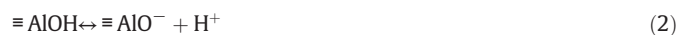
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1. Introduction

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 × 10⁶ TBq of radionuclides, including 1.80 TBq ²³⁷Np and 1.37 × 10³ TBq ²⁴¹Am (Smith et al., 2003); an estimated 1.06 × 10³ TBq ²⁴¹Am and 2.035 TBq ²³⁷Np 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., ²³⁷Np (t_{1/2} = 2.14 × 10⁶ 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 ²⁴¹Am decay to ²³⁷Np. 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., ≡AlOH, ≡Al₂OH, ≡Al₃OH, ≡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 (γ -Al(OH)₃), corundum (α -Al₂O₃), and γ -alumina (γ -Al₂O₃) and show that surface acidity follows the trend corundum > gibbsite > γ -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 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 pK_{a1} and pK_{a2} values shown in Table 1 are derived from reactions 1 and 2, respectively, and suggest that distinct sorption behavior should be observed for corundum, gibbsite, and γ -alumina.



Understanding the role of aluminum (hydr)oxide surface acidities is further complicated by the tendency of these minerals to undergo phase

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transformations in aqueous environments. In particular, γ -alumina slowly changes to gibbsite or bayerite (α -Al(OH)₃) 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 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 9.0×10^{-8} M– 3.1×10^{-5} M at constant solid concentration ($3.6 \text{ g} \cdot \text{L}^{-1}$) and ionic strength (0.1 M NaClO₄), 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 et al. (2012) report the formation of monodentate europium complexes with γ -alumina at pH 6. The formation of inner-sphere complexes is further supported by time-resolved laser fluorescence spectroscopy (TRLFS) measurements (Tan et al., 2008; Kupcik et al., 2016). 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 (NpO₂CO₃⁻) 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 prevailing carbonate concentrations, 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, ionic strength, 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. Materials and methods

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 (α -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. The minerals were also characterized using a Bruker D8 Advance Davinci pXRD (2 θ increments of 0.02 and a 7 second time step) to verify the purity of the mineral phases. Diffraction patterns are provided in the Supporting Information.

2.2. Batch hydration experimental conditions and methods

Phase transformations of γ -Al₂O₃ were monitored with batch hydration experiments. Suspensions of γ -Al₂O₃ ($1170.1 \pm 8.5 \text{ m}^2 \text{ L}^{-1}$) 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 (FT-IR) spectroscopy. 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^{-1} .

2.3. Neptunium and europium working solution preparation

To prepare the 1.098×10^{-6} M neptunium working solution, a small aliquot of a 2.467×10^{-5} M ²³⁷Np 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 ± 0.005 M europium working solution was prepared through dilution of a 1001 ± 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.

2.4. Batch sorption experimental conditions and methods

Batch experimental conditions are summarized in Table 3. All suspensions were prepared in 0.01–0.1 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 homogeneous 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

Table 1
pK_{a1} and pK_{a2} values (see reactions 1 and 2 in the main text) for corundum, gibbsite, and γ -alumina as reported by Yang et al. (2007).

Mineral	pK _{a1}	pK _{a2}
Corundum (α -Al ₂ O ₃)	6.03 ± 0.25	7.47 ± 0.42
Gibbsite (γ -Al(OH) ₃)	6.78 ± 0.4	10.10 ± 0.43
γ -Alumina (γ -Al ₂ O ₃)	8.50 ± 0.29	9.20 ± 0.52

Table 2
N₂(g)-BET surface areas of corundum, γ -alumina, bayerite, and gibbsite.

Mineral	Surface area (m ² g ⁻¹)
Corundum (α -Al ₂ O ₃)	4.80 ± 0.06
γ -Alumina (γ -Al ₂ O ₃)	58.10 ± 2.66
Bayerite (α -Al(OH) ₃)	9.49 ± 0.05
Gibbsite (γ -Al(OH) ₃)	64.47 ± 0.01

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