

## U(VI) Interactions with Partially Fe(III)- or Ti(IV)-coated Silica

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### 1. Introduction

There has been great interest in the immobilizations and adsorption mechanisms of various toxic ions in aqueous solutions by using silica-based sorbents [1-2]. The adsorption reaction of a metal ion onto a metal (hydr)oxide surface is explained in terms of surface complexation. Due to their ubiquity in soils and sediments and high specific surface area, iron or titanium hydroxides (Fe or Ti oxides) around silicate minerals may play a role in the migration of actinides in groundwater. The interactions of actinides on immobile solid surfaces are important processes that determine retardation during transport.

In our previous published paper, Fe(III)- or Ti(IV)-ion effects on the adsorption behaviors of Eu(III), which is a chemical analogue of actinides, Am(III) and Cm(III), onto silica surface in the aqueous solution were investigated [3]. Here, the sorption of  $\text{UO}_2^{2+}$  from an aqueous solution on Fe(III)- or Ti(IV)-coated silica is discussed to understand the radionuclide migration which occurs in groundwater.

### 2. Experimental

Pretreated silica (particle size 40 to 63  $\mu\text{m}$ ; surface area 550  $\text{m}^2/\text{g}$ ), which was prepared by being dispersed in 3.7 M  $\text{HNO}_3$  for one day and washed with distilled water until wet silica surface was neutral, was dried in an oven at 120  $^\circ\text{C}$  for 6 h.

For the partial Fe(III) coating on the dried silica surface, proper amount of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was added with stirring to each silica with pH adjusting to 4.5. The partially Fe(III)-coated silica was filtered, washed with a pH 4.5  $\text{HClO}_4$  solution and distilled water three times each, and dried at 120  $^\circ\text{C}$  for 6 h sequentially.

For the partial Ti(IV) coating on the dried silica surface, certain amount of  $\text{Ti}(\text{O}i\text{Bu})_4$  was added with stirring to each silica. The partially Ti(IV)-coated silica was also filtered, washed with a  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{C}_6\text{H}_5\text{CH}_3$  (1:1) mixed solution three times, and dried in sequence at 120  $^\circ\text{C}$  for 6 h.

In each test, 500 mg of dissimilar Fe(III)- or Ti(IV)-coated silica was placed in 0.10 mM  $\text{UO}_2^{2+}$  in 0.16 mM  $\text{HClO}_4$  with a controlling ionic strength with 0.1 M  $\text{NaClO}_4$ . At this point, for the observation of a pH-dependent adsorption, 0.1 M  $\text{NaOH}$  under the  $\text{N}_2$  gas flow was properly added to each mixture, and the pH went up to 7 for U(VI) adsorption tests. Fluorescence of

U(VI) on Fe(III)- or Ti(IV)-coated silica was obtained from the sediments.

### 3. Results and discussion

Based on UV-vis absorption spectra and ICP-AES analysis, 0, 2.05, 3.81, 7.38, 13.8, and 21.3  $\mu\text{mol/g}$  (Fe/silica) Fe-coated silica and 0, 16.1, 40.5, 63.9, 324 and 407  $\mu\text{mol/g}$  (Ti/silica) Ti-coated silica were obtained when appropriate amounts of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Ti}(\text{O}i\text{Bu})_4$  were added in each silica for sample preparation.

At first,  $\equiv\text{Si-OH}$  in the pretreated dried silica ( $\text{SiO}_2$ ) is dissociated into surface  $\equiv\text{Si-O}^-$  and free  $\text{H}^+$ . Here, Fe(III) or Ti(IV) was primarily fixed on the negatively charged silica surface through the  $\equiv\text{Si-O-Fe}$  or  $\equiv\text{Si-O-Ti}$  structure. After then, hydrolyzed U-OH is assumed to be sorbed onto Fe(III)- or Ti(IV)-coated silica in aqueous U(VI) solutions. The U(VI) adsorption processes onto the partially Fe(III)- or Ti(IV)-coated silica involve the combination of U(VI) hydrolysis and the adsorption of the hydrolysis product,  $\text{U}^{\text{VI}}\text{-OH}$ , to produce  $\equiv\text{Si-O-Ti}(\text{or Fe})\text{-OH-U}^{\text{VI}}$  and/or  $\equiv\text{Si-O-Ti}(\text{or Fe})\text{-O-U}^{\text{VI}}$  in addition to  $\equiv\text{Si-OH-U}^{\text{VI}}$  and/or  $\equiv\text{Si-O-U}^{\text{VI}}$ , depending on the pH of the prepared solutions.

The adsorption of U(VI) onto the silica at various pH (ca. pH 3.5~pH 7) shows no influence of a surface coating by Fe(III). In contrast, Ti(IV)-coated silica showed higher U(VI) adsorption capacities as increasing the amount of Ti(IV) on silica surface.

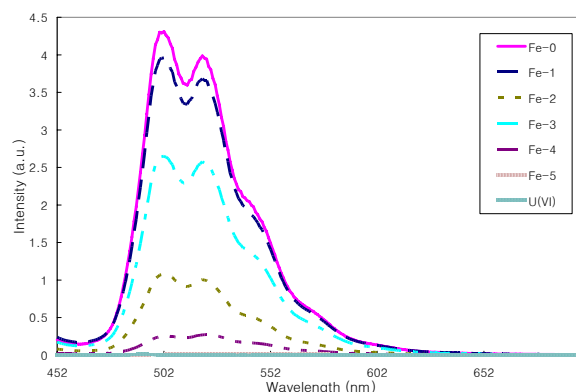


Fig. 1. Fluorescence spectra ( $\lambda_{\text{exc}} = 422 \text{ nm}$ ) of U(VI) on partially Fe(III)-coated silica according to the amount of coated Fe(III) at pH 5. (sample,  $\mu\text{mol/g}$  (Fe/silica); Fe-0 (0.0): Fe-1 (2.05): Fe-2 (3.81): Fe-3 (7.38): Fe-4 (13.8): Fe-5 (21.3): U(VI) (0.10 mM  $\text{UO}_2^{2+}$  in 0.16 mM  $\text{HClO}_4$  itself))

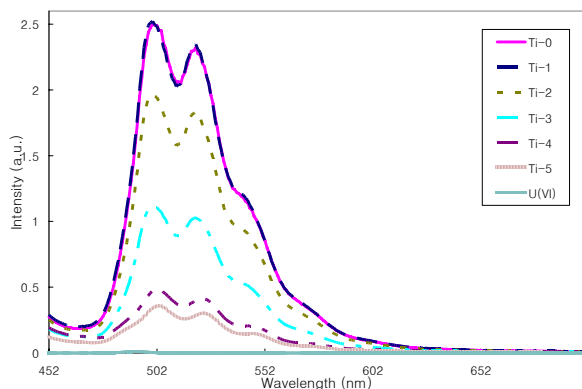


Fig. 2. Fluorescence spectra ( $\lambda_{exc} = 422$  nm) of U(VI) on partially Ti(IV)-coated silica according to the amount of coated Ti(IV) at pH 5. (sample,  $\mu\text{mol/g}$  (Ti/silica); Ti-0 (0.0): Ti-1 (16.1): Ti-2 (40.5): Ti-3 (63.9): Ti-4 (324): Ti-5 (407): U(VI) (0.10 mM  $\text{UO}_2^{2+}$  in 0.16 mM  $\text{HClO}_4$  itself))

However, as shown in Figures 1 and 2, the fluorescence decreased with an increased amount of coated Fe(III) as well as Ti(IV) even though the shape of the fluorescence spectra did not change.

Details addressing their possible interactions of U(VI) with partially Fe(III)- or Ti(IV)-coated silica will be discussed further.

#### 4. Summary

This study shows an example of foreign ion effects on the adsorption of  $\text{UO}_2^{2+}$  onto a mineral surface. Ti(IV) enhances U(VI) adsorption onto a silica surface. In contrast, Fe(III) coating on silica surfaces did not enhance adsorption of U(VI). In the fluorescence studies, it was found that Fe(III) and Ti(IV) considerably quenched the fluorescence of the adsorbed U(VI).

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