

## Effects of Calcium Ions on the Sorption of Am(III) and Eu(III) onto Kaolinite in the Presence of Humic Acid

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The sorption of actinides onto minerals depending on groundwater chemistry plays an important role in the safety aspects of geological disposal of high-level waste. The effects of Ca(II) on the sorption of Am(III) and Eu(III) onto kaolinite in the presence of humic acid (HA) were examined in this study. Distribution coefficients ( $K_d$ ) of Am(III) and Eu(III), and the fractional adsorption ( $f_{HA}$ ) of HA on kaolinite were determined by a batch method under initial Ca(II) concentrations of 0 to  $1.0 \times 10^{-3}$  M at a constant ionic strength of 0.1 M ( $\text{NaClO}_4$ ) and pH region from 3.5 to 10 in an  $\text{N}_2$  atmosphere at 298 K. The  $K_d$  increased with increasing Ca(II) concentrations in regions higher than  $1.0 \times 10^{-4}$  M and in the range of pH 7 to 10. In this pH region,  $f_{HA}$  was also enhanced by introducing Ca(II). Concentrations higher than  $1.0 \times 10^{-4}$  M Ca(II) can be regarded as a bridge between kaolinite and HA. It is very likely that the increase in the adsorbed HA on kaolinite, where the HA includes very stable Am(III) and Eu(III) humates, results in an increase in the Am(III) and Eu(III) distribution coefficients.

**KEYWORDS:** Americium, Europium, Humic acid, Sorption, Kaolinite, Calcium

### I. Introduction

Migration of actinides in the geosphere is an essential safety aspect of radioactive waste disposal. Aquatic transport of actinides is controlled by sorption on geologic media. Humic substances (HS) occur widely in subsurface regions and in some cases even in deep groundwater<sup>1,2</sup>. HS affects the sorption of metal ions on minerals due to both the formation of complexes with metal ions<sup>3,4</sup> and the adsorption of these complexes on minerals<sup>3,5</sup>.

Sorption behavior of various metal ions has been extensively studied for a number of minerals<sup>6-8</sup>) in a ternary system consisting of metal ions, HS, and a mineral. Drastic changes in metal ion sorption were observed by introducing HS. Murphy and Zachara<sup>9</sup>) clarified that the metal ion sorption in the ternary system is enhanced in the lower pH region while being depressed in the relatively higher pH region in comparison with sorption in the absence of HS.

In recent years, modeling approaches have attempted to clarify the sorption process in a similar ternary system using interactions between the respective components. Zachara *et al.*<sup>10</sup>) studied Co(II) sorption on minerals and concluded that sorption behavior was satisfactorily elucidated by a model based on the linear additivity rule. Samadfam *et al.*<sup>11</sup>) studied Am(III) and Cm(III) sorption and treated similarly. However, the linear additivity approaches were not always successful in the prediction of the metal ions sorption<sup>12,13</sup>). Vermeer *et al.*<sup>12</sup>) suggested that the electrostatic fields both of mineral surfaces and HS are affected by the respective charge, and the metal ions adsorptivity to the mineral and HS is different from the isolated ones.

Apart from the intrinsic question in the ternary system, there is a practical problem in the sorption. It is possible that a change in groundwater chemistry gives additional interactions in the ternary system. Calcium ions are common polyvalent cations in groundwater, where they are found in concentrations of  $10^{-5}$ - $10^{-3}$  M<sup>1</sup>). When Ca(II) is introduced into such a ternary system, a change in actinide sorption is conceivable, since the HS adsorption on minerals is influenced by the Ca(II) and competition of actinides with Ca(II) for binding sites on both the mineral surfaces and HS. However, the role of Ca(II) in this ternary system has not been studied. The purpose of this paper is to clarify the effects of Ca(II) on distribution coefficients ( $K_d$ ) in such ternary systems consisting of Am(III) or Eu(III), as an analogue for trivalent actinides, together with humic acid (HA), and kaolinite.

### II. Experimental

#### 1. Materials

Humic acid (HA) was obtained from the Aldrich Co. (Lot No. 01828JZ). The carboxylic group capacity and ash content of the purified HA were 4.7 eq / kg and less than 1 percent, respectively. Kaolinite (2-5  $\mu\text{m}$ ) from the Iwamoto Mineral Co. was used after being washed with deionized water three times and dried. No contaminant minerals were detected in the kaolinite by X-ray diffraction. Commercially available Am-241, 10  $\mu\text{g}$  (1.06 MBq), in the form of  $\text{AmO}_2$  deposited on a thin silver foil was purchased from the Japan Radioisotope Association. An  $\text{NH}_4$ -type cation exchange column (Muromac AG50W  $\times$  8) was used to separate the silver from the Am. Europium-152 was purchased from the Japan Radioisotope Association as europium chloride in 0.1 M nitric acid. The activity of the solution was 1.05 MBq /

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mdm<sup>3</sup>. The solution was diluted 20 times by 0.1 M perchloric acid before use.

All other chemicals used in the experiment were of reagent grade and were obtained from Wako Pure Chemical Industries, Ltd. or Kanto Kagaku.

## 2. Procedure

Kaolinite suspensions of 0.20 dm<sup>3</sup> (1.0 g-kaolinite / dm<sup>3</sup>) were prepared with HA concentrations of 0 and 10 ppm, and CaCl<sub>2</sub> concentrations of 0, 1.0 × 10<sup>-5</sup>, 1.0 × 10<sup>-4</sup>, and 1.0 × 10<sup>-3</sup> M at a constant ionic strength of 0.1 M (sodium perchlorate). These suspensions were each stirred in a polypropylene beaker for 7 days and then placed in an N<sub>2</sub> atmosphere (CO<sub>2</sub>-free). The suspensions in the N<sub>2</sub> atmosphere were stored over night. After the addition of 50 μ dm<sup>3</sup> of the radionuclide solution, the suspensions were adjusted to a pH of 10. Then, aliquots of 5.0 × 10<sup>-3</sup> dm<sup>3</sup> were transferred from the suspensions to polypropylene vials with airtight caps. Repeated decreases in pH values in steps of about 0.5 allowed the removal of additional aliquots until the pH value reached about 3.5. Equilibrium was achieved by shaking for 48 h in a 298 K water bath. This period was sufficient, judging from the results of a preliminary kinetic experiment. When equilibrium was reached, the liquid and solid (kaolinite) phase were separated by centrifugation at 3000 rpm for 10 min. The final pH of the supernatant of the suspension was measured. The supernatant radioactivity was measured by γ-counting. Three molar hydrochloric acid was added to the solid phase and the suspension was shaken overnight. The eluate was again centrifuged and the radioactivity was measured by γ-counting. The distribution coefficients in the absence (K<sub>d</sub><sup>0</sup>) and presence of HA (K<sub>d</sub>) were obtained from liquid and solid phase radioactivity as

$$K_d^0, K_d = C_s / C_{aq} \quad (1)$$

where C<sub>s</sub> is the concentration of nuclides in the solid phase in mol / kg-kaolinite, and C<sub>aq</sub> is the concentration of nuclides in the aqueous phase in mol / dm<sup>3</sup>.

The adsorption of HA onto kaolinite was also determined. The absorbance of the HA solution equilibrated in kaolinite suspension prepared as above was measured using a Shimadzu UV / VIS spectrophotometer at 265 nm. The fractional adsorption (f<sub>HA</sub>) was derived using the following equation,

$$f_{HA} = (C_{HA-total} - C_{HA-aq}) / C_{HA-total} \quad (2)$$

where C<sub>HA-total</sub> is the initial HA concentration, and C<sub>HA-aq</sub> is the HA concentration of the aqueous solution after separation from the kaolinite.

The experimental details are described elsewhere<sup>11</sup>.

## III. Results and Discussion

### 1. Adsorption of Humic Acid on Kaolinite

In Fig. 1, the fractional adsorption (f<sub>HA</sub>) of humic acid (HA) onto kaolinite is plotted as a function of pH at different initial Ca(II) concentrations. When the Ca(II) concentration in the solution is low (0 and 1.0 × 10<sup>-5</sup> M), f<sub>HA</sub>

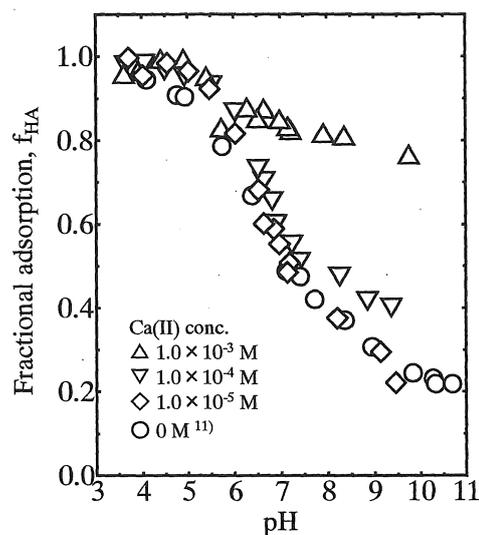
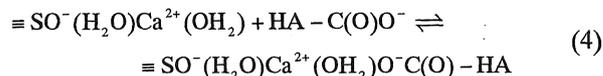
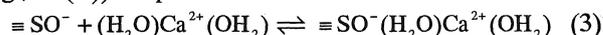


Fig. 1. Fractional adsorption of humic acid on kaolinite (f<sub>HA</sub>) as a function of pH with varying initial Ca(II) concentrations at 298 K. The system contains 1.0 g kaolinite and 10 mg humic acid per liter of solution.

significantly decreases as the pH increases above a pH of 6. Moreover, the fraction of HA in the solution phase at a pH of 10 is 80 percent. The decrease of f<sub>HA</sub> is regarded as the result of the electrostatic effect. Both the HA functional groups and kaolinite surface hydroxyl groups dissociate and are negatively charged as pH values increase.

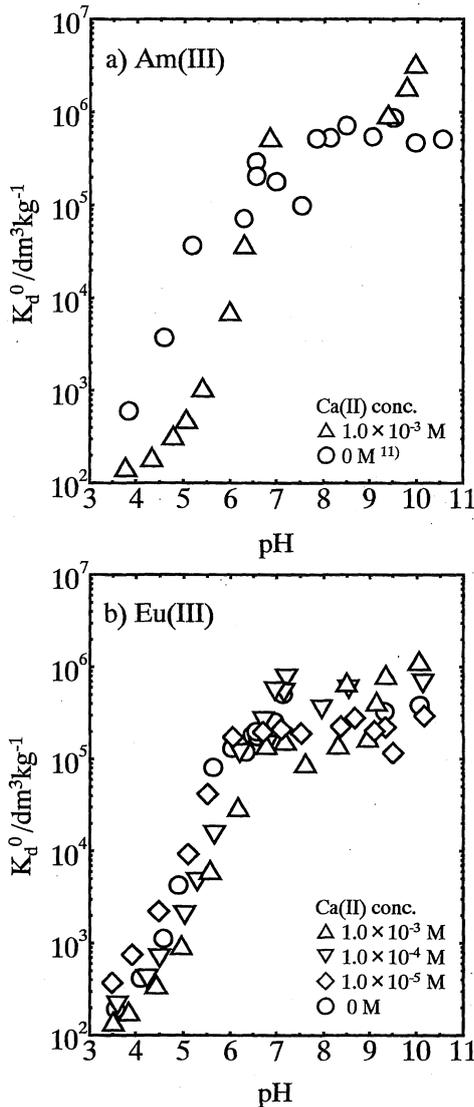
When Ca(II) concentrations are higher than 1.0 × 10<sup>-4</sup> M, f<sub>HA</sub> is enhanced when pH values are above 6. Over 70 percent of the HA remains adsorbed on kaolinite at a pH of 10 with a Ca(II) concentration of 1.0 × 10<sup>-3</sup> M. This suggests that in alkaline conditions the bridging of Ca(II) between HA and kaolinite has an important role in HA adsorption. Enhancement of HA adsorption on minerals in the presence of Ca(II) has previously been reported by several authors. Tipping<sup>14</sup>, for example, observed enhanced humic adsorption on iron oxides. Schlautman and Morgan<sup>15</sup> described the adsorption reactions when bivalent cations (e.g., Ca(II)) are present as



where ≡SO<sup>-</sup> represents deprotonated surface hydroxyl groups of kaolinite. The cation(II) attaches an HA carboxyl group to the kaolinite surface site. The enhancement of HA adsorption on kaolinite with increasing Ca(II) can be understood when viewed from the perspective of the bridging reaction process.

### 2. Sorption of Am(III) and Eu(III) on Kaolinite

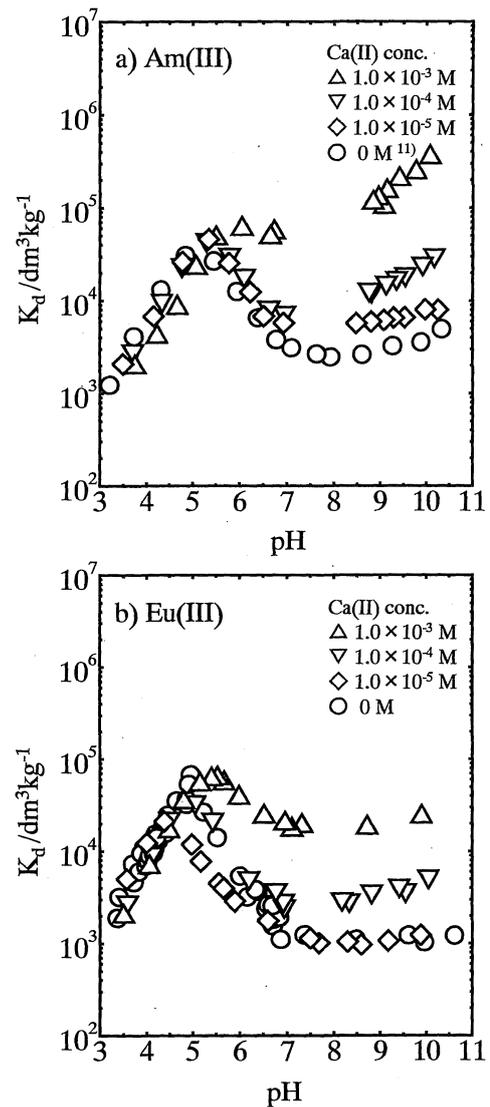
Figure 2 shows the distribution coefficients (K<sub>d</sub><sup>0</sup>) of Am(III) and Eu(III) onto kaolinite in the absence of HA as a function of pH and Ca(II) concentrations. The data for



**Fig. 2.** Distribution coefficients of a) Am(III) and b) Eu(III) for kaolinite (1.0 g / liter) in the absence of humic acid as a function of pH with varying initial Ca(II) concentrations at 298 K.

Am(III) are slightly dispersed but reliable because they are similar to those for Eu(III), which are easily available and reproducible. As general observations<sup>11, 16)</sup>, sorption increases with increasing pH,  $K_d^0$  remarkably increases in the pH region from 3 to 7, and sorption nearly reaches saturation at pH values over 7. Fairhurst *et al.*<sup>16)</sup> reported that the zeta potential of kaolinite surfaces decreased with increasing pH due to deprotonation of the surface hydroxyl groups of kaolinite. Both electrostatic interaction and site-specific binding occur between the positively charged Eu(III) species and the oppositely charged mineral surfaces.

Trivalent actinide sorption onto kaolinite is not much sensitive to the presence of Ca(II). This indicates that substantially no or very weak competition of Ca(II) with tracer actinides(III) occurs on the kaolinite surfaces when the concentration of Ca(II) is below  $1.0 \times 10^{-3}$  M. It is possible that inner-sphere type sorption occurs in this



**Fig. 3.** Distribution coefficients of a) Am(III) and b) Eu(III) for kaolinite (1.0 g / liter) in the presence of humic acid (10 ppm) as a function of pH with varying initial Ca(II) concentrations at 298 K.

system. Stumpf *et al.*<sup>15)</sup> investigated the sorption process of Cm(III) onto kaolinite by time-resolved laser fluorescence spectroscopy. In the low pH region, the outer-sphere complex of Cm(III) with kaolinite occurs, while, with a pH rise, the sorption processes change to the inner-sphere complex on the aluminol edge sites.

### 3. Sorption of Am(III) and Eu(III) in the Presence of Humic Acid and Ca(II)

**Figure 3** shows the effects of Ca(II) on the distribution coefficient ( $K_d$ ) of Am(III) and Eu(III) for kaolinite in the presence of HA as a function of pH. The sorption behavior for Am(III) is similar to that for Eu(III). An enhancement of  $K_d$  at a low pH and a decrease at higher pH values are observed as compared with the system with no HA. Several reports showing the same behavior are available<sup>9, 11, 16)</sup>.

Between pH values of 3 and 5,  $K_d$  values increase steeply with pH and are independent of Ca(II) concentrations. Around a pH of 5, there is a distinct sorption peak. When the Ca(II) concentrations in the solution are low ( $0$  and  $1.0 \times 10^{-5}$  M),  $K_d$  values markedly decrease with an increase in pH beyond the peak. With Ca(II) values higher than  $1.0 \times 10^{-4}$  M,  $K_d$  is enhanced with increasing Ca(II) at pH values of 6 to 10. The  $K_d$  value at a pH of 10 and a Ca(II) concentration of  $1.0 \times 10^{-3}$  M is two orders of magnitude larger than that in the absence of Ca(II).

In comparison between Fig. 1 and 3, one can notice some relationship between the adsorption of HA and the sorption of Am(III) and Eu(III). Between pH values of 3 and 5, the values of both  $f_{HA}$  and  $K_d$  are not affected by introducing Ca(II). At pH values of 6 to 10, the values both of  $f_{HA}$  and  $K_d$  increase as Ca(II) concentrations increase higher than  $1.0 \times 10^{-4}$  M. Since actinides(III) have a strong affinity to HA, these observations allow the following assumption that Am(III) and Eu(III) sorb on kaolinite as humate. The bridging between both the negatively charged HA and a mineral by the addition of Ca(II) enhances the sorption of actinides(III) humate onto the mineral.

#### IV. Conclusions

In the presence of humic acid, sorption of Am(III) and Eu(III) onto kaolinite was measured at varying Ca(II) concentrations as a function of pH. The derived distribution coefficients increased when the Ca(II) concentrations exceeded  $1.0 \times 10^{-4}$  M in the pH regions from 6 to 10. In this pH region, the adsorption of humic acid on kaolinite was also enhanced by introducing Ca(II), which can be regarded as a bridge between kaolinite and humic acid. It is very likely that the increase in the adsorbed HA on kaolinite, where the HA includes very stable Am(III) and Eu(III) humates, results in an increase in the Am(III) and Eu(III) distribution coefficients. Consequently, Ca(II) plays a significant role for actinides(III) sorption on minerals, mainly through the adsorption/desorption process for HA.

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#### REFERENCES

- 1) Japan Nuclear Cycle Development Institute: H12 Project to Establish the Scientific and Technical Basis for HLW Disposal in Japan, Supporting Report 1, JNCTN 1410 2000-002, III 48- III 72 (2000).
- 2) C. H. Ho, N. H. Miller, "Effect of humic acid on uranium uptake by hematite particles," *J. Colloid Interface Sci.* 106, 281 (1985).
- 3) F.J. Stevenson, *HUMUS CHEMISTRY*, 2<sup>nd</sup> Edition, John Wiley & Sons, New York (1994).
- 4) V. Moulin, J. Tits, G. Ouzounian, "Actinide speciation in the presence of humic substances in natural water conditions," *Radiochim. Acta* 58/59, 179 (1992).
- 5) J. A. Davis, "Complexation of trace metals by adsorbed natural organic matter," *Geochim. Cosmochim. Acta.* 58, 553 (1994).
- 6) L. Righetto, G. Bidoglio, G. Azimonti, I. R. Bellobono, "Competitive Actinide Interactions in Colloidal Humic Acid-Mineral Oxide Systems," *Environ. Sci. Technol.* 25, 1913 (1991).
- 7) B. Allard, V. Moulin, L. Basso, M. T. Tran, D. Stammose, D. "Americium sorption on alumina in the presence of humic materials," *Geoderma.* 44, 181 (1989).
- 8) Y. Takahashi, Y. Minai, S. Ambe, Y. Makide, F. Ambe, "Comparison of adsorption behavior of multiple inorganic ions on kaolinite and silica in the presence of humic acid using the multitracer technique," *Geochim. Cosmochim. Acta.* 63, 815 (1999).
- 9) E. M. Murphy, J. M. Zachara, "The role of sorbed humic substances on the distribution of organic and inorganic contaminants in groundwater," *Geoderma* 67, 103 (1995).
- 10) J. M. Zachara, C. T. Resch, S. C. Smith, "Influence of humic substances on  $Co^{2+}$  sorption by a subsurface mineral separate and its mineralogic components," *Geochim. Cosmochim. Acta.* 58, 553 (1994).
- 11) M. Samadfam, T. Jintoku, S. Sato, H. Ohashi, T. Mitsugashira, M. Hara, Y. Suzuki, "Effects of humic acid on the sorption of Am(III) and Cm(III) on kaolinite," *Radiochim. Acta* 88, 717 (2000).
- 12) A. W. P. Vermeer, J. K. McCulloch, W. H. van Riemsdijk, L. K. Koopal, "Metal ion adsorption to complexes of humic acid and metal oxides: Deviations from the additivity rule," *Environ. Sci. Technol.* 33, 3892 (1999).
- 13) I. Christl, R. Kretzschmar, "Interaction of copper and fulvic acid at the hematite-water interface," *Geochim. Cosmochim. Acta* 65, 3435 (2001).
- 14) E. Tipping, "The sorption of aquatic humic substances by iron oxides," *Geochim. Cosmochim. Acta.* 45, 191 (1981).
- 15) M. A. Schlautman, J. J. Morgan, "Adsorption of aquatic humic substances on colloidal-size oxide particles: Influence of solution chemistry," *Geochim. Cosmochim. Acta* 58, 4293 (1994).
- 16) A. J. Fairhurst, P. Warwick, S. Richardson, "The effect of pH on Europium-mineral interactions in the presence of humic acid," *Radiochim. Acta* 69, 103 (1995).
- 17) Th. Stumpf, A. Bauer, F. Coppin, J. I. Kim, "Time-resolved laser fluorescence spectroscopy study of the sorption of Cm(III) onto smectite and kaolinite," *Environ. Sci. Technol.* 35, 3691 (2001).