

The Effect of Calcium Ions on Uranium (VI) Sorption onto Kaolinite

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1. Introduction

The groundwater is considered as the main pathway for migration of soluble radionuclides in deep geological nuclear disposal system. In weakly alkaline groundwater system which contains abundant calcium and carbonate ion, uranium (VI) is highly soluble according to the predominant formation of $\text{CaUO}_2\text{CO}_3^{2-}$ and $\text{Ca}_2\text{UO}_2\text{CO}_3(\text{aq})$ species. This work presents the effect of calcium metal ions on the uranium (VI) sorption onto kaolinite by means of time-resolved laser fluorescence spectroscopy (TRLFS) and inductively coupled plasma optical emission spectroscopy (ICP-OES).

2. Materials and Methods

2.1 Materials

Kaolinite (kGa-2) was used as obtained from The Clay Minerals Society (USA). The mineral was washed by using 0.5 M NaClO_4 with 3 times for 2 days to replace exchangeable cations as Na-form and then rinsed 5 times with deionized water. After washing and rinsing, kaolinite was air-dried. X-ray diffraction (XRD) analysis of the mineral showed that the major presence of kaolinite in the clay sample. N_2 -BET measurement revealed that a surface area of the mineral is $20.24 \pm 0.05 \text{ m}^2/\text{g}$.

Deionized water (18.2 M Ω) obtained from purification system (Milli-Q/Rios, Millipore) was used to prepare all solutions. An uranium(VI) stock solution was prepared by dissolution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck) in 1 M HClO_4 . A stock solution was diluted to prepare 8×10^{-5} M uranium(VI) solutions. By adding NaHCO_3 (99.7-100.3%), the concentration of initial carbonate ions in the solutions was kept at 0.05 mol/L. The concentration of initial calcium metal ions was controlled in the range between 0 to 15 mmol/L by adding CaCl_2 . The pH of solutions was buffered with 0.075 M TRIS at pH 8.1. Ionic strength of 0.1 M was controlled by using NaClO_4 . All chemicals utilized in the present work were analytical grade, and solutions equilibrated under atmospheric CO_2 .

2.2 Experiments

Prior to fluorescence and sorption experiments, the solutions were filtered by 0.02 μm syringe filter to remove possible calcite precipitates (CaCO_3). ICP-OES analysis showed the Ca concentration decreased after

filtration due to precipitation of calcium ions. However, the uranium concentration remained unchanged even by filtration. Thus, uranium (VI) concentration was not affected by the formation of calcite.

The fourth harmonic beam of Nd:YAG laser (266 nm) was used to measure the fluorescence emission of aqueous solutions. The emitted fluorescence was transferred to Czerny-Turner spectrometer coupled with ICCD camera through optic fiber. The fluorescence lifetimes were determined with time-resolved fluorescence intensities.

For the sorption experiments, pre-treated kaolinite was mixed with calcium uranyl carbonate solution with the S:L ratio of 0.5g/10 ml in 15 ml centrifugal vial. The suspensions were continuously shaken at 200 rpm to homogenize the sample for 60 hours. For the phase separation, samples were centrifuged at 3000 rpm for 30 min and successively filtrated with 0.02 μm syringe filter. All experiments were conducted in duplicate. The concentrations of Ca and U in supernatants were determined with ICP-OES. In addition, the uranium concentration results evaluated with ICP-OES were compared with those obtained by means of fluorescence spectroscopy based on the URAPLEX- UO_2^{2+} complexation in 0.1 M HNO_3 medium

3. Result and Conclusions

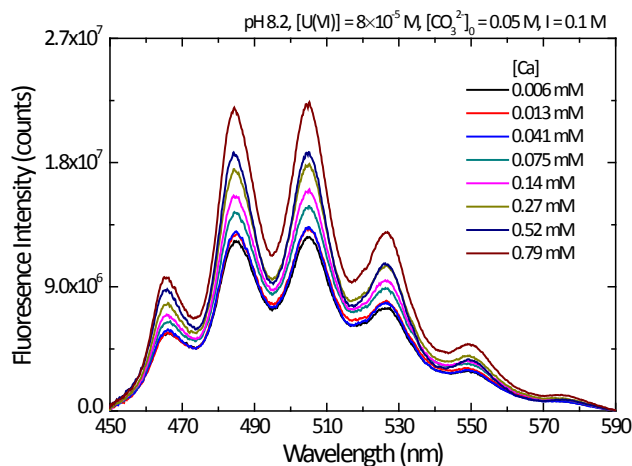


Fig. 1. $\text{Ca-UO}_2\text{-CO}_3$ spectra at various Ca concentration. Fluorescence is increasing at high Ca concentration.

The uranium(VI) fluorescence spectra measured at various calcium ion concentrations in aqueous solutions are given in Fig. 1. The fluorescence peak positions were determined by means of the Voigt peak

deconvolution, revealing five well-resolved fluorescence peaks located at 465, 484, 504, 526, and 550 nm. The fluorescence lifetimes were increased from 12.0 ns to 20.6 ns as increasing calcium concentration. The fluorescence peak positions and lifetimes determined in the present work indicates the major presence of $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ species, according to the reported spectroscopic data of $\text{Ca-UO}_2\text{-CO}_3$ complexes [1,2]. An increasing tendency of lifetimes with calcium concentration reveals that the U(VI) species with longer fluorescence lifetime becomes predominant as $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$. The spectroscopic properties determined in the present work along with data taken from the other literature are given at Table I.

Table I: Spectroscopic data of $\text{Ca-UO}_2\text{-CO}_3$

[Ca] (mM)	FL lifetime	[U] ($\times 10^{-4}$ M)
0.006	12.0 ns	0.80
0.013	12.2 ns	0.81
0.04	13.6 ns	0.81
0.08	14.9 ns	0.81
0.14	16.6 ns	0.80
0.27	18.0 ns	0.80
0.52	19.4 ns	0.87
0.79	20.6 ns	0.89
Reported data [2]	FL lifetime	Peak positions
$\text{UO}_2(\text{CO}_3)_3^{4-}$	11.6 ± 0.1	466-485-505-526-549
$\text{CaUO}_2(\text{CO}_3)_3^{2-}$	12.7 ± 0.2	466-485-505-527-550
$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$	29.2 ± 0.4	466-485-505-527-551

Fig. 2 shows the sorbed uranium concentration ratio after sorption reaction determined with the supernatant sample by using ICP-OES and URAPLEX- UO_2^{2+} fluorescence analysis method. Almost all of the samples showed that ca. 50 % of uranium was sorbed onto the kaolinite regardless of the initial calcium concentration. The distribution coefficient (K_d) was determined to be $(10.7 \pm 0.3) \times 10^{-3} \text{ m}^3/\text{kg}$. At that moment, the calcium concentration in the supernatant sample decreased and the decreased amount of Ca was more significant at higher initial calcium concentration (Table 2). Sorption of calcium metal ions onto kaolinite buffered the calcium concentration, therefore, even at high concentration of calcium, the formation of $\text{Ca-UO}_2\text{-CO}_3$ species was inhibited.

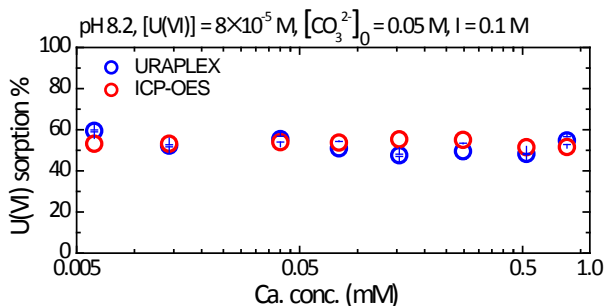


Fig. 2. Uranium(VI) sorption as a function of calcium concentration. Quantitative analysis of U was conducted by ICP-OES and URAPLEX- UO_2^{2+} fluorescence intensity.

Table II: Change in calcium concentration before and after sorption experiments. ($\times 10^{-5}$ M)

Ca conc. before sorption	Ca conc. after sorption	Decreased amount of Ca
0.60	1.92	- 1.32
1.27	2.12	- 0.85
4.07	3.94	0.13
7.53	6.57	0.96
13.6	12.1	1.50
26.7	13.4	13.3
52.4	10.7	41.7
79.3	11.3	68.0

Finally, it has been addressed that the formation of $\text{Ca-UO}_2\text{-CO}_3$ species hindered the sorption of uranium (VI) onto minerals such as natural bentonite [3] and goethite surface [4]. However, at sub-millimolar calcium concentration, the effect of the formation of $\text{Ca-UO}_2\text{-CO}_3$ on the uranium sorption to kaolinite is insignificant due to the sorption of Ca^{2+} ion predominant than uranium(VI).

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