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# Sorption of Cm(III) and Gd(III) onto gibbsite, $\alpha$-Al(OH)$_3$: A batch and TRLFS study

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ABSTRACT

Gd(III) and Cm(III) sorption onto a pure aluminum hydroxide, gibbsite ($\alpha$-Al(OH)$_3$), is studied by batch experiments and time-resolved laser fluorescence spectroscopy (TRLFS). The experiments are conducted under argon atmosphere to exclude the influence of atmospheric $CO_2$ on solution and surface speciation. Batch experiments are done in two different electrolytes 0.1 M $NaClO_4$ and 0.1/0.01 M NaCl at a constant gibbsite concentration of 2.2 g/L. Gadolinium concentrations are varied from $6.4 \times 10^{-9}$ to $6.4 \times 10^{-5}$ M. pH-dependent sorption is found to be congruent at Gd(III) concentrations up to $6.4 \times 10^{-7}$ M and a shift of the pH edge to higher pH values is observed for higher metal ion concentrations. Type of background electrolyte anion and ionic strength do not affect the metal ion sorption. The spectroscopic investigations are performed with Cm(III) and gibbsite concentrations of $2 \times 10^{-7}$ M and 0.5 g/L, respectively. From the strongly red-shifted emission spectra two different inner-sphere surface complexes can be identified. A third species appearing at pH 6–11 is assigned to a coprecipitated or incorporated Cm(III) species. This incorporated species is most likely formed as a consequence of the applied experimental procedure. By continuously increasing the pH from 4 we move from high to low gibbsite solubility domains. As a result, aluminum hydroxide precipitates from oversaturated solutions, either covering already adsorbed curium or forming a Al/Cm(OH)$_3$ coprecipitate. Fluorescence lifetimes for the surface-bound Cm(III) complexes and the incorporated species are at 140–150 and 180–200 µs, respectively. Emission bands of the Cm(III) gibbsite surface complexes appear at comparable wavelengths as reported for Cm(III) species bound to aluminum oxides, e.g., $\gamma$-Al$_2$O$_3$; however, lifetimes are longer. This could presumably arise from either shorter binding distances of the Cm to Al–O sites or a coordination to more surface sites.

## 1. Introduction

Deep geological clay and bedrock formations are considered appropriate for the final disposal of nuclear waste. Scenarios assuming accidental groundwater inflow to the repository must take into account the release of radionuclides into the geosphere. Radionuclide retention or retardation can take place via various solid–solute interaction mechanisms. For nuclear safety assessment it is therefore imperative to understand the chemistry behind radionuclide reactions at the groundwater–mineral interface, including characterization of the surface species and determination of involved mechanisms. The long-term radiotoxicity of nuclear waste is dominated mainly by the transuranium elements. The prevailing geochemical conditions in the repository dictate their speciation and thus their mobility. Under the reducing conditions of deep geological formations, actinides are usually found in their reduced oxidation states III and/or IV.

Extensive studies of metal ion sorption on different aluminum oxides/hydroxides have been performed [1–5]. Pure aluminum oxides/hydroxides are rare in nature, but these minerals contain reactive aluminol groups also present at the surfaces of aluminosilicates which are abundant in natural systems. Furthermore, aluminum oxides/hydroxides display similar mineralogical structures as iron oxides/hydroxides and can thus be used as models for these iron-containing minerals, which are not transparent for visible light and therefore not suitable for investigation by a variety of spectroscopic studies such as Time-Resolved Laser Fluorescence Spectroscopy (TRLFS). The reactivity of aluminol groups differs with varying atomic arrangements on the mineral surface, leading to slightly different metal ion sorption behavior on different aluminum oxides/hydroxides. In aqueous solutions the surfaces of suspended oxides are hydrated, and surface transformations of oxides like $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ have been reported [6–8]. Investigations on $\gamma$-alumina show a surface transformation into bayerite,

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$\beta$-Al(OH)$_3$ [6,7], a secondary phase formation that presumably changes the reactivity of the mineral surface. A similar secondary phase formation has been reported for $\alpha$-alumina, where a surface transformation into bayerite or gibbsite, $\alpha$-Al(OH)$_3$, has been observed [8,9]. The aim of this work is to study trivalent metal ion sorption onto a pure aluminum hydroxide. For this purpose the mineral gibbsite was chosen. As noted before, gibbsite forms at the $\alpha$-alumina/water interface and is thermodynamically more stable in aqueous solution than the corresponding aluminum oxides. Results from previous work by Rabung et al. [10,11] and Stumpf et al. [12], where the sorption of trivalent actinides onto both $\alpha$- and $\gamma$-alumina has been investigated, are compared with the findings of the present study. Curium is a minor actinide element in the nuclear waste, but exhibits excellent fluorescent properties suitable for surface speciation investigation by means of TRLFS. It was therefore chosen in our experiments to represent trivalent actinides such as americium, which is far more abundant. Batch sorption studies were carried out with the trivalent lanthanide ion gadolinium, which is usually considered as a chemical homologue to curium and americium.

## 2. Materials and methods

### 2.1. Gibbsite—synthesis and characterization

The gibbsite used throughout this work was prepared through precipitation of Al(OH)$_3$ followed by subsequent dialysis of the suspension at 70 °C for a time span of 4 months. A 0.33 M aluminum chloride solution was titrated with 1 M NaOH until a pH value of 4.5, at which amorphous aluminum hydroxide precipitates. The precipitation was carried out in a glove box under argon atmosphere (O$_2$ $<1$ ppm) to eliminate possible contamination by atmospheric CO$_2$. The aluminum hydroxide precipitate was dialyzed against deionized water (MilliQ) at a temperature of 70 °C. Water exchange was done every day for the first four weeks, and 2–3 times per week for another 3 months. The pH and solid content of the final suspension were 4.2 and $41.9 \pm 1$ g/L, respectively. Gibbsite particles are shaped as hexagonal platelets, with predominant basal plane contribution to overall surface area, and comparatively small edge planes, Figs. 1a and 1b. The diameter and height of these particles were determined with atomic force microscopy, AFM, and N$_2$-BET analysis was done to evaluate the specific surface area of the mineral. Mineralogical purity and surface composition were examined with XRD (Bruker D8Advance) and X-ray photoelectron spectroscopy, XPS, respectively. To determine the isoelectric point, IEP of the mineral, i.e., the pH value at which the net surface charge equals zero, $\zeta$-potential measurements (Zeta Plus, Zeta Potential Analyser, Brookhaven Instruments Corporation) were performed in 0.1/0.01 M NaClO$_4$ and MilliQ water. The gibbsite suspension was diluted in the three different media to a final concentration of 1 g/L. pH adjustments were done from 4.95 to approximately 12 with NaOH.

For studies requiring solid gibbsite samples or freshly resuspended gibbsite, a fraction of the synthesized gibbsite batch was freeze-dried.

### 2.2. Batch sorption experiments

Batch sorption experiments were conducted in a glove box under argon atmosphere (O$_2$ $<1$ ppm) to exclude atmospheric CO$_2$ which influences the solution speciation of trivalent actinides through the formation of carbonate species at pH values above 6 [13] that may adsorb onto gibbsite. All reagents were prepared in the glove box and MilliQ water was stored in an open bottle inside the glove box to minimize the CO$_2$ content prior to use. Gadolinium sorption onto gibbsite was investigated as a function of pH in different electrolytes and ionic strengths (0.1 M NaClO$_4$ and 0.1/0.01 M NaCl). The gibbsite concentration was fixed to 2.2 g/L in each batch, while the Gd$^{3+}$ concentration was varied between $6.4 \times 10^{-9}$ and $6.4 \times 10^{-5}$ M. pH adjustments were done in small steps by addition of CO$_2$-free NaOH. The sample solutions were shaken periodically for 3–7 days to reach sorption equilibrium. After the equilibration time the samples were centrifuged at 18,000 rpm and the aluminum and gadolinium concentrations were analyzed in the supernatant by ICP-MS.

### 2.3. TRLFS study

Samples for TRLFS measurements were prepared under the same conditions as the batch experiments. Two series of three parallel samples were prepared in 0.1 M NaClO$_4$ with gibbsite and curium concentrations of 0.5 g/L and $2 \times 10^{-7}$ M, respectively. For one series the stock gibbsite suspension was diluted directly in the electrolyte. Those experiments are referred to in the following text as “gibbsite suspension.” The other series was prepared by using freeze-dried gibbsite resuspended in the electrolyte (referred to as “freeze-dried gibbsite I”). For comparison experiments were performed with another freeze-dried gibbsite (referred to as “freeze-dried gibbsite II”) previously characterized by Mitchell [14]. Suspensions were shaken periodically for 2–3 days to reach sorption equilibrium. The TRLFS measurements were performed with a pulsed Nd:YAG pumped dye laser system (Continuum, Powerlite, ND 6000, laser dye; Exalite 398). The Cm(III) fluorescence emission was detected using an optical multichannel analyzer consisting of a polychromator (Chromex 250) with a 1200 lines/mm grating. The emission spectra were recorded in the range 580–620 nm, 1 µs after the exciting laser pulse in a time window of 1 ms. The excitation wavelength used was 396.6 nm. For the lifetime measurements the time delay between the laser pulse and the camera gating was scanned between 1 and 1200 µs in intervals of 10–15 µs. The laser pulse energy, controlled by a photodiode, was between 2.5 and 3.5 mJ during all measurements.

## 3. Results

### 3.1. Gibbsite—synthesis and characterization

The XRD study showed the mineralogical purity and crystalline character of the synthetic bulk gibbsite. The analysis of the gibbsite surface composition with XPS revealed the presence of small amounts of chloride (0.16% of total atomic concentration) originating from the use of AlCl$_3$ for synthesis. As the gibbsite surface is positively charged under stock suspension conditions (pH 4.2) the presence of the respective amounts of Cl$^-$ is expected. The aluminum to oxygen ratio was analyzed from the peak intensities in the XPS spectrum, and was determined to be 0.329, in very good agreement with the theoretical value of 0.333. The gibbsite particle diameter and height assessed from 25 particles in the AFM survey were $250 \pm 60$ and $16.8 \pm 10.4$ nm, respectively. The specific surface area of the platelets was determined to be 49.5 m$^2$/g. The pH value 11.0 was obtained for the IEP of gibbsite. Respective pH-dependent $\zeta$-potential data are shown in Fig. 2.

### 3.2. Gadolinium sorption onto gibbsite

Figs. 3 and 4 present data for pH-dependent fraction of sorbed Gd (%) and $\log K_d$ vs pH, respectively, for Gd concentrations ranging from $6.4 \times 10^{-9}$ to $6.4 \times 10^{-5}$ M in 0.1 M NaClO$_4$. pH curves are congruent at Gd concentrations up to $6.4 \times 10^{-7}$ M. Uptake starts above pH 5.5 and is complete at around pH 7.5. At metal ion concentrations of $6.4 \times 10^{-6}$ and $6.4 \times 10^{-5}$ M a shift of the pH curve to higher pH values occurs and complete sorption is attained at