Sorption and desorption of Eu(III) on alumina


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Introduction

For long term performance assessment of radioactive waste management, knowledge of long half-life lanthanide and actinide ions interactions with mineral surfaces and humic substances is imperative.1–3 Sorption and migration processes of radionuclides are considered to be important since they control the distribution, mobility, cycling and bioavailability of lanthanides and actinides in the environment. Therefore, it is necessary to characterize the sorption properties of radionuclides on mineral surfaces and also the reaction mechanisms involved.

A batch technique was employed to study the sorption of Eu(III) on Al2O3 as a function of pH, ionic strength and presence of humic substances by NORDEN et al.4 and WANG et al.5 It was found that the sorption of Eu(III) onto alumina was strongly dependent on pH and weakly dependent on ionic strength. Humic substances could increase the sorption of Eu(III) at low pH values and reduce Eu(III) sorption at high pH values. The distribution of metal ions in ternary systems of metal ion/mineral particle/humic acid is mainly governed by humic substances, especially if it forms strong complexes with metal ions.5,6 The presence of humic acid increases the sorption of Eu, Yb, Am, Cm and U on mineral surfaces at acidic pH values but reduces the metal ions sorption at high pH values.5–11 The increase in sorption is explained by the adsorption of humic acid onto the mineral surfaces followed by the interaction of metal ions with humic acid sorbed onto the surfaces, whereas the reduction of sorption is explained by the formation of complexes by humic acid with metal ions in solution, which stabilize the metal ions in aqueous solution. Conversely, if the complexation of metal ion with functional groups of humic acid sorbed on the mineral surfaces is weaker than that with the surface hydroxyls of the mineral, a negative effect of humic acid on metal ion sorption is observed. The effects of different humic substances on the sorption of metal ions differ because of the different properties of humic substances.

The addition sequence of Yb(III) and fulvic acid (FA) to the alumina-NaNO3-Yb-FA-water system was changed to check for reversibility of the sorption process.5 In these experiments, Eu or FA was allowed to react with bare alumina first and the results showed that the distribution coefficients of Yb(III) sorption were different for the two different addition sequences. The distribution coefficients of Yb(III) in the system of prior FA addition were slightly higher than those with prior Yb(III) addition. The results were explained by the assumption that the fulvic acid sorbed primarily onto alumina exhibits higher affinity for Yb(III) than the interaction of Yb(III) or fulvic acid-Yb(III) complexes with alumina.

WANG et al.12 studied the effects of different addition sequences of Cm(III) and humic acid to alumina suspension on Cm(III) sorption and species in the ternary system by using time resolved life fluorescence spectroscopy (TRLFS) and found that in the solutions of different addition sequence different species of Cm(III) were formed with humic acid and alumina before equilibration. The equilibration time for microcosmic structural change was quite long (more than 10 days), and the same species of Cm(III) was found in the ternary systems afterwards. Consequently, no effect of addition sequence of Cm(III) and humic acid to alumina solution on the equilibrium sorption of Cm(III) onto alumina was found.

The two different results in References 5 and 12 may be attributed to the difference between humic acid and fulvic acid, and the differences between nuclides, alumina batches, etc. The complex interactions within the metal ions-humic acid-alumina ternary system can obviously be described by (1) metal complexation by free surface hydroxyls of alumina, (2) metal-humic substance complexation in solution and subsequent
sorption of the complex onto alumina, and (3) metal complexation with humic acid sorbed on the alumina surface.

Europium belongs to the lanthanide group and only the trivalent oxidation state is stable in water. The ionic radii are almost the same for all the trivalent lanthanide ions and Am$^{3+}$, which results in a similar chemical behavior. Eu is often taken as a chemical analog for trivalent actinide ions. Thus, it is necessary to study the behavior of Eu(III) in the environment.

This paper is an extension of our previous papers,\textsuperscript{5,13,14} where we studied the effects of pH, ionic strength and fulvic acid on Eu and Yb sorption onto alumina, bentonite and red earth, the diffusion of Eu in compacted bentonite. The main purpose of this paper is to study the effects of pH and fulvic acid on the sorption and desorption of Eu(III) onto alumina, and of the difference in addition sequences of fulvic acid and Eu(III) to alumina/fulvic acid/Eu ternary systems on the sorption of Eu(III) onto alumina/alumina-fulvic acid surfaces.

**Experimental**

Chromatographic Al$_2$O$_3$ (100–200 mesh) was purchased from the Wu-Xi chemical reagent factory (Shanghai, China). Prior to the experiments, the oxide was washed with distilled-deionized water until a constant electrical conductivity was obtained. The washed Al$_2$O$_3$ was dried at 105 °C for 2 hours, and then placed on a shallow dish inside a desiccator over saturated NaCl solution. The alumina was characterized by potentiometric titration and its pH$_{zpc}$ (zero point of charge) was found to be 7.5.\textsuperscript{5}

Fulvic acid from the dark loessial soil (Gansu province, China) was used in this work and characterized, by its elemental composition being C: 50.15%, H: 4.42%, N: 5.38%, S: 0.49%, O: 35.96%.\textsuperscript{15} The concentration of FA was determined by UV-vis spectrophotometric analysis at wavelength of 254 nm and in presence of 0.1M NaCl. The concentration of Eu(III) was analyzed by using inductively coupled plasma-mass spectroscopy (ICP-MS).

The sorption of Eu onto alumina was studied by a batch technique. The experiments were carried out at pH 4–6 and in 1M NaCl. Sodium chloride, alumina, Eu(III), fulvic acid, HCl or NaOH were added to achieve the desired background electrolyte concentration, FA concentration and pH of aqueous solutions.

Polyethylene tubes were used in the batch experiments. The test tubes were shaken for 3 days so as to reach the equilibration states. From kinetic study, the time was sufficient to achieve time-dependent equilibration. The solid phase was separated from the aqueous one by centrifugation for 15 minutes at 4000 rpm. (The sorption of Eu on the tube wall was negligible).

For desorption experiments, after centrifugation at the end of sorption experiments, half of the supernatant was pipetted and the equal volume of background electrolyte solution was added. The pH was adjusted with 0.01M HCl or NaOH to obtain the same pH values as in sorption experiments. Then the mixture was shaken and centrifugation at the same conditions as in sorption experiments.

The sequences of additions were, respectively: (1) alumina, water, NaCl solution, Eu, pH adjuster, 3 days, FA, pH adjuster, 3 days; (2) alumina, water, NaCl solution, FA, pH adjuster, 3 days, Eu, pH adjuster, 3 days.

The controlled column experiments were conducted with 1.5 g alumina which was packed in a 4×0.8 cm glass tube jacketed by constant temperature water (20 °C). It is necessary to note that radionuclide $^{152,154}$Eu(III) was used in the column experiments. Before the radionuclide injection, the columns were percolated with 1M NaCl solution at the fixed flow rate for two or three days.

**Results and discussion**

**Kinetic study**

The time dependent sorption of Eu(III) onto alumina was carried out at pH 4.4±0.1 in the presence of 1M NaCl. The results are shown in Fig. 1. From the figure it is clear that the sorption of Eu(III) to alumina is rather quick and thirty hours are enough to get time independent values. According to the kinetic results, in the batch experiments 3-day shaking was used.