



Sorption competition and kinetics of trivalent cations (Eu, Y and Cm) on corundum ($\alpha\text{-Al}_2\text{O}_3$): A batch sorption and TRLFS study

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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 NaClO₄ 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 (1×10^{-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.

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) (4×10^{-9} M, 1.4×10^{-13}) together with higher interfering metal (Nd(III) or Eu(III)) concentrations of 5×10^{-6} M - 1×10^{-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

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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 ($\alpha\text{-Al}_2\text{O}_3$), 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}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; Kupeik 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, $R_{\text{Y(III)}^{\text{VI}}} = 1.019 \text{ \AA}$; $R_{\text{Eu(III)}^{\text{IX}}} = 1.120 \text{ \AA}$; and $R_{\text{Cm(III)}^{\text{IX}}} = 1.146$ (Shannon, 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 $^6\text{D}_{7/2}$ 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 γ -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 γ -alumina in Lefèvre et al., (2002). For γ -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 (Kupeik 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 H_2O and 0.01–0.1 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-carbonate-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 M NaClO_4 was used as a background electrolyte in all the experiments and HClO_4 and NaOH were used for pH adjustments. TRIS (tris(hydroxymethyl)amino-methane) buffer (concentration 0.01 M) was used in the kinetic experiments to stabilize the suspension pH at pH 8. Eu(III) and Y(III) stock solutions used in the pH-edge experiments and Y(III) stock solution used in the TRLFS studies as competing metal were prepared by diluting commercial 1000 ppm ICP-MS standards (in 0.5 M HNO_3) to the final concentration. $^{248}\text{Cm(III)}$ stock solution in 0.1 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 $5 \times 10^{-6} \text{ M}$ or $1 \times 10^{-5} \text{ M}$ Eu(III) was added to a corundum suspension with a solid

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