

# Effect of aqueous acetic, oxalic, and carbonic acids on the adsorption of europium(III) onto $\alpha$ -alumina

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## Abstract

Chemical retention, i.e., partition of the element between aqueous solution and mineral surface, is a key phenomenon for assessing the safety of possible nuclear waste disposal. For this purpose, the sorption of Eu(III) onto a model mineral— $\alpha$ -alumina—is studied here, including the effects of groundwater chemistry: pH and concentrations of small organic and inorganic ligands (acetate, oxalate, and carbonate anions). This work presents some experimental evidence for a synergic mechanism of sorption of europium–ligand complexes onto the alumina. Only cationic complexes were necessary to consider to model experimental results. Using the ion-exchange theory (IET) and a corresponding restricted set of parameters—exchange capacities and thermodynamic equilibrium constants—the whole set of sorption experiments of Eu(III) cationic species onto the  $\alpha$ -alumina was modeled under various chemical conditions.

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## 1. Introduction

Sorption of radioactive species onto minerals will delay their migration in groundwaters. To assess the retention properties of the geochemical barriers about possible geologic repositories of radioactive wastes, it is necessary to understand the chemical behavior of radionuclides in this context, including the interactions with natural solids such as oxides or clays.

However, chemical retention (partition of the element between the aqueous and solid phases) will be modified by complexing agents. These complexing agents decrease the sorption as a result of complexation in the aqueous phase [1,2] or of competition for sorption sites on the solid; conversely, they in-

crease the sorption as a result of co-sorption with radionuclides (synergic effect) [3].

In the present study, we first focused on the effect of ionic strength and pH on europium(III) sorption. We then studied the effect of various typical complexing agents: anions  $\text{CH}_3\text{CO}_2^-$ ,  $\text{C}_2\text{O}_4^{2-}$ , and  $\text{CO}_3^{2-}$  of respectively acetic, oxalic, and aqueous carbonic acids. Our aim is to model the effects of the parameters pH, ionic strength, and concentrations of ligands on europium(III) sorption.

Isotopes of lanthanides are fission products of uranium-235 and trivalent actinides (mainly Am and Cm isotopes) are activation products of uranium-238. Lanthanides are also studied as nonradioactive analogues of trivalent actinides.

$\text{Al}_2\text{O}_3$  was chosen as a model mineral. It does not occur frequently as a pure mineral in natural systems; however, the sorption properties are compared with those of hematite and goethite [4]. Aluminum oxide was chosen for its amphoteric properties in the pH range of underground water. In contrast to iron oxides, it is transparent to exciting laser light, which

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allows study  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> by time-resolved laser fluorescence spectroscopy (TRLFS).

The anions of carboxylic acids were chosen as ligands because simple organic acids in soils may be released by decay of plant, animal, and microbial tissues [5] and their anionic forms are complexing agents for hard cations such as Eu<sup>3+</sup>. We also studied carbonate ion (CO<sub>3</sub><sup>2-</sup>), which is the most reactive species toward Eu(III) in natural carbonate systems (CO<sub>2</sub>(g)/HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>).

## 2. Materials and methods

### 2.1. Materials

Synthetic mineral,  $\alpha$ -alumina, from Interchim (pure 99.99%) was used. However, its surface could be carbonated. Consequently, a protocol was used to obtain a homoionic Na<sup>+</sup>- and carbonate-free surface: the solid was first washed with a 0.1 M NaOH carbonate-free solution and rinsed with deionized water.

The surface was analyzed by X-ray photoelectron spectroscopy (XPS) to know the crystalline form of alumina at the interface: no modification was detected. The point zero net proton charge (PZNPC) was measured by titrations at three different NaClO<sub>4</sub> ionic strengths (0.001, 0.01, and 0.1 M). It was found to be pH<sub>PZNPC</sub> = 9.1, which confirms that no carbonate was adsorbed onto  $\alpha$ -alumina [6]. Finally, the N<sub>2</sub>-BET surface area was measured as 12(±0.2) m<sup>2</sup>/g.

### 2.2. Solutions

#### 2.2.1. Radioisotope <sup>152</sup>Eu solution

Liquid scintillation was used to count isotope 152 of europium, a  $\beta$  emitter (half-life 13.5 yr). The used solution contains equal natural europium.

#### 2.2.2. Other aqueous solutions

To avoid carbonation from atmospheric CO<sub>2</sub>, we worked with carbonate-free aqueous solutions in closed batches, and the volume of air over the aqueous solutions was limited (less than 10% volume of solution) and replaced by argon.

The NaCl or HCl solutions were prepared by diluting weighted amounts of Suprapur products (Merck) with Millipore water purged with argon. NaOH aqueous solutions were prepared similarly from weighted amounts of 50% NaOH from Aldrich as developed by Sipos et al. [7].

The solutions of ligands were prepared by weighting NaCl, NaCH<sub>3</sub>COO, Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and NaHCO<sub>3</sub> Suprapur products (Merck). These products were dissolved in Millipore water purged with argon.

The pH of the different batches was adjusted with HCl or NaOH carbonate-free solutions and measured with a combination microelectrode (Mettler Toledo). The outer reference cell was filled with a saturated NaCl/KCl solution. The combined glass microelectrode was calibrated with solutions of known [H<sup>+</sup>] and same ionic strength as the working solutions, which means that it was calibrated in  $-\log_{10}[\text{H}^+]$  units, not in pH ( $-\log_{10} a_{\text{H}^+}$ ).

## 3. Procedures and techniques

### 3.1. Experiments with radionuclides at trace concentrations (<10<sup>-9</sup> mol L<sup>-1</sup>)

The protocol used to study europium(III) sorption with trace radionuclide concentrations on  $\alpha$ -alumina in different binary and ternary systems is the same as described elsewhere for americium and uranium [8–10]. Trace concentrations are defined as total concentrations of an element negligible with regard to exchange capacity of the surface.

Sorption on the batch walls was checked, and found not significant for different  $-\log_{10}[\text{H}^+]$ , ionic strength. The time necessary to achieve equilibrium conditions was verified and is less than 1 day. Sorption measurements were carried out as a function of pH in 10-ml polycarbonate centrifuge tubes. After being spiked with <sup>152</sup>Eu and shaken for at least 2 days, the samples were centrifuged for 2 h at 60,000 rpm before sampling of the supernatant solutions and pH measurements.

The samples were analyzed by beta counting with a Packard Tricarb 2700 liquid scintillator enough time for obtaining an error of less than 1%. This counting follows a Poisson law: relative error is inversely proportional to count number. The data uncertainties were estimated by considering the error in each operation (weighting, volume, counting) in batch sorption experiments.

Concerning the ternary systems, preliminary measurements showed that oxalic, acetic, and aqueous carbonic acids did not change the time needed to achieve equilibrium conditions of Eu(III) sorption on  $\alpha$ -alumina. The influences of ligand concentrations were studied by sorption experiments of metal with other chemical conditions fixed. Sorption isotherms were determined as a function of ligand concentrations.

### 3.2. Studying the influence of europium(III) concentration

We checked if europium(III) sorption behavior is the same whatever its concentration. The aim was not to refit the model, but rather to check whether the data measured at high europium concentrations could still be interpreted with the model and the thermodynamic constants determined from data at trace concentrations.

The solutions were always spiked with <sup>152</sup>Eu. To adjust its concentration, natural Eu<sub>2</sub>O<sub>3</sub> was added to reach a total concentration of up to 10<sup>-4</sup> M. All the parameters were fixed excepted the Eu(III) concentration.

## 4. Theoretical calculations

### 4.1. Description of the sorption model

Surface complexation formulas (SCFs) are very popular for interpreting sorption of aqueous ions on oxide and others minerals. However, ion-exchange theory (IET) can also be used [8–10]. Both models are able to describe such mechanisms as surface complexation, ion exchange, and any other chemical surface reactions. However, ion-exchange theory assumes

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