

**Sorption competition and kinetics of trivalent cations (Eu, Y and Cm) on corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>): a batch sorption and TRLFS study**

Virtanen, S.; Meriläinen, S.; Eibl, M.; Rabung, T.; Huittinen, N.;

Originally published:

May 2018

**Applied Geochemistry 92(2018), 71-81**

DOI: <https://doi.org/10.1016/j.apgeochem.2018.02.011>

Perma-Link to Publication Repository of HZDR:

<https://www.hzdr.de/publications/Publ-26331>

Release of the secondary publication  
on the basis of the German Copyright Law § 38 Section 4.

CC BY-NC-ND

## Sorption competition and kinetics of trivalent cations (Eu, Y and Cm) on corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>): a batch sorption and TRLFS study

S. Virtanen<sup>1</sup>, S. Meriläinen<sup>1</sup>, M. Eibl<sup>2</sup>, T. Rabung<sup>3</sup>, J. Lehto<sup>1</sup> and N. Huittinen<sup>2</sup>

<sup>1</sup>Department of Chemistry - Radiochemistry, University of Helsinki, P.O. Box 55, 00014 University of Helsinki, Finland

<sup>2</sup>Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, Bautzner Landstrasse 400, 01328 Dresden, Germany

<sup>3</sup>Institut für Nukleare Entsorgung, Karlsruhe Institute of Technology, P.O. Box 3640, 76021 Karlsruhe, Germany

### Abstract

In this study we have combined batch sorption and laser spectroscopic investigations to study the sorption of Eu(III) and Cm(III), on the aluminum oxide corundum in single- and multi-metal systems. Experiments were performed using a constant equilibrium time as a function of pH (pH-edges) or at constant pH as a function of equilibrium time (kinetic experiments) in 0.01 M NaClO<sub>4</sub> and carbonate free conditions. The objective was to investigate how the sorption behavior of trivalent actinides and lanthanides is affected by the presence of another trivalent metal, Y(III). Our hypothesis was that the addition of higher concentrations of trivalent Y(III) together with a chemically similar trivalent metal, Eu(III) or Cm(III), would affect the sorption behavior of that metal. Batch experiments show that when the concentration of competing Y(III) is high enough ( $1 \times 10^{-4}$  M) to occupy most of the surface sites, there is a clear shift in the position of the Eu(III) pH-edge to higher pH. Spectroscopic

studies using time-resolved laser fluorescence spectroscopy (TRLFS) clearly confirm sorption competition between the trivalent metals Cm(III) and Y(III), but they also indicate a change in the surface speciation of the trivalent actinide in the presence of the competing metal if the concentration of that competing metal is high enough.

Keywords: Sorption competition, Eu(III), Cm(III), Y(III), TRLFS, corundum,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>

## 1 Introduction

Sorption onto immobile, solid surfaces is an important factor limiting the mobility of heavy metals and radionuclides in the environment. The uptake of a contaminant by a solid surface is usually reported as the sorption percentage or the sorption distribution coefficient ( $K_d$  or  $R_d$ ) at a given pH value, where high sorption percentages or  $K_d$ -values correspond to a high removal of the contaminant from the aqueous phase. Such uptake studies, determining the degree of sorption of hazardous (for example toxic or radioactive) elements in the environment are often conducted under simplified experimental conditions considering a single element on a single solid phase at a time and projecting the obtained results on an environmental scale. In reality, conclusions about the mobility and the retention of metals onto mineral surfaces should be derived from experiments performed in more complex systems, where the uptake of a contaminant is investigated in the presence of other dissolved elemental or molecular species that may hinder or otherwise affect the uptake of the metal ion under consideration through e.g. complexation reactions in solution or sorption competition reactions on the solid surface.

Bradbury and Baeyens (2005) performed extensive investigations of the sorption competition between various metal cations on the clay mineral montmorillonite. By investigating the competition of metals with similar and dissimilar chemical behavior (e.g. tendency to hydrolysis and oxidation state), the authors concluded that metal cations with dissimilar chemical properties do not affect the uptake of one another by the clay mineral, whereas

metals with similar chemistries do. For example, the divalent metals Co(II) and Zn(II) were not found to affect the sorption of Eu(III), tested at various pH values and interfering metal concentrations. U(VI)/Co(II), Th(IV)/U(VI), Th(IV)/Eu(III) or Th(IV)/Co(II) pairs were neither found to result in sorption competition. On the other hand the authors could show that trivalent metals compete for the same surface sites on montmorillonite in experiments using trace concentrations of Eu(III) or Am(III) ( $4 \times 10^{-9}$  M,  $1.4 \times 10^{-13}$ ) together with higher interfering metal (Nd(III) or Eu(III)) concentrations of  $5 \times 10^{-6}$  M -  $1 \times 10^{-4}$  M. Even though these particular experiments were performed as single-point batch sorption competition experiments with only a small number of samples to account for the competition between trivalent cations, the results imply that the uptake and retention of metal cations on a solid surface may be overestimated when considering only one element at a time. Thus, sorption competition reactions and potential changes in the metal ion speciation in the presence of multiple solutes should be accounted for when describing the fate of contaminants in the environment.

In our previous study (Virtanen et al. 2016) we investigated the sorption of neptunium(V) on the aluminum oxide corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>), in the presence and absence of trivalent Eu(III) or Gd(III). In accordance with the study by Bradbury and Baeyens (2005), no competitive behavior for the surface sorption sites could be observed between the metal cations with differing oxidation states. In X-ray absorption spectroscopic (XAS) investigations of the Np(V) speciation on the corundum surface, however, we did observe slight changes in the presence of the trivalent metal. These changes were tentatively assigned to a change in the Np(V) binding mode to the surface, implying that even though no competitive behavior was observed between the metals on the macroscopic scale, there may be changes occurring on the molecular level.

In the present study, we have investigated the sorption and speciation of Eu(III) or Cm(III) on the corundum surface in the presence and absence of the trivalent metal cation Y(III). Based on the results by Bradbury and Baeyens (2005) sorption competition can be expected to occur between these metal cations. The trivalent actinides Pu(III), Am(III) and Cm(III) are important long lived radionuclides in the spent nuclear fuel. Another important trivalent radionuclide relevant in the spent nuclear fuel is the fission product  $^{151}\text{Sm}$  (half-life 90 y). Also the mobility and migration of the rare earth elements, REE, (Sc(III), Y(III) and lanthanides) in the environment is becoming an increasingly important topic in environmental research after the great increase of industry using these metals. These REE exist primarily as trivalent cations and they are chemically very close to trivalent actinides. Although there are several published studies on the sorption and speciation of trivalent actinides and lanthanides on aluminum oxides (for example Stumpf et al. 2001; Rabung et al. 2006; Kumar et al. 2013; Kupcik et al. 2016), none of these experiments have been performed from the perspective of sorption competition.

This study includes sorption competition investigations on a macroscopic scale (batch sorption studies) but the focus of this work is on understanding the molecular level changes occurring in a sorption competition scenario using time-resolved laser fluorescence spectroscopy (TRLFS) for speciation investigations. Eu(III) was chosen as an analogue element for the trivalent actinides in the batch sorption studies, while Cm(III) was used in the spectroscopic investigations, because of the high luminescence yield of its  ${}^6\text{D}_{7/2}$  transition to the  ${}^8\text{S}_{7/2}$  ground state, that takes place after excitation by laser light. This  ${}^6\text{D}_{7/2} \rightarrow {}^8\text{S}_{7/2}$  transition is very sensitive to changes in the Cm(III) ligand field, resulting in a shift of the luminescence emission spectra maximum of the Cm(III) aqua ion (593.8 nm) to longer wavelengths, thus, enabling the detection of changes occurring in the metal ion speciation. Y(III) was used as competing metal cation. Even though Y(III) does not belong to the actinide or lanthanide series, its chemical properties are very close to those of Eu(III) and Cm(III), due

to the similar metal cation radii and charge,  $R_{Y(III)}^{VIII} = 1.019 \text{ \AA}$ ;  $R_{Eu(III)}^{IX} = 1.120 \text{ \AA}$ ; and  $R_{Cm(III)}^{IX} = 1.146$  (Shannon et al. 1976; David and Vokhmin 2003), where the superscript indicates the coordination number of the metal cation under consideration. The major advantage of using Y(III) in the TRLFS experiments is that it will not interfere with the detection of Cm(III) luminescence emission, since it does not have accepting energy levels below and close to the emitting  ${}^6D_{7/2}$  term that could potentially cause quenching of the Cm(III) luminescence through cross relaxation via intermetallic energy transfer.

## 2 Materials and methods

### 2.1 Mineral and chemicals

#### 2.1.1 Corundum

The aluminum oxide corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) was chosen for the study because it is isomorphous to hematite, a more common mineral in the environment, but unlike hematite, corundum does not quench the Cm(III) luminescence signal in the laser fluorescence spectroscopic investigations. Iron has been shown to induce significant quenching effects even at low impurity concentrations, presumably due to non-radiative energy transfer from curium to iron through dipole-dipole interactions [Claret et al. 2005; Rabung et al., 2005; Hartmann et al. 2008].

The surface of corundum consists of aluminol (Al-OH) functional groups that are also present as functional groups in many other minerals such as aluminosilicates and clay minerals. The surface of aluminum oxides can change during the hydration process in contact with aqueous solution.  $\alpha\text{-Al}_2\text{O}_3$  represents the end structure of alumina dehydration where transformation from gibbsite to boehmite to  $\gamma$ -alumina and finally corundum occurs. Thus, surface hydration of  $\alpha\text{-Al}_2\text{O}_3$  may be regarded as a reversible process of gibbsite dehydration (Yang et al. 2007). Surface hydration and the subsequent transformation to hydroxide phases have further been shown to impact the surface reactivity, as demonstrated for  $\gamma$ -alumina in Lefèvre et al. 2002.

For  $\gamma$ -alumina, such transformations were shown to occur within 4 days of contact with water. To our knowledge, similar data is not available for corundum, implying that the corundum surface transformation process has not been studied, or it is too slow to be detected in the time-frame of typical (adsorption) experiments. To avoid the alteration of the mineral surface and unnecessary aging of the mineral suspension, the corundum suspension was always freshly prepared from dry powder for batch sorption experiments and laser spectroscopic investigations. Commercially available corundum (Taimicron, Japan) was used in the experiments. Characterization of the mineral used in this study has already been described more closely in recent publications (Kupcik et al. 2016; Virtanen et al. 2016). The specific surface area of the mineral was determined to be  $14.5 \text{ m}^2/\text{g}$  and the average grain size was ranging from 100 nm to 200 nm. The isoelectric point of the mineral, determined in  $\text{H}_2\text{O}$  and  $0.01 - 0.1 \text{ M NaClO}_4$  was found at pH 9.7.

### 2.1.2 Chemicals

All sorption and TRLFS samples were prepared and equilibrated in a glove box, under nitrogen or argon atmosphere, to exclude the formation of metal-carbonato-complexes that could affect the uptake of the metals by the corundum mineral. All chemicals used in the study were carbonate free and at least of analytical grade.  $0.01 \text{ M NaClO}_4$  was used as a background electrolyte in all the experiments and  $\text{HClO}_4$  and  $\text{NaOH}$  were used for pH adjustments. TRIS (tris(hydroxymethyl)aminomethane) buffer (concentration  $0.01 \text{ M}$ ) was used in the kinetic experiments to stabilize the suspension pH at pH 8.  $\text{Eu(III)}$  and  $\text{Y(III)}$  stock solutions used in the pH-edge experiments and  $\text{Y(III)}$  stock solution used in the TRLFS studies as competing metal were prepared by diluting commercial  $1000 \text{ ppm ICP-MS}$  standards (in  $0.5 \text{ M HNO}_3$ ) to the final concentration.  $^{248}\text{Cm(III)}$  stock solution in  $0.1 \text{ M HClO}_4$  was used in the TRLFS experiments.

## 2.2 Batch sorption experiments

### 2.2.1 *pH dependent sorption investigations in the absence and presence of Y(III)*

Eu(III) batch sorption experiments as a function of pH were conducted both in the absence and presence of Y(III) as competing element. In a first set of experiments, the batch sorption studies as a function of pH were conducted for Eu(III) only. In these experiments  $5 \times 10^{-6}$  M or  $1 \times 10^{-5}$  M Eu(III) was added to a corundum suspension with a solid concentration of either 0.5 g/l or 5 g/l and the pH was adjusted over the pH range 3-11. The samples were thereafter equilibrated for 3 days before phase separation by centrifugation at 30 000 rpm for one hour and the metal ion concentration in the supernatant was determined by inductively coupled-mass spectrometry (ICP-MS). In the ICP-MS measurements, external standards were used for calibration and internal standards were used to confirm stability of the signal. Independent reference samples were used to verify the validity of the results. The detection limit for Eu(III) was  $3.5 \times 10^{-11}$  M.

In a second set of experiments, the competing metal, Y(III), was introduced to the corundum suspension and allowed to adsorb on the mineral surface before the addition of Eu(III). For that, the pH of the corundum suspensions with the interfering metal was adjusted in the pH range of 3-11 and the samples were allowed to equilibrate for 2-3 days before Eu(III) addition and subsequent readjustment of the pH. After the Eu(III) addition, the batch sorption samples were equilibrated for an additional time of 3 days before sample separation was done according to the procedure explained above. The same Eu(III) concentrations of  $5 \times 10^{-6}$  M or  $1 \times 10^{-5}$  M used in the single element studies explained above were used, while the Y(III) concentration was varied over a larger range, between  $5 \times 10^{-6}$  M -  $1 \times 10^{-4}$  M. The experiments were conducted for both corundum concentrations of 0.5 g/l or 5.0 g/l, to compare low and high surface site saturation scenarios. Taking into account the specific surface area of corundum ( $14.5 \text{ m}^2/\text{g}$ ) and the solid concentration in our competitive batch sorption



experiments, the highest Y(III) concentration of  $1 \times 10^{-4}$  M would saturate 8.3 sites/nm<sup>2</sup> for the lower solid concentration of 0.5 g/l and 0.83 sites/nm<sup>2</sup> for the higher corundum concentration of 5 g/l. 8.3 sites/nm<sup>2</sup> is larger than the theoretical surface site concentration of 2.31 sites/nm<sup>2</sup> (recommended for oxide minerals by Davis and Kent, 1990), which would imply that not all added Y(III) can adsorb on the mineral surface. This could lead to a possible precipitation of M(III) as hydroxides, especially in the higher pH-region. However, as significantly larger surface site densities have been reported for corundum, e.g. 5.94 sites/nm<sup>2</sup> (Das et al. 2004), 10 sites/nm<sup>2</sup> (Hayes et al. 1991) or 30.5 sites/nm<sup>2</sup> (Criscenti and Sverjensky, 2002), we chose to conduct both competitive batch sorption investigations as well as spectroscopic studies (see description later in the text) for this high Y(III) concentration to ensure a sufficiently high surface site coverage and subsequently ideal competitive conditions for the various trivalent cations on the corundum surface. Great care was taken during the pH adjustments, where small volumes of NaOH was added to the corundum suspensions at a time over the course of a day, to avoid precipitation of metal hydroxides from oversaturated solutions.

### *2.2.2 Kinetic sorption investigations in the absence and presence of Y(III)*

Kinetic batch experiments both for single element (Eu(III) only) and competing scenarios (Eu(III) and Y(III)) were conducted as a function of time at a constant pH (pH ~ 8, TRIS). These experiments were performed for the 0.5 g/l corundum concentration only. The Eu(III) concentrations in the experiments were the same as used in the pH-dependent sorption investigations, i.e.  $5 \times 10^{-6}$  M or  $1 \times 10^{-5}$  M. In addition, one kinetic experiment was run for  $1 \times 10^{-7}$  M Eu(III) in order to be able to directly compare the results with the spectroscopic investigations conducted for  $1 \times 10^{-7}$  M Cm(III) (see detailed explanation in the following chapter). In the single metal experiments, Eu(III) was added to a suspension and the equilibration time of the samples was varied between 1 hour and 86 days. Phase separations

were performed as described previously. Two different sets of competitive kinetic experiments were performed. In the first set the potential influence of the metal addition order was investigated by adding  $5 \times 10^{-6}$  M Y(III) either together with the same amount of Eu(III), or 2 – 3 days before Eu(III) addition, and sorption of Eu(III) was followed as a function of time. The second set of experiments was performed to mimic kinetic TRLFS experiments (see description in the following section). Here, the sorption of  $1 \times 10^{-7}$  M Eu(III) in the absence and presence of  $1 \times 10^{-5}$  or  $1 \times 10^{-4}$  M Y(III) (added 2 – 3 days before Eu(III)) was investigated as a function of time at pH 8.3. All the kinetic experiments were executed by preparing multiple batch samples that were separated as a function of time.

### 2.3 Laser spectroscopic investigations

TRLFS was used to investigate the surface complexation and *in situ* speciation of Cm(III) on the corundum surface at varying pH or equilibrium times. The luminescence emission band of Cm(III) is sensitive to changes in the first coordination sphere. In case the metal ion coordination sphere changes, for example in case of hydrolysis or inner-sphere surface complexation, the Cm(III) emission band is shifted from 593.8 nm for the aqua ion to longer wavelengths, which is called a bathochromic shift or a redshift. Peak deconvolution of the luminescence emission spectra at various pH values allows the extraction of single components and derivation of the Cm(III) species distribution.

Investigation of the luminescence lifetimes enables the determination of the number of luminescence quenching entities, mainly  $\text{OH}^-$  and/or  $\text{H}_2\text{O}$ , in the first coordination sphere of the metal. In general, the luminescence lifetime increases if these quenching entities are replaced by other ligands, for example in case of inner-sphere surface complexation onto mineral surfaces, where some of the  $\text{H}_2\text{O}/\text{OH}^-$  units are displaced. The number of  $\text{H}_2\text{O}/\text{OH}^-$  units can be determined by using an empirical relationship (Eq. 1) between the luminescence decay constant  $k_{\text{obs}}$  and the number of these units (Kimura and Choppin, 1994).

$$n(\text{H}_2\text{O}) = 0.65 \times k_{\text{obs}}(\text{Cm}) - 0.88 \quad (\text{Eq. 1})$$

In Eq. 1  $k_{\text{obs}}(\text{Cm})$  is  $\tau^{-1}$ ,  $\tau$  being the luminescence lifetime in milliseconds.

Surface complexation of Cm(III) and competition between Cm(III) and Y(III) was investigated as a function of pH or as a function of time, at a constant corundum concentration of 0.5 g/l. The pH dependency of Cm(III) emission spectra and sorption species formation was investigated with two independent samples: one sample containing  $1 \times 10^{-7}$  M Cm(III) and the other with  $1 \times 10^{-4}$  M Y(III) and  $1 \times 10^{-7}$  M Cm(III). The pH of the sample with only Cm(III) was increased stepwise from pH 4 to pH 12 and with Y(III) + Cm(III) from pH 5 to pH 10. After each NaOH addition the samples were equilibrated for two days.

The influence of equilibration time on Cm(III) surface complexation at constant pH (sorption kinetics) was investigated by preparing three samples, one with  $1 \times 10^{-7}$  M Cm(III), one with  $1 \times 10^{-7}$  M Cm(III) and  $1 \times 10^{-5}$  M Y(III) and one with  $1 \times 10^{-7}$  M Cm(III) and  $1 \times 10^{-4}$  M Y(III). In the competitive samples Y(III) was added three days before the Cm(III) addition, and the pH was increased to ~8 in small steps to avoid precipitation of  $\text{Y}(\text{OH})_3$ . After the Cm(III) addition, the pH was readjusted and TRIS buffer was added to the suspension to fix the pH at 8.3. TRLFS measurements were performed after various Cm(III) equilibration times, from 1 hour to 51 days. To exclude the potential influence of the TRIS buffer on Cm(III) complexation, we also performed investigations without the use of a buffer, at pH 8.5 and 8.9 using  $5 \times 10^{-7}$  M Cm(III) and  $1 \times 10^{-4}$  M Y(III). In these samples Y(III) was added before or at the same time as Cm(III). However, these experiments yielded the same results as the experiments with the buffer and will not be discussed further in this paper.

To account for the solution speciation of Cm(III) (mainly hydrolysis), additional experiments were performed in the absence of the solid phase and the competing metal cation. These experiments were performed with  $5 \times 10^{-7}$  M Cm(III) solutions, at pH 5.5 – 8.5.

For the TRLFS measurements the samples were pipetted into cuvettes which were sealed in the glove box. After the measurements, the samples were brought back into the glove box and pipetted back to the sample vials, followed by pH adjustments of the complete sample volume. The TRLFS measurements were performed at two different laser systems with a pulsed Nd:YAG (Continuum Surelite II or Powerlite Precision II 9020) pump laser coupled to either a dye laser (Radiant dyes Narrow Scan) with Exalite 398 laser dye or a solid-state optical parametric oscillator (OPO, PANTHER EX OPO, Continuum). The Cm(III) luminescence emission spectra were recorded between 580 – 620 nm, 1  $\mu$ s after of the exiting laser pulse ( $\lambda_{\text{ex}}=396.6$  nm). The laser pulse energy was controlled by photodiode to be between 2 – 3 mJ. Luminescence emission was detected by an optical multichannel analyzer with 1200 lines/mm grating and an ICCD-Camera (iStar, Andor). Lifetime measurements were performed by monitoring the luminescence emissions with 5  $\mu$ s – 20  $\mu$ s time delay steps between the laser pulse and the camera gating.

### 3 Results

#### 3.1 Eu(III) sorption on corundum in the absence and presence of Y(III)

##### 3.1.1 pH dependent investigations

###### 3.1.1.1 Total metal ion concentration $\leq 10^{-5}$ M

When keeping the total metal ion concentration at a maximum of  $10^{-5}$  M, oversaturation conditions where the metal ion concentration exceeds the number of available sorption sites (discussed previously) should not be reached for any of the corundum concentrations used in the batch sorption experiments. The pH edges for  $5 \times 10^{-6}$  M and  $1 \times 10^{-5}$  M Eu(III) (closed and open black symbols, respectively) are shown in Figure 1 together with the obtained sorption data for  $5 \times 10^{-6}$  M Eu(III) in the presence of  $5 \times 10^{-6}$  M Y(III) (red symbols) for two corundum

concentrations of 0.5 g/l (left) and 5 g/l (right). In the competitive samples the total metal ion concentration was kept at  $1 \times 10^{-5}$  M by addition of  $5 \times 10^{-6}$  M Y(III) prior to Eu(III) addition.

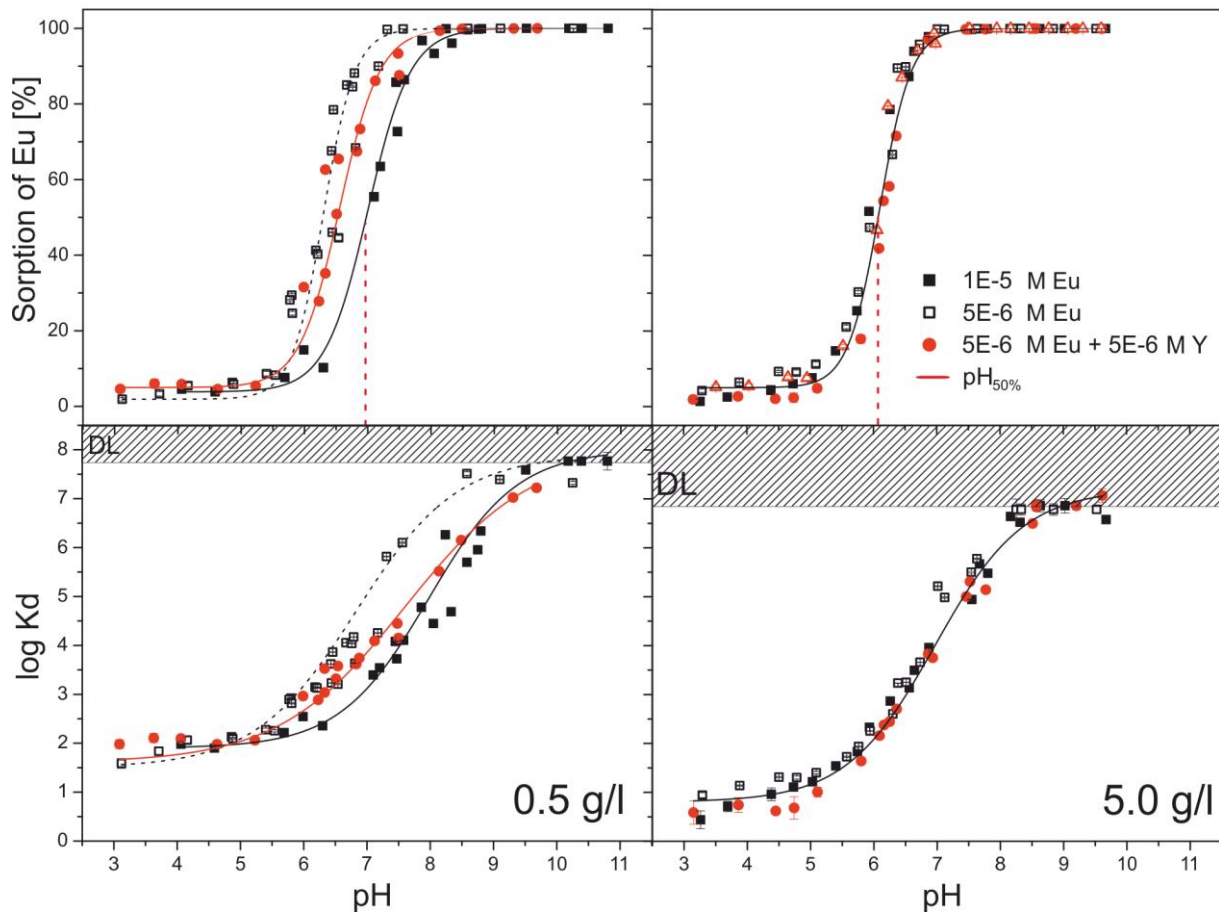


Figure 1: Sorption of  $1 \times 10^{-5}$  M or  $5 \times 10^{-6}$  M Eu(III) on 0.5 g/l (left) and 5.0 g/l (right) corundum in the absence and presence of  $5 \times 10^{-6}$  M Y(III) added before Eu(III) presented as pH-edges (top) and  $\log K_d$  [l/kg] plots (bottom). Lines are added as trend lines.

In the absence of Y(III), the pH-edge is clearly shifted to higher pH for the  $1 \times 10^{-5}$  M Eu(III) concentration when going from the higher solid concentration of 5 g/l ( $pH_{50} = 6$ , a pH value where 50% of the Eu(III) is adsorbed) to the lower one of 0.5 g/l ( $pH_{50} = 7$ ). A shift of the pH edge is also obtained when increasing the total metal ion concentration in the samples with 0.5 g/l corundum, while no concentration effect can be observed for the 5 g/l solid content. This shift of the pH-edge can be attributed to either saturation of available sorption sites, to the heterogeneity of the sites (e.g. strong vs. weak sites) or to steric (electrostatic) effects,

where the attached metal exerts a repulsive force on metal ions remaining in solution (Dzombak and Morel, 1990; Davis and Kent, 1990). An area, where sorption is independent of the used metal ion concentration or the available sorption sites, is called an ideal sorption range. For the higher mineral concentration (5.0 g/l) there is no visible difference between the uptake of  $5 \times 10^{-6}$  M Eu(III),  $1 \times 10^{-5}$  M Eu(III) or Eu(III)+Y(III), implying that the number of available surface sites is sufficient to accommodate the metals on the mineral surface, i.e. Eu(III) sorption occurs in an ideal sorption range. For the lower mineral concentration (0.5 g/l) the presence of Y(III) does influence the uptake of Eu(III) on the corundum surface, implying that sorption competition does occur in the samples as a result of a more limited amount of available surface sites. Interestingly, the results show a slightly different uptake behavior for  $1 \times 10^{-5}$  M Eu(III) on the corundum surface when solely present in the system in comparison to the competing samples where the total metal ion concentration is the same, i.e.  $1 \times 10^{-5}$  M. Whether this is due to a lower affinity of Y(III) to the surface in comparison to Eu(III) or a kinetic influence will be discussed in more detail in connection to the time-dependent batch sorption studies.

### *3.1.1.2 Total metal ion concentration $\geq 10^{-5}$ M*

In order to obtain sorption competition conditions, especially for the higher mineral content in the samples, the total metal ion concentration in the samples had to be increased. These conditions may not be directly comparable to environmental conditions where the concentration of trivalent actinides and REE is expected to be very low. However, to understand sorption competition phenomena, saturation of the available surface sites had to be achieved. As previously discussed, when increasing the metal ion concentration and approaching the surface saturation region, precipitation reactions from oversaturated solutions may occur. Thus, special care had to be taken when preparing the following samples, especially where the mineral concentration was kept low (0.5 g/l).

In Figure 2 the uptake ( $\log K_d$ ) of  $1 \times 10^{-5}$  M Eu(III) on 0.5 g/l (left) and 5 g/l (right) corundum in the absence and presence of  $1 \times 10^{-5}$  M or  $1 \times 10^{-4}$  M Y(III) is presented. As already mentioned in the previous section, the competing (blocking) metal has been added to the mineral suspension prior to Eu(III) addition.

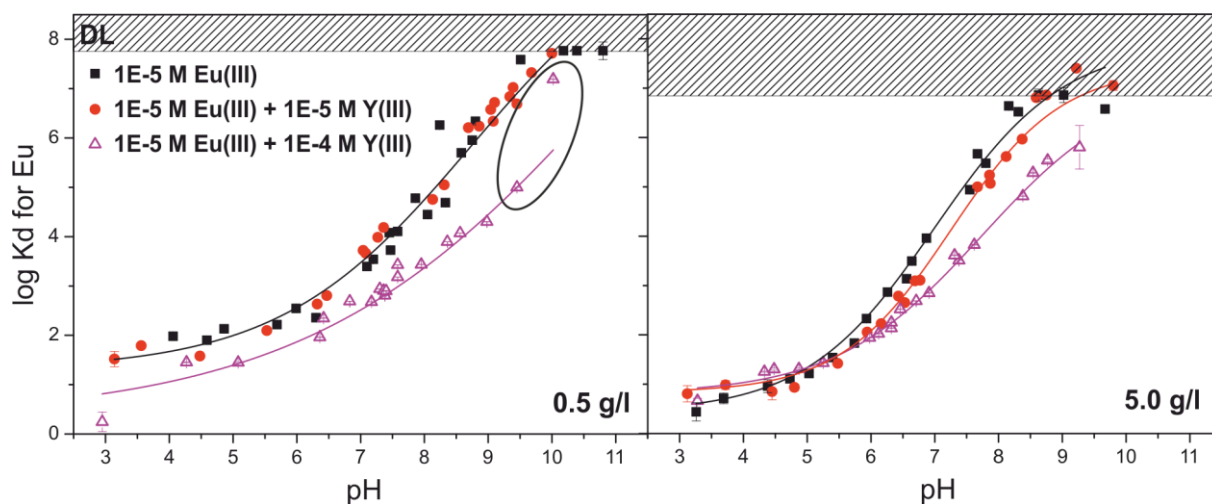


Figure 2: Sorption of  $1 \times 10^{-5}$  M Eu(III) on 0.5 g/l (left) or 5.0 g/l (right) corundum in the absence (black symbols) and presence (red symbols) of  $1 \times 10^{-5}$  or  $1 \times 10^{-4}$  M Y(III) (added before Eu(III)) in 0.01 M  $\text{NaClO}_4$ .

There is a clear shift of the sorption  $K_d$  edge for both mineral concentrations. The shift is particularly apparent for the lower mineral concentration of 0.5 g/l, however, in contrast to our results where the total metal ion concentration was kept at  $10^{-5}$  M and below, an influence of Y(III) on the uptake of Eu(III) can be seen in the 5 g/l corundum samples as well. The pH value where 50% of the Eu(III) is adsorbed on the corundum surface for  $1 \times 10^{-5}$  M Eu(III) on 0.5 g/l corundum (i.e.  $\text{pH}_{50} = 7$ , discussed in the previous paragraph) is in concordance with the results obtained for a total Eu(III)+Y(III) concentration of  $2 \times 10^{-5}$  M in both the 0.5 g/l and 5 g/l suspensions. The shift from the edge-position around  $\text{pH}_{50} = 6$  (indicative for the ideal sorption range, Figure 1) implies that sorption occurs in the non-ideal sorption range in these competitive sorption samples. However, the absence of an additional shift of the pH edge in

the competitive sample with  $2 \times 10^{-5}$  M (Eu(III)+Y(III)) in comparison to  $1 \times 10^{-5}$  M (Eu(III) only) on 0.5 g/l, is somewhat surprising. This would mean that a small increase of the total metal ion concentration from  $5 \times 10^{-6}$  M to  $1 \times 10^{-5}$  M is sufficient to shift the pH-edge from the ideal sorption range to the non-ideal one for the 0.5 g/l mineral concentration (Figure 1), whilst a larger increase is required to impact the metal ion sorption behavior in the non-ideal sorption range. This phenomenon could arise from the larger amount of available weak surface sites (non-ideal sorption range) in comparison to strong sites (ideal sorption range). Hence, due to a large excess of available (weak) surface sites, site-saturation effects will not be equally pronounced in this sorption range and, consequently small changes in the total metal ion concentration will not influence the total amount of sorption. When the metal ion concentration changes significantly, such as in our competitive samples with  $1 \times 10^{-4}$  M Y(III), a clear shift of the pH-edge is again obtained in the weak-site regime, indicative of site-saturation or steric effects at the mineral surface.

In the 0.5 g/l Kd plots, a rather steep, unexpected increase of the Eu(III) sorption distribution coefficient close to pH 10 can be seen in the presence of  $10^{-4}$  M Y(III) (circled in Figure 2). This rapid increase in the uptake is in concordance with the rapid removal of Eu(III) from solution as a result of precipitation or coprecipitation as a hydroxide when exceeding the hydroxide solubility limit in the alkaline pH-range. In none of the other Kd plots a similar rapid increase of the Eu(III) uptake can be seen, implying that oversaturation conditions are reached only when combining a high Y(III) concentration of  $10^{-4}$  M, a low mineral concentration of 0.5 g/l and a rather alkaline pH range above pH 9.5. The oversaturation can be verified from the Y(III) sorption data (supporting information SI Figure 3) where a similar rapid increase of Y(III) uptake is observed in the alkaline pH range (pH~10). From these results, a rough estimate of the surface site density on the corundum surface can be calculated when taking into account the total adsorbed metal ion concentration (97 % of Y(III) and 98 % of Eu(III) is sorbed with an initial concentration of  $10^{-4}$  M and  $10^{-5}$  M for Y(III) and Eu(III),



respectively) in the 0.5 g/l corundum sample at a pH value just below 9.5. This would correspond to a surface site density of 11 sites/nm<sup>2</sup>.

Due to clearly visible competitive influence of 10<sup>-4</sup> M Y(III) in 0.5 g/l corundum suspensions, these mineral and blocking metal concentrations were chosen for most of the laser spectroscopic experiments with Cm(III), see chapter 3.2, however, bearing in mind that the solubility limit could be exceeded for pH values approaching 10 and beyond.

### *3.1.2 Kinetic investigations*

To investigate the influence of kinetics on the sorption competition observed in the pH dependent batch sorption studies, kinetic sorption experiments were conducted for varying Eu(III) and Y(III) concentrations. In kinetic experiments where the total metal ion concentration was kept at  $\leq 1 \times 10^{-5}$  M, Eu(III) concentrations of  $5 \times 10^{-6}$  M and  $1 \times 10^{-5}$  M in non-competitive samples and  $5 \times 10^{-6}$  M together with  $5 \times 10^{-6}$  M Y(III) in competitive ones, were used. In addition, sorption kinetics of 10<sup>-7</sup> M Eu(III) solely and in the presence of 10<sup>-4</sup> M Y(III) was investigated in order to allow for direct comparison of batch sorption and spectroscopic experiments. All kinetic investigations were conducted at a constant pH of approximately 8, i.e. well below the pH value where Eu(III) precipitation was found to occur in our pH-dependent sorption studies. The results of all kinetic investigations are presented in Figure 3. Only the results of 10<sup>-7</sup> M Eu(III) solely on corundum were omitted from Figure 3, as the results were all below the detection limit (DL).

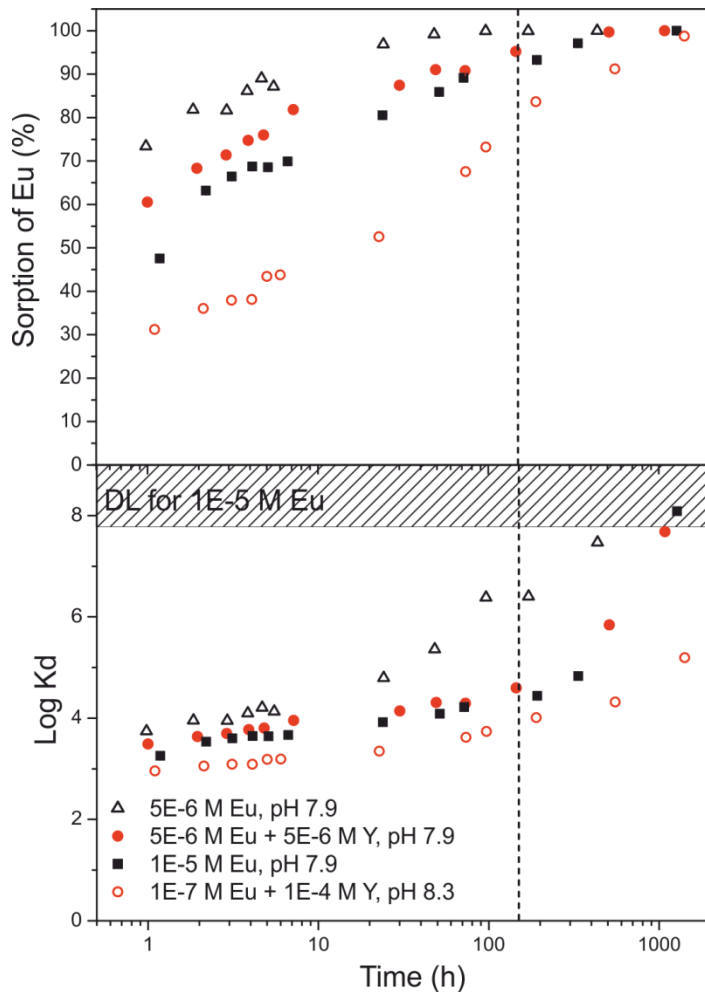


Figure 3: Sorption kinetics of Eu(III) in non-competitive samples with Eu(III) concentrations of  $5 \times 10^{-6}$  M and  $1 \times 10^{-5}$  M (black symbols) on 0.5 g/l corundum at pH 8 as a function of time, compared to the  $5 \times 10^{-6}$  M Eu(III) sorption with  $5 \times 10^{-6}$  M Y(III) and  $1 \times 10^{-7}$  M Eu(III) sorption with  $1 \times 10^{-4}$  M Y(III) added before Eu(III) (red symbols). Dashed line shows the time point of 150 h.

When looking at the Kd plots (Figure 3, below), it seems like no real sorption equilibrium is achieved even after very long equilibrium times, but the extent of sorption is increasing until the DL for Eu(III) is reached (except for the total M(III) concentration of  $1 \times 10^{-4}$  M, where Eu(III) concentrations are well above the DL at all equilibration times). As previously mentioned, the aluminum oxide surface is known to change when the mineral is contacted

with aqueous solutions, leading to the formation of a hydroxide layer on the oxide surface. This hydroxide layer may alter the surface reactivity of the mineral, which in turn compromises the interpretation of long-term sorption experiments such as our kinetic study. Furthermore, dissolution and re-precipitation reactions leading to the formation of a hydroxide layer on the mineral surface has previously been shown to cause partial incorporation of the metal ion at the interface (Huittinen et al. 2009). Thus, in order not to over-interpret our results, we focus our discussion on the time region used in our pH-dependent sorption studies, i.e. 6 days, or approximately 150h (3d equilibrium time after Y(III) addition followed by 2-3d equilibrium time after Eu(III) addition). This time region is shown in Figure 3 by a dashed line.

The kinetic results for a total metal ion concentration of  $\leq 10^{-5}$  M are in concordance with the pH-dependent results (Figure 1) for the same metal ion concentrations. When  $5 \times 10^{-6}$  M Y(III) has been added to the corundum suspension before Eu(III), Y(III) has time to occupy free surface sites causing a decrease of the Eu(III) uptake in comparison to the non-competitive case where only  $5 \times 10^{-6}$  M Eu(III) is present on the mineral surface. Interestingly, this competitive scenario does not seem to be governed by kinetics as Eu(III) uptake increases in parallel in the non-competitive and competitive samples. Thus, sorption kinetics cannot be used to explain the pH-dependent uptake of Eu(III) in the absence and presence of Y(III), where a difference between  $10^{-5}$  M Eu(III) and  $5 \times 10^{-6}$  M Y(III) +  $5 \times 10^{-6}$  M Eu(III) (i.e. a total metal ion concentration of  $10^{-5}$  M) could be observed (Figure 1).

## 3.2 Laser spectroscopic investigations of Cm(III) speciation on corundum in the absence and presence of Y(III)

### 3.2.1 Cm(III) speciation on corundum in the absence and presence of Y(III)

A comprehensive study on the sorption and speciation of Cm(III) on corundum using TR-LFS has recently been published (Kupcik et al. 2016). However, to enable direct comparison of Cm(III) emission spectra measured with the same laser set-up in the absence and presence of the competing metal cation Y(III) we conducted a pH dependent series on Cm(III) complexation on corundum also in the absence of Y(III) over the pH range 4 – 12. The reader is referred to the supporting information for the normalized and background corrected Cm(III) luminescence spectra in the corundum suspensions at varying pH-values (supporting information SI Figure 4 and 5). Peak deconvolution of the emission spectra in the absence of Y(III) (Figure 4, left) identifies four different Cm(III) species in addition to the aqua ion, with peak maxima at 597.5 nm, 600.7 nm, 602.6 nm and 605.0 nm. The latter three peak positions are reasonably comparable to the pure component spectra reported in Kupcik et al. (2016) for Cm(III) complexation on corundum, 600.7 nm, 603.0 nm and 605.4 nm. These single species were identified as *surface*···Cm(OH)<sub>x</sub>(H<sub>2</sub>O)<sub>5-x</sub> (x=0, 1, 2) complexes, in agreement with earlier work on Cm(III) sorption on other aluminum (hydr)oxides:  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Al(OH)<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> single crystals (Stumpf et al. 2001; Huittinen et al. 2009, Rabung et al. 2004 and 2006). However, the first species with a peak maximum at 597.5 nm has not been reported in any of the above mentioned Cm(III) sorption studies on aluminum (hydr)oxide minerals. This species appears at pH < 7 and its contribution to the emission spectra is minor. Nevertheless, the origin of this species is discussed later in the text.

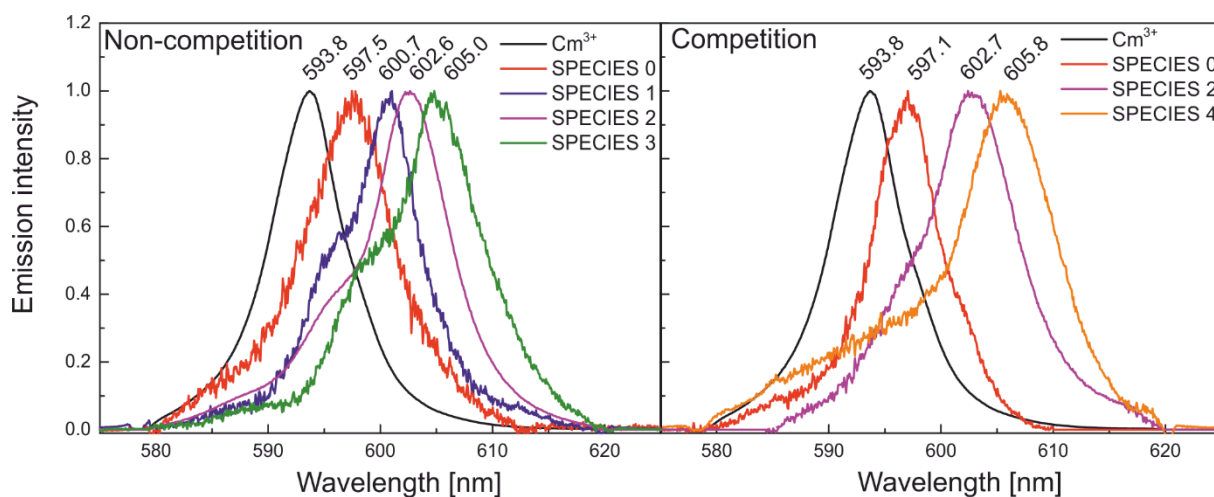


Figure 4: Pure component spectra of  $1 \times 10^{-7}$  M Cm(III) in the absence of Y(III) (left) and in the presence of  $1 \times 10^{-4}$  M Y(III) (right) on 0.5 g/l corundum derived by deconvolution of the sum spectra (supporting information SI Figure 4 and 5).

At first glance, the Cm(III) luminescence emission spectra collected at pH 5 – 10 of the sample where  $1 \times 10^{-4}$  M Y(III) was added simultaneously with  $1 \times 10^{-7}$  M Cm(III) to the corundum suspension resembles the spectra presented for Cm(III) emission without yttrium (supporting information SI Figure 4 and 5). However, a closer look on the individual emission spectra of only Cm(III) and Cm(III) together with Y(III) reveals that the spectra at the same pH values are not completely identical as shown in Figure 5.

At pH < 5, there is no difference between the emission spectra between competitive and non-competitive samples and only the non-sorbed Cm(III) aqua ion is detected. At pH > 5, the spectra of the non-competitive samples start to slowly move to higher wavelengths as a result of Cm(III) surface complexation, while a much weaker peak shift is observed for the competitive samples at similar pH. This more pronounced peak shift (larger bathochromic shift) at intermediate pH for the non-competitive samples follows the shift of the pH edge to lower pH values at lower metal ion concentrations (see Figure 1). However, at higher pH the spectra of the competitive samples are broader compared to the non-competitive ones and exhibit an even larger peak shift (Figure 5 d). This implies that the speciation of Cm(III) is

different in these two systems. The deconvolution of the emission spectra (Figure 4, right) reveals that in addition to the aqua ion, the competitive emission spectra of Cm(III) consist of only three species at  $\lambda_{\text{max}}$  597.1 nm, 602.7 nm and 605.8 nm. The distribution of the species both in the absence and presence of Y(III) will be discussed later in the text.

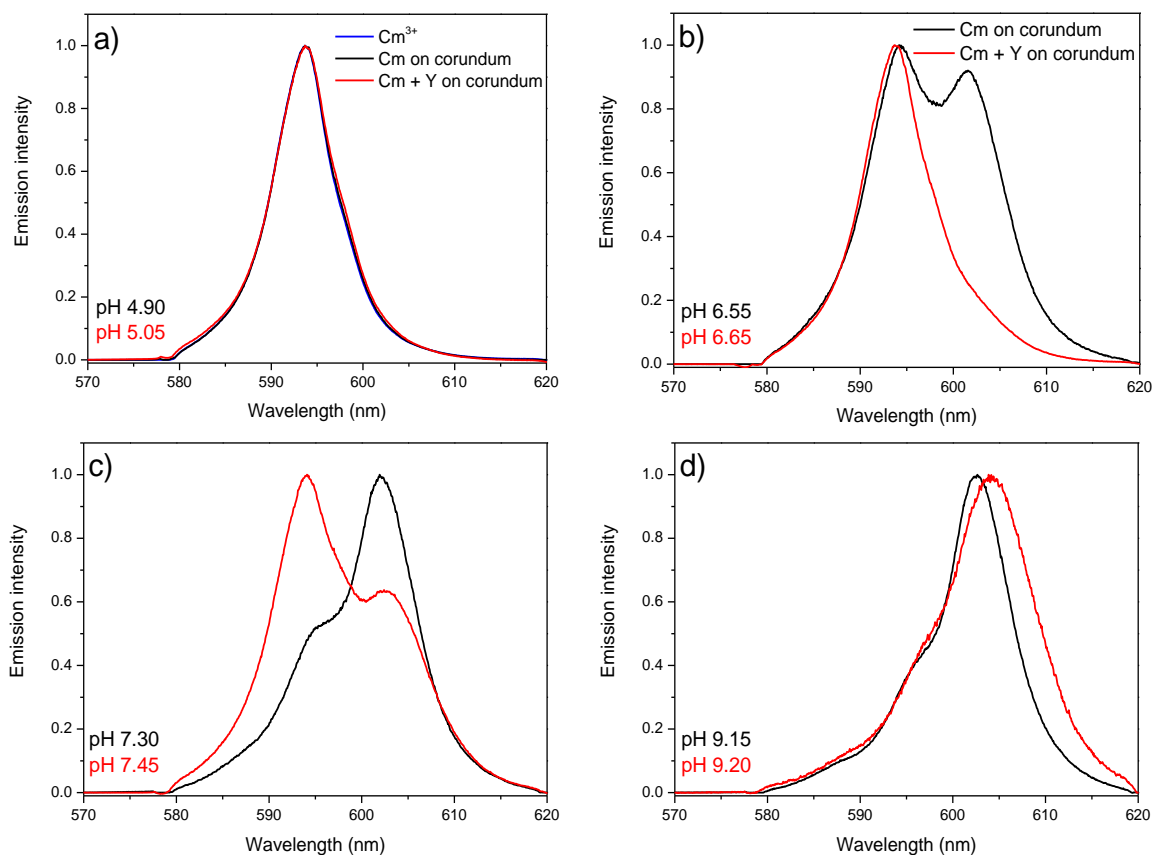


Figure 5 a) – d) Comparison of luminescence emission spectra at selected pH values between 5 and 9 for only  $1 \times 10^{-7}$  M Cm(III) on corundum (black) and for  $1 \times 10^{-7}$  M Cm(III) +  $1 \times 10^{-4}$  M Y(III) (red) added simultaneously to the mineral suspension. The Cm(III) aqua ion spectrum,  $\text{Cm}(\text{H}_2\text{O})_9^{3+}$ , collected at pH 1 is presented together with the spectra a) at pH  $\approx$  5.

### 3.2.2 *Cm(III) solution speciation in the absence of Y(III) and corundum*

The Cm(III) solution speciation was investigated for two reasons. Firstly, we detected a species at 597.5 nm (without Y(III)) and 597.1 nm (with Y(III)) that cannot be directly associated to any other sorbed species identified in earlier studies on the sorption of Cm(III) on aluminum minerals. Hence we wanted to explore the possibility of this species being an aqueous Cm(III) species such as the first hydrolysis complex,  $\text{Cm}(\text{OH})^{2+}$ . Secondly, from the batch experiments with Eu(III) and Y(III), we know that higher Y(III) concentrations can decrease the sorption of Cm(III) at a given pH, leading to higher amounts of unsorbed Cm(III). Therefore, it is important to examine the aqueous speciation of Cm(III).

In Figure 6 we see the deconvoluted pure component spectra, extracted from the emission spectra of  $5 \times 10^{-7}$  M Cm(III) in 0.01 M  $\text{NaClO}_4$  at pH 5.5 – 8.5. With increasing pH, the intensity of the Cm(III) emission spectra decreases, most likely caused by increasing sorption of Cm(III) onto vial walls or the pH-electrode (unlike in the presence of a sorbing mineral phase when the metal sorption onto container walls is strongly suppressed). Thus, investigations at pH > 8.5, using the batch method for sample preparation in rather large polyethylene vials (20 ml) with large surface areas, followed by pH measurements and sample transfer to the cuvettes for the spectroscopic investigations, were not possible to conduct. In addition, the Cm(III) concentration of  $5 \times 10^{-7}$  M does not allow for much higher pH values for solution speciation investigations as the solubility limit of  $\text{Cm}(\text{OH})_3$  may be exceeded at pH > 9.

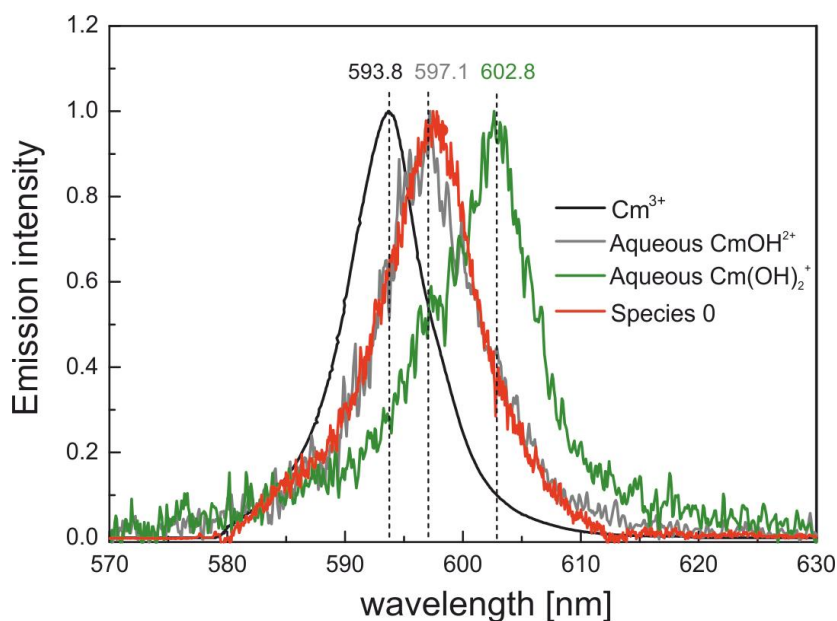


Figure 6: Normalized pure component emission spectra of the suggested Cm(III) ( $5 \times 10^{-7}$  M) hydrolysis species in 0.01 M NaClO<sub>4</sub>, at pH 5.5 – 8.5

Two solution species were found in the investigated pH range, with peak maxima at 597.1 nm and 602.8 nm. There are only two possible complex-forming ligands in the solution, ClO<sub>4</sub><sup>-</sup> and OH<sup>-</sup>, of which the perchlorate anion is known to be a much weaker complexing ligand compared to the hydroxide anion. Based on this, the two aqueous species are most likely the first two curium hydrolysis complexes, CmOH<sup>2+</sup> and Cm(OH)<sub>2</sub><sup>+</sup>. The position of the first hydrolysis complex at 597.1 nm corresponds very well with the position of *species 0* found in the sorption samples, at 597.5 nm and 597.1 nm without and with Y(III), respectively, implying that this species could in fact be the non-sorbed aqueous hydrolysis complex of Cm(III) in the corundum suspension. However, these results are in some contradiction to earlier work by Wimmer et al. (1992) and Fanghänel et al. (1994), who found the Cm(OH)<sup>2+</sup> and Cm(OH)<sub>2</sub><sup>+</sup> emission maxima at 598.7 – 598.8 nm and 603.5 nm, respectively. In the framework of this study, however, we cannot explain the relatively large discrepancies



between the emission peak maxima of the deconvoluted hydrolysis complexes (597.1 – 597.5 nm, this work, vs. 598.7 – 598.8 nm, earlier work).

### 3.2.3 The Cm(III) species distribution on corundum in the absence and presence of Y(III)

To calculate the species distribution for Cm(III) at different pH, we need to derive the relative fluorescence intensity factors (FI) for the species in question. FI-correction takes into account differences in the molar absorptivity at the excitation wavelength and the fluorescence quantum yield of the individual species (Rabung et al. 2005). In case of inner-sphere complexation of Cm(III) on alumina the absorption band is shifted away from the fixed excitation wavelength which was set to the maximum absorptivity of the free aqua ion (396.6 nm). This leads to a general decrease in the fluorescence intensity with larger peak shifts (Wang et al. 2004). Relative FI's can be calculated using least-squares fitting, by considering the measured integrated fluorescence intensity of each emission spectra referring to the integrated emission spectra of a Cm(III) aqua ion reference sample, determined before each measurement. The FI of Cm(III) aqua ion was fixed to 1 whereas the intensity factors for the first *species 0* could not be obtained by this method, since its contribution to the total emission intensity is too low. For *species 1*, *species 2* and *species 3*, we obtained  $FI_{\text{species } 1} = 0.56$ ,  $FI_{\text{species } 2} = 0.33$  and  $FI_{\text{species } 3} = 0.19$ , which are in agreement with earlier work by Kupcik et al. (2016) ( $FI_{\text{species } 1,2,3} = 0.55, 0.21$  and  $0.22$ ) and Rabung et al. (2006) ( $FI_{\text{species } 1,2,3} = 0.45, 0.29$  and  $0.26$ ) for Cm(III) complexes on aluminum oxides. For *species 0* we had to estimate the intensity factor to be somewhere between  $FI_{\text{aqua ion}}$  and  $FI_{\text{species } 1}$ , (based on its peak shift located between these two species). Thus we selected  $FI = 0.75$  for *species 0* for the species distribution calculations. For *species 4* found in the competitive samples at 605.8 nm we used the same value as for *species 3*, since the position of the peak maxima are very close to each other.

The obtained species distribution (Figure 7) of only Cm(III) in contact with corundum compared to the species distribution of Cm(III) added to corundum suspension at the same time with Y(III) are quite different. *Species 1* does not appear at all in the competitive samples, which is reasonable as sorption is shifted to higher pH values where *species 1* does not occur anymore. Noticeable is, that *species 2* is clearly more suppressed in the presence of Y(III) than in the absence of the competing metal. This implies that a larger amount of Cm(III) is remaining in solution due to the presence of Y(III), i.e. Y(III) does indeed occupy the same surface sites as Cm(III) and, thus, hinders or at least retards the uptake of Cm(III) by the aluminum mineral. Above pH 8, both of the Cm(III) emission spectra peak maxima are completely shifted from the original peak position of the aqua ion, however, the surface speciation of the actinide is completely different. In the non-competitive samples *species 2* dominates pH > 6 while the competitive samples show a dominance of *species 4* for pH > 8, which is not accounted for at all in the absence of Y(III). The underlying reasons for the different speciation and the presence of *species 4* will be discussed later in the text.

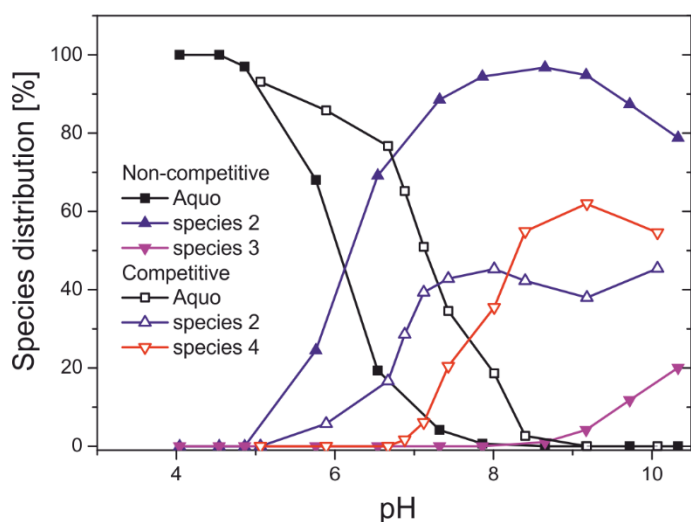


Figure 7: The Cm(III) species distribution, derived by peak deconvolution of the luminescence emission spectra for  $1 \times 10^{-7}$  M Cm(III) in the absence of Y(III) (closed symbols) and  $1 \times 10^{-7}$  M Cm(III) in the presence of  $1 \times 10^{-4}$  M Y(III) (open symbols) in 0.5 g/l

corundum suspension. The *Species 0* and *1* were left out from the graph because the low abundance of the species (less than 10 %).

### 3.2.4 Kinetic investigations of Cm(III) sorption on corundum in the presence of Y(III)

Curium sorption kinetics investigated by TRLFS (Figure 8, left) for only  $1 \times 10^{-7}$  M Cm(III) in contact with 0.5 g/l corundum at pH 8.3 show that the Cm(III) surface complex formation is rapid, characterized by an almost identical emission spectrum at all time points between 1 hour – 20 days after Cm(III) addition. Conversely, in the presence of  $1 \times 10^{-4}$  M Y(III) added before  $1 \times 10^{-7}$  M Cm(III), the sorption kinetics is very different (Figure 8, right). In this sample, one hour after Cm(III) addition the emission spectra are mainly consisting of the Cm(III) aqua ion and the alleged aqueous hydrolysis species (*species 0*), and there is only a small shoulder denoting surface complex formation. However, the shape of the spectra is significantly changing during the 1 – 51 days of equilibration time. The fraction of aqueous species decreases when Cm(III) is forming inner sphere surface complexes on corundum and after 51 days, the emission peak maximum is clearly shifted in the direction of the sorption species.

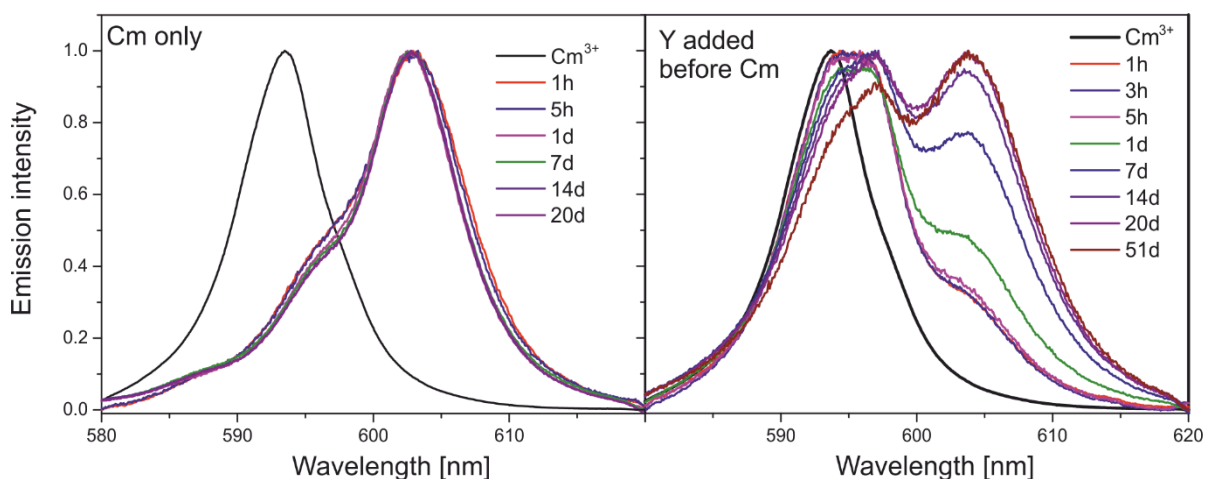


Figure 8: Comparison of luminescence emission spectra of only  $1 \times 10^{-7}$  M Cm(III) on corundum (left) at pH 8.3 in TRIS buffered 0.01 M NaClO<sub>4</sub> to the emission spectra where  $1 \times 10^{-4}$  M Y(III) is also present (right; Y(III) added before Cm(III)) determined at different times after Cm(III) addition. The Cm(III) aqua ion, Cm(III), recorded at pH 1 is presented as a reference.

The results are in concordance with the kinetic results obtained for Eu(III) sorption on corundum in the absence and presence of Y(III) (Figure 3). Clearly, the sorption kinetics become slower with increasing metal ion concentration. In order to compare the obtained results from the batch sorption experiments and the spectroscopic investigations, the Cm(III) sorption percentage in the two kinetic samples was calculated using the derived FI factors and the known species distribution (Figure 7) at the pH-value of 8.3. The results are plotted in Figure 9, together with the corresponding Eu(III) data. In the non-competitive samples both Eu(III) and Cm(III) show a rapid uptake as a function of time. As already mentioned in connection to the Eu(III) results, the concentration of Eu(III) remaining in the solution was below the instrumental detection limit already after one hour (detection limit for Eu(III) was  $3.5 \times 10^{-11}$  M), indicative of high and fast sorption. In the presence of Y(III), Eu(III) and Cm(III) sorption is less than 40 % after one hour of Cm(III) or Eu(III) addition to the corundum suspension, yet increasing to approximately 90 % after 51 and 86 days, respectively. The absence of an apparent sorption equilibrium or a steady-state even after 86 days could be a consequence of e.g. surface alteration, as explained previously.

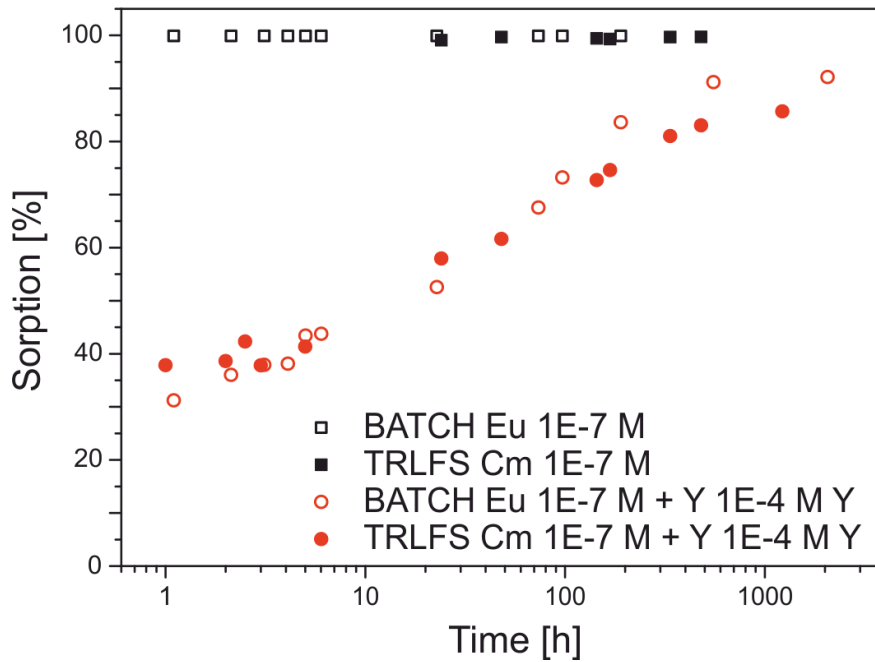


Figure 9 Sorption percentages of  $1 \times 10^{-7}$  M Eu(III) (open symbols) in the batch experiments compared to the sorption percentages of  $1 \times 10^{-7}$  M Cm(III) (closed symbols) calculated from the TRLFS data in contact with 0.5 g/l corundum in the absence and presence of  $1 \times 10^{-4}$  M Y(III) (added before Eu(III), Cm(III)). Sorption recorded 1 hour up to 86 days after the addition of Eu(III) or Cm(III) to the mineral suspension.

## 4 Discussion

### 4.1 Batch sorption investigations

The results from Bradbury and Baeyens (2005), showing that metals with similar chemistries compete for the same mineral sorption sites, have been confirmed in our batch experiments with trivalent metals, where the results clearly show the decreasing effect that the presence of Y(III) has on Eu(III) sorption. We used two corundum concentrations of 0.5 g/l and 5g/l in our experiments, since the number of sorption sites is directly dependent on the mineral concentration. The effect of competing metal was very pronounced for the lower mineral concentration which can easily be understood when regarding the total number of available

surface sites for metal ion attachment. The absolute value of surface sites was not determined in the present study, but we calculated a rough number of sites based on the results in our batch sorption studies, where an apparent precipitation reaction from oversaturated solutions could be observed as an abrupt increase of Eu(III) uptake on corundum at a pH-value close to 10 (Figure 2). In this batch sorption experiment the mineral concentration was 0.5 g/l and the total metal ion concentration (Eu(III) + Y(III)) was  $1.1 \times 10^{-4}$  M, respectively. The batch sorption data showed that approximately 98 % of the added Eu(III) and 97 % of the added Y(III) were adsorbed on the corundum surface at a pH-value of 9.5 (just below the pH value where the noticeable increase of Eu(III) occurred), leading to an estimated number of 11 sites/nm<sup>2</sup> assuming 100 % site saturation by the adsorbed metal ions and one trivalent metal ion per available site. This site density is considerably larger than the theoretical site density of 2.31 sites/nm<sup>2</sup> commonly used for oxide minerals (Davis and Kent, 1990), however, it is still well within the range of reported values for corundum (see discussion in section 2.2.1).

Sorption competition was also found to occur for concentrations well below our estimated surface saturation concentration (calculated by using the theoretical site density of 2.31 sites/nm<sup>2</sup>), e.g. for  $5 \times 10^{-6}$  M Y(III) and  $5 \times 10^{-6}$  M Eu(III) on 0.5 g/l corundum (36 % coverage) (Figure 1) or for  $10^{-4}$  M Y(III) and  $10^{-5}$  M Eu(III) on 5 g/l corundum (40 % coverage) (Figure 2), implying that other factors besides mere site saturation are responsible for the observed shifts in the pH-edges. We may have to regard sorption onto different site types (so called strong and weak sites) or steric effects arising from the electrostatic repulsion of metals to be able to explain the competitive sorption behavior of Eu(III) and Y(III).

Furthermore, the total concentration of metal ions in the batch sorption experiments is clearly not the only factor that needs to be taken into account when considering competitive sorption between metals. In our batch sorption studies, we found that the sorption of  $5 \times 10^{-6}$  M Eu(III) together with  $5 \times 10^{-6}$  M Y(III) did not completely equal the sorption of  $1 \times 10^{-5}$  M Eu(III)

(Figure 1). As sorption kinetics could be a probable cause for this discrepancy, we conducted Eu(III) sorption investigations in the presence and absence of Y(III) as a function of time. These kinetic investigations showed that the total metal ion concentration had an influence on the sorption kinetics, where low concentrations of the metal cation were adsorbed faster than larger concentrations. Nevertheless, a different kinetic behavior could not be observed in the non-competitive sample with  $5 \times 10^{-6}$  M Eu(III) in comparison to the competitive sample with  $5 \times 10^{-6}$  M Y(III) and Eu(III), thus, other reasons must be considered to understand this phenomenon. However, the kinetics of Y(III) sorption show slightly different properties compared to Eu(III) sorption (see SI Figure 1 and 2), since the presence of Eu(III) slows down Y(III) sorption when metals are added together. Whether Y(III) has a lower affinity for the surface groups than Eu(III) caused by e.g. slight differences in the hydrolysis behavior between the metals or small differences in the character of the chemical bond formed to the surface (such as the degree of covalency) we cannot estimate based on the rather limited set of batch sorption data for these two metal cations. Kinetic experiments also show that no steady state was obtained even after 80 days which might be attributed to slow modifications of the corundum surface and subsequent changes of the surface reactivity as previously discussed in section 2.1.1.

## **4.2 Spectroscopic investigations**

The speciation of Cm(III) in 0.5 g/l corundum suspensions in the absence and presence of Y(III) as competing cation, was investigated using TRLFs. Our results without the competing cation are well in concordance with a recent publication on Cm(III) sorption on corundum by Kupcik et al. (2016). The authors identified three pH-dependent Cm(III) sorption species on the mineral surface at pH 3 – 13, and these same three species were identified in the present study with emission peak maxima at 600.7 nm, 602.6 nm, and 605.0 nm, however, a fourth minor component (maximum of 9%) was found in the present work at an emission

wavelength of 597.5 nm that had not been accounted for in any of the aforementioned studies. After investigations of the solution speciation of Cm(III), we observed two aqueous Cm(III) species at 597.1 nm and 602.8 nm that could be assigned to the first two hydrolysis species of Cm(III);  $\text{CmOH}^{2+}$  and  $\text{Cm}(\text{OH})_2^+$ , even though slightly different peak positions for these hydrolysis complexes have been reported in earlier studies (Wimmer et al., 1992, Fanghänel et al., 1994). The first hydrolysis complex is most likely also responsible for the peak in the corundum suspension at 597.5 nm (non-competitive samples) or 597.1 nm (competitive samples).

As already mentioned, in addition to the aqua ion, four Cm(III) species could be extracted from our non-competitive samples at pH 4 – 12, with emission peak positions at 597.5 nm, 600.7 nm, 602.6 nm, and 605.0 nm. In the competitive samples at pH 5 – 10 only three species with peak positions at 597.1 nm, 602.7 nm, and 605.8 nm were found. When comparing the species distributions of the adsorbed species (i.e. excluding the alleged hydrolysis species at 597.1 or 597.5 nm) (Figure 7) we conclude that the species found at 602.6 nm and 602.7 nm in non-competitive and competitive samples, respectively, is the same species, identified as *surface*... $\text{Cm}(\text{OH})(\text{H}_2\text{O})_4^+$  by Kupcik et al. (2016). The aqua ion and *species 2* appear in same pH region in both the competitive and non-competitive samples. However, the fraction of *species 2* in competitive samples is smaller because the presence of the rather high concentration of Y(III) decreases the overall sorption of Cm(III) and forces Cm(III) to remain in the solution. Hence the fraction of aqua ion is greater in the competitive sample. Furthermore, in our solution speciation experiments (Figure 6) we see that the second aqueous hydrolysis species  $\text{Cm}(\text{OH})_2^+$  has peak maximum at 602.8 nm that would superimpose with *species 2* at 602.6 nm. Thus *species 2* may be a combination of surface-adsorbed and solution species which cannot be distinguished from one another, leading to an overestimation of adsorbed Cm(III) on the corundum surface.



*Species 1*, found at 600.7 nm in the non-competitive samples is not present in the competitive samples, which is reasonable as its contribution is small and the presence of Y(III) further decreases the sorption of Cm(III) in the competitive samples in the pH range of this species.

So far we have not yet discussed *species 4* in the competitive samples found at 605.8 nm at  $\text{pH} > 7$ . If we regard only the peak position, *species 4* resembles very much *species 3* in the non-competitive samples with a peak maximum at 605.0 nm. However, these species appear in completely different pH-ranges, i.e. above pH 9 (*species 3*) in the non-competitive case and already above pH 7 (*species 4*) in the competitive one. Between pH 7 and 9 in the non-competitive samples, *species 2* is predominant. This leaves two possibilities for the formation of *species 4*: (i) either it is equivalent to *species 3* in which case an explanation for the different pH-dependent behavior of this species in the non-competitive and competitive environments has to be found or (ii) *species 4* is formed from *species 2* when the surface loading is high enough and this species differs in terms of coordination/complexation strength/proximity to the surface etc. from *species 2*.

Based on recorded luminescence lifetime data above pH 7 in competitive and non-competitive samples, no indications of different surface speciation of in terms of gain/loss of water molecules around the Cm(III) cation could be obtained (the reader is referred to supporting information for lifetime measurements, SI Figure 6). In both cases a biexponential decay of the luminescence intensity was observed for corundum suspension samples with Cm(III) or Cm(III) + Y(III), with a long-lived component of  $140 \pm 30 \mu\text{s}$  and a shorter-lived one ( $< 60 \mu\text{s}$ ). The origin of the shorter lived component is not clear, but it might arise from non-radiative energy transfer from the excited Cm(III) state to the solid phase (Huittinen et al. 2010, Huittinen et al. 2012). According to Eq. 1, the lifetime of  $140 \mu\text{s}$  corresponds to 3.8  $\text{H}_2\text{O}/\text{OH}^-$  units in the first coordination sphere of Cm(III). According to Wang et al. (2003) the replacement of water molecules by hydroxyl groups from the Cm(III) ligand field

increases the fluorescence lifetime and, therefore, reducing the number of quenching entities estimated by Eq 1. This means that in case of multiple OH<sup>-</sup> groups instead of H<sub>2</sub>O groups, the empirical equation could underestimate the number of quenching entities in the Cm(III) ligand field, and thus, the lifetime of 140 μs might correspond to more than 3.8 quenching units. Huittinen et al. (2012) obtained comparable lifetimes ( $47 \pm 2 \mu\text{s}$  and  $132 \pm 5 \mu\text{s}$ ) for Cm(III) luminescence on kaolinite and in this study the longer component was attributed to 5 H<sub>2</sub>O/OH<sup>-</sup> units based on the lower quenching properties of OH<sup>-</sup> ligands in comparison to the water molecule. Following the same assignment of 5 H<sub>2</sub>O/OH<sup>-</sup> molecules in the first coordination sphere of *species 2-4*, a tetradentate coordination would be required to preserve the coordination number of nine, typically found for Cm(III) in aqueous solution (e.g. Kimura and Choppin, 1994; David and Vokhmin 2003; Skanthakumar et al. 2007). This coordination is supported by quantum chemical studies by Polly et al. (2010, 2013) for trivalent actinides on corundum, where tri- or tetradentate surface complexes were found using density functional theory.

The surface coordination alone, if we only regard a tetradentate surface complex, does not explain the bathochromic shift of *species 4* compared to *species 2* in the competitive samples as the observed lifetimes do not change. However, if we regard the possibility of differing surface coordination between the hydrolyzed curium surface complex (*species 2*) in the non-competitive samples and the hitherto unidentified complex in our competitive samples (*species 4*), we may be able to explain the observed bathochromic shift between the species. A red-shift due to a change in the Cm(III) coordination number in aqueous solution has previously been observed in Lindqvist-Reis et al. (2005). The authors studied the hydration of Cm(III) in aqueous solutions from 20 to 200 °C by measuring the luminescence of Cm(III). Increasing temperature was followed by a spectral shift of Cm(III) emission maximum from 593.8 nm to 594.2 nm (from deconvolution) which was associated to a possible change in the local structure from a nonhydrated Cm(III) species to an octahydrated one. The lower

amount of coordinating ligands allows for a closer location of the water molecules around the curium cation, causing the oxygen ligands to exert a stronger ligand field on the actinide cation with a subsequent shift of the emission-peak position to longer wavelengths. In other words, a reduction of coordination number could explain the small shift of 0.8 nm observed between species 3 ( $\lambda_c = 605.0$  nm) and species 4 ( $\lambda_c = 605.8$  nm). Unfortunately, the TRLFS method does not allow for a more precise identification of the present species on the corundum surface, and additional information about the complex structures must be obtained with other spectroscopic methods. Thus, for example x-ray absorption spectroscopic investigations (XAS) would be urgently required to provide further insight into the complex structures in the non-competitive and competitive samples.

## 5 Conclusions

In this study, we obtained clear evidence of sorption competition between the trivalent metals Eu(III) and Y(III) with batch experiments performed at different metal ion concentrations as a function of pH and time. Our results imply that these trivalent metals are sorbing on the same surface sites on the corundum surface and that the competing metal concentration can influence the adsorption kinetics of the metal ion under consideration. Spectroscopic studies using the TRLFS method to investigate the Cm(III) speciation on the corundum surface in the absence and presence of Y(III) confirm the findings observed in our batch sorption studies. The presence of Y(III) significantly impacts the adsorption kinetics of Cm(III), as well as the direct speciation of Cm(III) on the corundum surface. This difference in Cm(III) speciation on the mineral surface might be caused by a change in the surface coordination of the Cm(III)-complex, leading to an reduction of the overall actinide coordination number from nine to eight. To verify the hypothesis, however, additional spectroscopic methods, such as extended X-ray absorption spectroscopy (XAS) providing information on the complex structure,

coordination numbers, and nearest neighbor atoms and their intermolecular distances, are needed to confirm our hypotheses.

#### Acknowledgements

This work was supported by the Finnish Doctoral Programme for Nuclear Engineering and Radiochemistry (YTERA).

#### References

Bradbury M. H. and Baeyens B. (2005) Experimental measurements and modelling of sorption competition on montmorillonite. *Geochimica et Cosmochimica Acta*, 69, 4187 – 4197.

Claret, F., Schäfer, T., Rabung, T., Wolf, M., Bauer, A. and Buckau, G. (2005) Differences in properties and Cm(III) complexation behavior of isolated humic and fulvic acid derived from Opalinus clay and Callovo-Oxfordian argillite. *Applied Geochemistry* 20, 1158–1168.

Criscenti, L. J. and Sverjensky, D. A. (2002) A single-site model for divalent transition and heavy metal adsorption over a range of metal concentrations. *Journal of Colloid and Interface Science* 253, 329-352.

Das, M. R., Sahu, O. P., Borthakur, P. C. and Mahiuddin, S. (2004) Kinetics and adsorption behaviour of salicylate on  $\alpha$ -alumina in aqueous medium. *Colloids and Surfaces A* 237, 23-31.

David, F. H. and Vokhmin, V. (2003) Thermodynamic properties of some tri- and tetravalent actinide aquo ions. *New Journal of Chemistry*, 27, 1627 –1632.

Davis, J.A. and Kent D. B. (1990) Surface complexation modelling in aqueous geochemistry. Mineral-Water Interface Geochemistry, Rev. Mineral., Hochella M.F. and White, A.F. (Eds.), 23 pp. 177 – 260.

Dzombak D. and Morel F. (1990) Surface Complexation Modeling: Hydrous Ferric Oxide, Wiley, USA.

Fanghänel, Th., Kim, J. I., Paviet, P., Klenze, R., and Hauser, W. (1994) Thermodynamics of radioactive trace elements in concentrated electrolyte solutions: Hydrolysis of Cm<sup>3+</sup> in NaCl-solutions. Radiochimica Acta 66/67, 81 – 87.

Hartmann, E., Baeyens, B., Bradbury, M. H., Geckeis, H. and Stumpf, T. (2008) A Spectroscopic characterization and Quantification of M(III)/Clay Mineral Outer-Sphere Complexes. Environmental Science and Technology 42, 7601–7606.

Hayes, K. F., Redden, G., Ela, W. and Leckie, J. O. (1991) Surface complexation models: An evaluation of model parameter estimation using FITEQL and oxide mineral titration data. Journal of Colloid and Interface Science 142, 448-469.

Huittinen, N., Rabung, Th., Lützenkirchen, J., Mitchell, S. C., Bickmore, B. R., Lehto, J. and Geckeis H. (2009) Sorption of Cm(III) and Gd(III) onto gibbsite,  $\alpha$ -Al(OH)<sub>3</sub>: A batch and TRIFS study. Journal of Colloid and Interface Science 332, Iss 1, pp. 158 – 164.

Huittinen, N., Rabung, Th., Andrieux, P., Lehto, J. and Geckeis, H. (2010) A comparative batch sorption and time-resolved laser fluorescence spectroscopy study on the sorption of Eu(III) and Cm(III) on synthetic and natural kaolinite. Radiochimica Acta 98, 613 – 620.

Huittinen, N., Rabung, Th., Schnurr, A., Hakanen, M., Lehto, J. and Geckeis, H. (2012) New insight into Cm(III) interaction with kaolinite – Influence of mineral dissolution. Geochimica et Cosmochimica Acta 99, 100 – 109.

Kimura, T. and Choppin, G. (1994) Luminescence study on determination of the hydration number of Cm(III). *Journal of Alloys and Compounds* 213/214, 313 – 317.

Kumar, S., Godbole, S. V. and Tomar B. S (2013) Speciation of Am(III)/Eu(III) sorbed on  $\gamma$ -alumina: effect of metal ion concentration. *Radiochimica Acta* 101, 73 – 80.

Kupcik T., Rabung, Th., Lützenkirchen J., Finck, N., Geckeis H., Fanghänel Th., (2016) Macroscopic and spectroscopic investigations on Eu(III) and (Cm(III) sorption onto bayerite ( $\beta$ -Al(OH)<sub>3</sub>) and corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>). *Journal of colloid and Interface Science* 461, 215 – 224.

Lefèvre, G., Duc, M., Lepeut, P., Caplain, R. and Fédoroff, M. (2002) Hydration of  $\gamma$ -Alumina in Water and Its Effects on Surface Reactivity. *Langmuir* 18, 7530-7537.

Lindqvist-Reis, P., Klenze, R., Schubert, G. and Fanghänel, Th. (2005) Hydration of Cm<sup>3+</sup> in aqueous solution from 20 to 200 °C. A time-resolved laser fluorescence spectroscopy study. *Journal of Physical Chemistry B*, 109, 3077 – 3083.

Polly R., Schimmelpfenning, B., Rabung, T., Flörsheimer, M., Klenze, R. and Geckeis, H. (2010) Quantum chemical study of inner-sphere complexes of trivalent lanthanide and actinide ions on the corundum (0001) surface. *Radiochimica Acta* 98, 627 – 634.

Polly R. Schimmelpfenning, B., Flörsheimer, M., Rabung, T., Kupcik, T., Klenze, R. and Geckeis, H (2013) Quantum chemical study of inner-sphere complexes of trivalent lanthanide and actinide ions on the corundum (110) surface. *Radiochimica Acta* 101, 561 – 570.

Shannon, R. D., (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallographica*. A32, Pages 751 – 767.

Skanthakumar, S., Antonio, M. R., Wilson, R. E., and Soderholm, L. (2007) The Curium Aqua Ion. *Inorganic Chemistry*, 46 (9), pp 3485–3491.

Stumpf, Th., Rabung, Th., Klenze, R., Geckeis, H. and Kim, J. I. (2001) Spectroscopic study of Cm(III) sorption onto  $\gamma$ -alumina. *Journal of Colloid and Interface Science* 238, 219 – 224.

Rabung, Th., Schild, D., Geckeis, H., Klenze, R. and Fanghänel, Th. (2004) Cm(III) sorption onto sapphire ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) single crystals. *Journal of Physical Chemistry B* 108 (44), 17160 – 17165.

Rabung, Th., Pierret, C., Bauer, A., Geckeis, H., Bradbury, M. h. and Baeyens, B. (2005) Sorption of Eu(III)/Cm(III) on Ca-montmorillonite and Na-illite. Part 1: Batch sorption and time-resolved laser fluorescence spectroscopy experiments. *Geochimica et Cosmochimica Acta* 69, no 23, 5393 – 5402.

Rabung, Th., Geckeis, H., Wang, X. K., Rothe, J., Denecke, M. A., Klenze, R., and Fanghänel, Th. (2006) Cm(III) sorption onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>: New insight into sorption mechanisms by time-resolved laser fluorescence spectroscopy and extended X-ray absorption fine structure. *Radiochimica Acta* 94, 609 – 618.

Wang Z., Felmy A. R., Xia Y. X. and Mason M. J. (2003) A fluorescence spectroscopic study on the speciation of Cm(III) and Eu(III) in the presence of organic chelates in highly basic solutions. *Radiochimica Acta* 91, 329-337.

Wang X. K., Rabung, Th., Geckeis, H., Panak, P. J., Klenze R. and Fanghänel Th. (2004) Effect of humic acid on the sorption of Cm(III) onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> studied by TRLFS, *Radiochimica Acta* 92, 691 – 695.

Wimmer, H., Klenze, R. and Kim, J.L. (1992) A study of hydrolysis reaction of curium(III) by time resolved laser fluorescence spectroscopy. *Radiochimica Acta* 56, 79 – 83.

Virtanen, S., Bok, F., Ikeda-Ohno, A., Rossberg, A., Lützenkirchen, J., Rabung, T., Lehto, J. and Huittinen, N. (2016) The specific sorption of Np(V) on the corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) surface

in the presence of trivalent lanthanides Eu(III) and Gd(III): a batch sorption and XAS study. *Journal of Colloid and Interface Science* 483, 334 – 342.

Yang, X., Sun, Z., Wang, D. and Forsling, W. (2007) Surface acid-base properties and hydration/dehydration mechanism of aluminum (hydr)oxides. *Journal of Colloid and Interface Science* 308, 395 – 404.