

Macroscopic and spectroscopic investigations on Eu(III) and Cm(III) sorption onto bayerite (β -Al(OH)₃) and corundum (α -Al₂O₃)



Tomas Kupcik^{a,*}, Thomas Rabung^a, Johannes Lützenkirchen^a, Nicolas Finck^a, Horst Geckeis^a, Thomas Fanghänel^{b,c}

^a Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, P.O. Box 3640, 76021 Karlsruhe, Germany

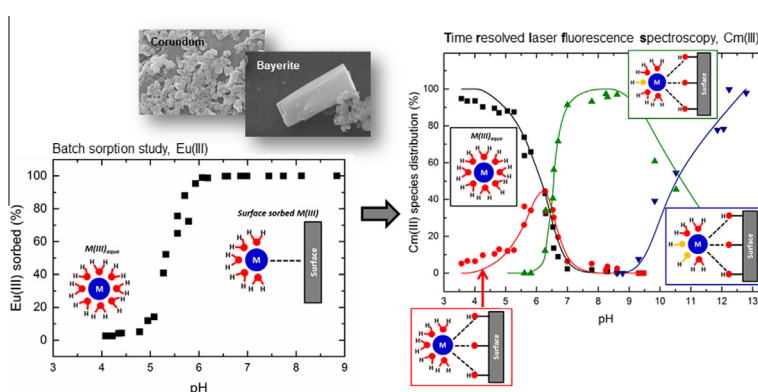
^b University of Heidelberg, Institute of Physical Chemistry, Im Neunheimer Feld 253, 69120 Heidelberg, Germany

^c Joint Research Centre – JRC, Rue du Champs de Mars 21, 1050 Brussels, Belgium

HIGHLIGHTS

- Sorption studied by macroscopic (batch sorption) and microscopic (TRLFS) techniques.
- Similar pH dependent sorption behaviour at trace metal ion concentrations.
- Surface transformation of the oxide surface into an hydroxidic structure.
- Metal ion sorption via singly coordinated aluminol groups.

GRAPHICAL ABSTRACT



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ABSTRACT

The interaction of trivalent Cm and Eu with the aluminum hydroxide bayerite (β -Al(OH)₃) and the aluminum oxide corundum (α -Al₂O₃) was investigated by batch sorption experiments and time resolved laser fluorescence spectroscopy (TRLFS). The experimental methods for both polymorphs show similar pH dependent sorption behavior at trace metal ion concentrations ($\sim 10^{-7}$ M), i.e. similar Eu sorption edges and nearly identical Cm speciation between pH = 3 and 13. In this pH range the Cm aquo ion as well as the Cm(III) surface species $surface \cdot \cdot Cm(OH)_x(H_2O)_{5-x}$ ($x = 0, 1, 2$) can be distinguished by TRLFS. The similar sorption data point to a (surface) transformation of the thermodynamically unstable Al₂O₃ surface into bayerite, in agreement with the similar isoelectric points obtained for both minerals ($pH_{IEP} = 8.6$ – 8.8). The pH dependent surface charge is most likely due to the protonation/deprotonation of singly coordinated Al–OH surface groups, prevailing on the edge planes of the rod-like bayerite crystals and the surface of the colloidal Al₂O₃ particles. These surface groups are also believed to act as ligands for lanthanide/actinide(III) surface complexation. In contrast to the similar sorption behavior at trace metal ion concentrations, discrepancies are observed at higher Eu levels. While similar sorption edges occur up to 7×10^{-7} M Eu for corundum, the pH edge on bayerite is gradually shifted to higher pH values in this Eu concentration range. The latter behavior may be related either to the existence of multiple sorption sites

* Corresponding author at: Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology (KIT), Postfach 36 40, D-76021 Karlsruhe, Germany.

E-mail addresses: tomas.kupcik@kit.edu (T. Kupcik), thomas.rabung@kit.edu (T. Rabung), johannes.luetzenkirchen@kit.edu (J. Lützenkirchen), nicolas.finck@kit.edu (N. Finck), horst.geckeis@kit.edu (H. Geckeis), Thomas.Fanghaenel@ec.europa.eu (T. Fanghänel).

with different sorption affinities, or to the influence of an additional amorphous Al-phase, forming in the course of the bayerite synthesis.

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1. Introduction

Fundamental knowledge of the parameters controlling the interaction of aquatic species with mineral surfaces is crucial for assessing the fate of pollutants in geosystems. In this respect, the chemical nature and reactivity of mineral/water interfaces are decisive for the retention of metal ions. Frequently α -Al₂O₃ (corundum) and γ -Al₂O₃ have been taken as model minerals for the investigation of metal ion sorption at variable metal ion concentration and pH [1–5]. Even though pure aluminum oxides are not very abundant in nature, reactions with aluminol groups are thought to be relevant for natural systems. They exist at surfaces of aluminosilicates and their alteration products which are present in soil and subsoil environments [6,7]. Especially the secondary minerals of aluminosilicates belonging to the clay group are known to be highly efficient in metal ion retention [8,9]. In addition, aluminum oxides hold as isomorphous model phases for ferric oxides/hydroxides, known for their strong sorptive properties in geosystems. Aluminum oxides are available as high purity solids with well-defined crystal cuts so that their crystal/solution interface can be studied in great detail.

The structure of corundum and the aluminum hydroxides gibbsite (α -Al(OH)₃) and bayerite (β -Al(OH)₃) consists of hexagonal close packed layers of AlO₆ octahedra, where 2/3 of the octahedral sites are occupied by Al atoms. In the case of corundum, the aluminum atoms are slightly displaced toward the free octahedral sites, thus lie slightly above and below the mid-plane between the oxygen layers. In contrast, the aluminum atoms are located directly in the mid-plane of the adjacent oxygen layers for the aluminum hydroxides, with a hydrogen attached to each oxygen forming a hydroxyl ion. A structural difference is apparent for γ -Al₂O₃, where Al is also located in tetrahedrally coordinated interstitial sites (AlO₄) [10,11].

Investigations with aluminum oxides are complicated by their instability with regard to dissolution and secondary phase formation when in contact with aqueous solution for more than 10 h [12]. The thermodynamically more stable gibbsite (α -Al(OH)₃) appears to form predominantly in the acidic pH range, while bayerite (β -Al(OH)₃) forms as a kinetically favoured phase at near-neutral pH and above. Lee and Condrate [13] observed the presence of a mixture of gibbsite and bayerite on α -Al₂O₃ in an aqueous solution using diffuse reflectance Fourier transformed infrared (DR-FTIR) spectroscopy. In the case of aged γ -Al₂O₃ suspensions, the surface is transformed into bayerite as indicated by acid-base and dissolution rate measurements [14], Raman spectroscopy and X-ray diffraction [14,15], as well as Fourier transformed infrared (FTIR) spectroscopy [15–17]. Based on the results of Lefèvre et al. [14], surface transformation is characterized by an induction period of about four days with the formation of a transient amorphous hydrated phase, after which the bayerite content increases until it levels off after two months. Gibbsite was not found by these authors, indicating that under a wide pH range bayerite is a kinetically stabilized polymorph being formed in aqueous suspensions.

Different types of surface groups are present in different ratios on the surfaces of the crystalline aluminum oxides and hydroxides. Bayerite crystals appear as rods usually well developed in *z* direction, which yields a strong contribution from 010 and 100 faces

[18]. On these crystal planes, singly and doubly coordinated aluminum groups can be found, i.e. the surface hydroxyl is bound to one (Al–OH) or two Al atoms (Al₂–OH) of the solid structure. As the latter are “set deeper in the surface”, they are believed to be sterically hindered and therefore less reactive [11]. In contrast, only doubly coordinated aluminum groups exist on the ideal 001 basal plane. In the case of crystalline α - and γ -Al₂O₃, triply coordinated Al₃–OH entities may also occur on the hydroxylated surfaces [19]. However, spherical aluminum oxide powders consist of edges, steps, vacancies and defect sites and are composed of a high fraction of singly coordinated aluminum groups [11].

As indicated above, there is a structural difference between the latter minerals, in that effect that also tetrahedrally coordinated Al is present in γ -Al₂O₃. Due to the lower coordination compared to the AlO₆, these sites are assumed to have a different reactivity. However, as γ -Al₂O₃ is, at least superficially, transformed into an hydroxidic structure [14–16], these sites are not relevant for metal ion sorption.

Which specific types of surface aluminol moieties act as coordinating surface ligands to bind metal ions still appears to be under debate (see. e.g. [19,20], or [21] for the case of Pb(II) adsorption). Their affinities toward metal ion sorption is to some extent related to the reactivity of the respective aluminol sites with regard to protonation/deprotonation. As a result of experiments and modeling, the coordination of surface oxygen groups to Al-atoms in the crystal structure is believed to mainly determine the acidity of the aluminol groups. The singly and triply coordinated aluminol groups are charged and/or proton reactive over a broad pH range [18], the corundum (001) plane (as the isomorphous bayerite and gibbsite basal plane) exclusively exposes doubly coordinated hydroxyl groups and is expected to be uncharged and of low reactivity. However, an unexpected pH dependent charge has been observed and mono- and divalent ions appear to adsorb on this crystal plane [22,23]. The doubly coordinated hydroxyl groups on gibbsite basal planes were also postulated to be proton active with pK_a values around 4–5.2 [24–26], in line with a pH_{IEP} at about 4–5 observed by streaming potential measurements on the corundum (001) plane [23]. Moreover, surface roughness, or steric aspects concerning the ordering of surface functional groups at the crystal plane might as well play a significant role for hydrated metal cation sorption as the structure of surface bound water layers [27] and crystal imperfections [28].

The aim of the present work is to apply a comprehensive approach combining classical batch sorption experiments with spectroscopy in order to provide insight into surface speciation of metal ions on model mineral phases, acting as surrogates for naturally occurring minerals (e.g. clays or iron oxides). Hence, trivalent metal ion sorption onto corundum (present work) and γ -alumina [29,30] is compared to the secondary polymorph bayerite (β -Al(OH)₃) in order to identify differences and similarities. We focus on trivalent metal ions such as lanthanide and actinide ions, which strongly adsorb on metal oxide surfaces. Notably the actinide ions are of specific interest in the context of radionuclide behavior in nuclear waste disposal systems. The present study covers wet chemistry (batch sorption studies with the lanthanide Eu) and spectroscopic investigations (using time resolved laser fluorescence spectroscopy (TRLFS) with the actinide Cm as a fluorescent probe) on corundum and bayerite. The latter yields spectroscopic

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