

# Immobilization of trivalent actinides by sorption onto quartz and incorporation into siliceous bulk: Investigations by TRLFS

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## Abstract

The adsorption of Cm(III) on quartz is studied by time resolved laser fluorescence spectroscopy (TRLFS) in the pH range from 3.75 to 9.45. The raw spectra are deconvoluted into three single components. The first one has a peak maximum at 593.8 nm and can be attributed to the Cm(III) aquo ion with an emission lifetime of  $68 \pm 3 \mu\text{s}$ . The second one corresponds to an adsorbed species and has a peak maximum at 601.4 nm and an emission lifetime of  $123 \pm 10 \mu\text{s}$ . The peak maximum of the third component is shifted to higher wavelength (603.6 nm) while the lifetime remains constant. Additionally, the adsorption of Am(III) on quartz is investigated in batch experiments. Based on the spectroscopic data a sorption mechanism is suggested. In addition, the obtained Am uptake data and the Cm-TRLFS data are modeled simultaneously using a single site Basic Stern model in combination with the charge distribution concept of Pauling. The finally suggested model consists of two bidentate surface complexes where the second one is the product of hydrolysis of the first sorption species. In a separate set of experiments the influence of silicic acid at different concentrations on the Cm(III) speciation in a quartz system is investigated by TRLFS. In suspension silicic acid at low concentration ( $3.5 \times 10^{-4} \text{ mol/L}$ ) has no influence on the Cm(III) speciation. At high concentration ( $3.5 \times 10^{-2} \text{ mol/L}$ ) the Cm(III) speciation is definitely influenced. The results at higher concentration indicate the formation of Cm(III)/silicic acid complexes and the incorporation of Cm(III) into siliceous bulk. This is confirmed by measurements at a quartz single crystal surface. Moreover, these measurements indicate the formation of quartz/Cm(III)/silicic acid ternary complexes at the mineral surface.

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## 1. Introduction

Radionuclide migration in natural aqueous systems is an ongoing concern in environmental research in particular in the context of the long term performance of nuclear waste repositories. The transport of actinides is strongly influenced by adsorption onto mineral surfaces and interaction with organic and inorganic ligands. Fundamental insight into sorption and complexation mechanisms such as identification of dissolved and adsorbed species is of cardinal importance for reliable prediction of actinide reactions in natural systems. Therefore it is

necessary to characterize the different actinide species and to elucidate the reaction mechanisms involved.

Time resolved laser fluorescence spectroscopy (TRLFS) enables the speciation of lanthanides like Eu(III) and actinides like U(VI), Am(III) and Cm(III) [1] in aqueous solution and on the water/mineral interface. Due to the high fluorescence yield of Cm(III) TRLFS allows speciation studies in the nanomolar concentration range corresponding to a surface loading far below a monolayer. Up to now the interaction of Cm(III) with mineral surfaces like  $\gamma$ -alumina [2], clay minerals [3], feldspars [4], CSH phases [5], cement [6], calcite [7] and  $\alpha$ -alumina single crystal surfaces [8] has been investigated. The characterization of the adsorbed species is deduced from excitation and emission spectra and from the fluorescence emission lifetime of Cm(III).

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TRLFS investigations of the interaction of Eu(III) with amorphous silica led to the conclusion that the trivalent lanthanide is not adsorbed but incorporated into the bulk structure [9]. Comparable results have been found for the interaction of Cm(III) with amorphous silica colloids [10]. These results indicate different mechanisms for the interaction of trivalent lanthanides/actinides with amorphous silica and with the aforementioned minerals. One possible explanation is the presence of dissolved silica from weathering of silicate minerals as described in literature [11–13]. The solubility of amorphous silica is known to be  $2 \times 10^{-3}$  M at pH < 9, dominated by monosilicic acid and increases rapidly with pH via deprotonation and through formation of polysilicic acid [14–16]. The different Si species may be involved in various reactions like complexation [17], formation of colloids [18,19] and precipitation [13]. These reactions have to be taken into account when the speciation of Cm(III) is investigated in the presence of silicate minerals.

The present TRLFS investigation is part of a study, which intends to give a complete Cm(III) speciation in a natural system mainly composed of silicates like quartz. Hereby, Cm(III) was selected as a representative of a trivalent actinide ion. Because of their omnipresence in nature silicates can have a dominating influence on the aqueous chemistry and hence on the migration behavior of actinides in the natural environment. In this study the adsorption of Cm(III) on quartz and the influence of silicic acid, which can be generated by the dissolution of the silicate mineral, at different concentrations on the Cm(III) speciation was investigated in dependence on pH. The studies of the Cm(III) speciation were performed on quartz particles in suspension as well as on quartz single crystal surfaces. In addition to TRLFS measurements the adsorption of Cm(III) and Am(III) was investigated by batch experiments and  $\alpha$ -spectrometry. The batch sorption and TRLFS data for the quartz particles in absence of silicic acid are described by a surface complexation model.

### 1.1. Surface complexation model

Adsorption of cations on oxides has been the subject of many studies. A number of different models have been used to describe the adsorption behavior [20]. Most models interpret the adsorption as an interaction of metal ions with functional groups at the surface. Those models usually consider competitive adsorption of protons and metal ions in proton–metal ion–adsorbent systems. Before interacting with the surface functional groups the metal ions have to overcome a potential difference between the bulk solution and the interface. A surface complexation model is therefore composed of two parts: a description of the electric double layer (e.g., that by Gouy and Chapman [21]) and conventional mass law equations and balances for the reactions at the surface. With this, the overall reaction for the absorption of a metal ion to a surface functional group can be separated into a chemical (intrinsic) and a variable electrostatic part:

$$K = e^{-\Delta G_{\text{ads}}/RT} = e^{-(\Delta G_{\text{el}}^{\circ} + \Delta G_{\text{el}})/RT} \\ = K_{\text{in}} e^{-\Delta G_{\text{el}}/RT} = K_{\text{in}} K_{\text{el}}, \quad (1)$$

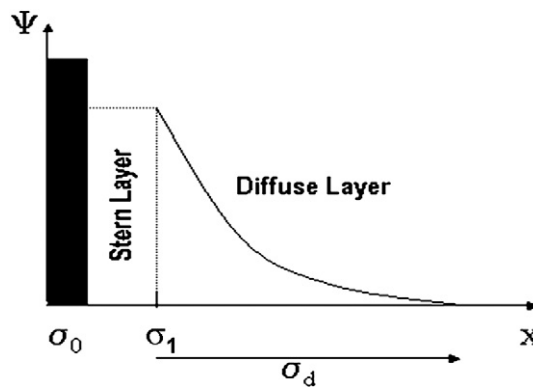


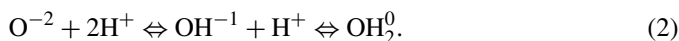
Fig. 1. Electrostatic double layer model for the interpretation of the sorption data.

where  $K$ : overall reaction constant,  $K_{\text{in}}$ : intrinsic reaction constant,  $K_{\text{el}}$ : electrostatic reaction constant,  $\Delta G_{\text{ads}}$ : Gibbs free energy for the adsorption,  $\Delta G_{\text{el}}^{\circ}$ : standard Gibbs free energy,  $\Delta G_{\text{el}}$ : electrostatic energy.

The electrostatic energy change,  $\Delta G_{\text{el}}$ , is variable due to the change in charge upon adsorption of ions and is determined by the electrostatic potential  $\Psi$  which is calculated by the use of an electrostatic model, in which the charge distribution (CD) of ions is involved [22].

Models may differ in the formulation of the surface chemical reactions (stoichiometries) and the assumed structure of the electrostatic double layer. In this study the basic Stern model was used as the electrostatic double layer model for the interpretation of the adsorption data (Fig. 1). Two electrostatic planes are considered that are separated from each other by a charge free layer in between called the Stern layer. The charges of protons are allocated to the surface ( $\sigma_0$ ). Adsorption of background electrolyte ions is considered by treating them as point charges and placing that charge at the head end of the diffuse part of the double layer ( $\sigma_1$ ). The sum of  $\sigma_0$  and  $\sigma_1$  is compensated by the charge  $\sigma_d$  of the diffuse part of the electrostatic double layer, which is calculated from the Gouy–Chapman equation. The Stern layer is characterized by a capacitance. This capacitance is usually determined from model fits to acid base titration data [23].

As demonstrated in Eq. (2) the interface of an oxide may be composed of several functional groups, which are coordinated to one or more metal ions of the solid.



This picture leads to a discrete surface heterogeneity because each group has its own proton affinity and charge characteristics, which may even vary with the crystallographic plane. For the determination of the overall charge  $\sigma_0$  at the surface one must take into account that the surface oxygen is not only partially neutralized by protons but also by the metal ions in the mineral structure. Vice versa, the charge of the cation is compensated by the charge of the surrounding oxygens. As it was introduced by Pauling [24] for neutralization, the charge is distributed over the surrounding ligands, which can be expressed per bond. With this, the bond valence  $v$  is defined as the charge

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