

## Sorption of Th(IV) ions onto TiO<sub>2</sub>: Effects of contact time, ionic strength, thorium concentration and phosphate

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The sorption of Th(IV) onto TiO<sub>2</sub> was studied by the batch technique as a function of pH and ionic strength at moderate concentration ( $10^{-4}$ – $10^{-5}$  mol/l) and in the presence and absence of phosphate. It was found that the sorption rate of Th(IV) was relatively slow, the sorption percent was abruptly increased from pH 2 to 4, and the sorption was decreased with increasing ionic strength as a whole. In the concentration range of Th(IV) from trace concentration to  $1.4 \cdot 10^{-4}$  mol/l and in the absence of phosphate, the sorption isotherms were roughly fitted the Freundlich equation at different ionic strengths and approximately constant pH. These sorption characteristics of Th(IV) onto TiO<sub>2</sub> were compared with those of uranyl on the same sorbent. In addition, the positive effect of phosphate on the sorption of Th(IV) onto TiO<sub>2</sub> was demonstrated obviously and can be attributed to strong surface binding of phosphate, and the subsequent formation of ternary surface complexes of Th(IV). The difference between the sorption characteristics of Th(IV) ions and uranyl ions onto TiO<sub>2</sub> is discussed.

### Introduction

Over the past few decades considerable interest was devoted to the studies of titanium dioxide (TiO<sub>2</sub>) as a sorbent. The sorption of alkali metals (<sup>22</sup>Na, <sup>134</sup>Cs, <sup>137</sup>Cs) onto TiO<sub>2</sub> was studied by BILEWICZ et al.,<sup>1</sup> SHABANA et al.,<sup>2</sup> and HASANY et al.,<sup>3</sup> and the Li<sup>+</sup><K<sup>+</sup><Rb<sup>+</sup><Cs<sup>+</sup> selectivity sequence was found in slightly acidic and neutral solutions, whilst in alkaline solutions it was partly reversed. The sorption of alkaline earth metal <sup>85</sup>Sr on TiO<sub>2</sub> from chloride medium was studied by SHABANA et al.<sup>2</sup> The sorption of transition elements (Zn, Ni, Cd, Mn, Hg, Zr, Hf, Cu, Co) and lanthanides(III) on TiO<sub>2</sub> was studied by many authors.<sup>3–7</sup> It was found that titanium oxide can be used to preconcentrate Zn(II), Cu(II), Ni(II), Mn(II), Zr(IV), Hf(IV) and lanthanides(III) by eluting them from the oxide column with a suitable eluant after their sorption on the oxide surface and in treatment of liquid radwaste containing radiocesium and radiostrontium. The sorption of actinides (UO<sub>2</sub><sup>2+</sup>, NpO<sub>2</sub><sup>+</sup>, Th<sup>4+</sup>) onto TiO<sub>2</sub> was studied by LIESER et al.,<sup>8</sup> JAKOBSSON et al.,<sup>7,9</sup> and GUPTA et al.,<sup>10</sup> respectively. The sorption and desorption of Th(IV) onto TiO<sub>2</sub> was investigated as a function of pH (1–11), ionic strength (0.005–0.1 mol/l NaCl, NaClO<sub>4</sub>), thorium concentration (from  $1 \cdot 10^{-9}$  to  $3 \cdot 10^{-2}$  mol/l), and carbonate concentration (up to  $10^{-2}$  mol/l) using <sup>234</sup>Th tracer and at ratio of solution volume to mass of adsorbent 100 ml/g.<sup>9</sup> It was found that the Th(IV) sorption onto TiO<sub>2</sub> is not dependent on the ionic strength at initial Th(IV) concentrations of  $10^{-7}$ – $10^{-9}$  mol/l and in the ionic strength range of 0.005–0.1 mol/l, that over a short pH interval (1–3). The distribution coefficient ( $K_d$ ) increases four orders of magnitude from 10 to  $10^5$  ml/g, that at pH 1.3, 2 and

ionic strength 0.1 mol/l NaClO<sub>4</sub>, a clear plateau, at which the surface is saturated, cannot be observed, and carbonate has no measurable influence on the sorption in the pH interval of 5 to 10.5 for a carbonate concentration below  $1 \cdot 10^{-2}$  mol/l.<sup>9</sup>

Laboratory studies in simple electrolytes have shown that metal oxides and clay minerals are strong sorbents of phosphate from aqueous solution<sup>11–15</sup> and that the thorium phosphate complexes are stable in the pH range of 0.7–3.<sup>16</sup> Therefore, a strong effect of phosphate may be expected on the extent of sorption of metal ions onto oxides.<sup>3</sup>

In our previous papers,<sup>17–19</sup> the sorption of UO<sub>2</sub><sup>2+</sup> and phosphate on silica were studied, the effects of contact time, pH and ionic strength, the absence and presence of phosphate and the sorption isotherms of UO<sub>2</sub><sup>2+</sup> at different pH values were determined.<sup>17</sup> The effects of pH, ionic strength and concentration on the sorption of Th(IV) on alumina and silica were investigated and the sorption isotherms of Th(IV) at different pH values were determined.<sup>18</sup> The sorption of UO<sub>2</sub><sup>2+</sup> onto TiO<sub>2</sub> was studied as a function of pH and ionic strength at moderate concentration ( $10^{-4}$ – $10^{-5}$  mol/l) and in the presence and absence of fulvic acid.<sup>19</sup> The present paper is an extension of these previous papers.<sup>17–19</sup> The aims were (1) to examine the effects of contact time between the TiO<sub>2</sub> and the aqueous solution phases, pH, ionic strength and concentration of aqueous solution on Th(IV) sorption onto TiO<sub>2</sub>; (2) to compare the sorptions of Th(IV) ions onto TiO<sub>2</sub> in the absence and presence of phosphate and hence to study the effect of phosphate on the Th(IV) sorption, and (3) to compare the sorption characteristics of Th(IV) and UO<sub>2</sub><sup>2+</sup> onto TiO<sub>2</sub>.

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## Experimental

Commercial TiO<sub>2</sub> (A.R. reagent) was purchased from the Beijing Chemical Plant. The conditioning and the storage of TiO<sub>2</sub>, and the experimental procedures of the batch experiments were identical to those already applied.<sup>17-20</sup> Batch experiments were performed in polyethylene test tubes sealed with screwcaps. It was found that the sorption of Th(IV) ions on the wall of the polyethylene test tubes is negligible under the experimental conditions used. The stock solutions of Th(NO<sub>3</sub>)<sub>4</sub> and of phosphate were prepared by dissolving Th(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O (A.R. reagent) and KH<sub>2</sub>PO<sub>4</sub> (A.R. reagent) in distilled-deionized water. The total concentration of Th(IV) or phosphate was determined by spectrophotometric analysis with Arsenazo-III or phosphomolybdate blue using ascorbic acid as a reducing agent.<sup>17,18</sup> The exact concentration of the stock solution of Th(IV) was determined gravimetrically. The pH value of initial solution was adjusted by adding a small amount of HNO<sub>3</sub> or KOH.

The sorption percent, the solid phase concentration,  $q$  (mol/g) and the distribution coefficient  $K_d$  (ml/g) were calculated from the difference between the initial concentration and the equilibrium concentration of the supernatant. The formulas of these calculations were identical to those already applied.<sup>17-20</sup> All chemicals are analytically or chemically pure. All experimental data were the average of duplicate experiments and the relative errors of sorption percent were within 5% in the range of 10–90%.

## Results

### *The effect of contact time*

The relative sorption rates of Th(IV) and phosphate onto TiO<sub>2</sub> at ionic strength ( $I$ ) 0.1 mol/l KNO<sub>3</sub>, initial concentrations  $C_{\text{Th}}^0 = 1.46 \cdot 10^{-4}$  mol/l and  $C_{\text{PO}_4}^0 = 3.5 \cdot 10^{-4}$  mol/l, pH  $2.44 \pm 0.06$  and  $2.65 \pm 0.02$  and ratio of solution volume ( $V$ ) to mass ( $m$ ) of TiO<sub>2</sub>,  $V/m = 200$  ml/g are shown in Fig. 1. It is seen that the equilibration time of Th(IV) onto TiO<sub>2</sub> is about 10 hours. The relative sorption rate of Th(IV) is slower than that of UO<sub>2</sub><sup>2+</sup> onto TiO<sub>2</sub>, and the equilibration time of UO<sub>2</sub><sup>2+</sup> ions is only 3 hours.<sup>19</sup> From Fig. 1 it is also seen

that the relative sorption rate of phosphate is very fast, 0.5 hour is sufficient to reach the sorption equilibrium under the experimental conditions used here, while the equilibration time of phosphate sorption on SiO<sub>2</sub> is 1 hour.<sup>17</sup> Therefore, the contact time between TiO<sub>2</sub> and aqueous solution containing Th(IV) and phosphate should be 12 hours to reach equilibrium states.

### *The effect of pH in the absence and presence of phosphate*

The sorption percents of Th(IV) ions and the corresponding solid phase concentration ( $q$ , mol/g) as a function of pH at ionic strength 0.1 mol/l KNO<sub>3</sub>,  $V/m = 200$  ml/g and initial concentration  $C_{\text{Th}}^0 = 1.46 \cdot 10^{-4}$  mol/l in the absence and presence of phosphate are shown in Fig. 2. It is seen that the sorption percent is abruptly increased from 40% at pH 2.2 to 67% at pH 2.8 and the corresponding solid phase concentration,  $q$  (mol/g) is abruptly increased from  $1.17 \cdot 10^{-5}$  mol/g at pH 2.2 to  $1.95 \cdot 10^{-5}$  mol/g at pH 2.8 in the absence of phosphate. The sorption percent is abruptly increased from 58% at pH 2.0 to 97% at pH 2.9 and corresponding solid phase concentration  $q$  (mol/g) is abruptly increased from  $1.65 \cdot 10^{-5}$  mol/g at pH 2.0 to  $2.8 \cdot 10^{-5}$  mol/g at pH 2.9 in the presence of phosphate. It was found that there are two big gaps between both curves in the presence and absence of phosphate and the sorption edge is moved to the left by about 0.8 pH by the addition of phosphate. Thus the strong effects of pH and phosphate on the sorption of Th(IV) onto TiO<sub>2</sub> are demonstrated clearly. While the sharp sorption edges of Th(IV) onto TiO<sub>2</sub> are in contrast to the relatively slow sorption edges of uranyl ions onto the same adsorbent.<sup>19</sup> The phosphate causes a relative enhancement in the sorption of Th(IV) at pH < 3.

The sorption percent of Th(IV) onto TiO<sub>2</sub> as a function of initial concentration of phosphate at  $V/m = 200$  ml/g,  $C_{\text{Th}}^0 = 1.46 \cdot 10^{-4}$  mol/l, pH  $2.50 \pm 0.05$ ,  $I = 0.1$  mol/l KNO<sub>3</sub> and 25 °C is shown in Fig. 3. It is seen that the sorption is increased with increasing initial concentration of phosphate, and the increase in the sorption percent is relatively sharp at  $C_{\text{PO}_4}^0 < C_{\text{Th}}^0$  and the increase in the sorption percent is relatively slow at  $C_{\text{PO}_4}^0 > C_{\text{Th}}^0$ .

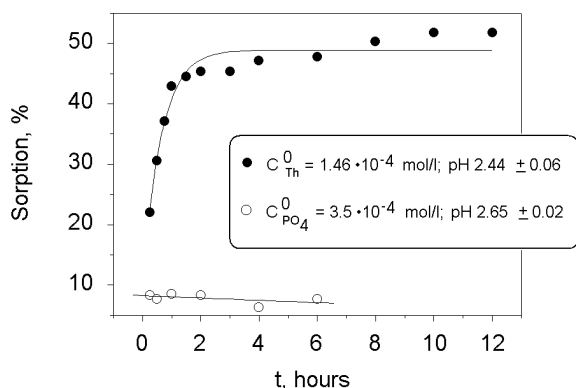


Fig. 1. Sorption percent of Th(IV) and phosphate on TiO<sub>2</sub> as a function of contact time,  $I = 0.1$  mol/l KNO<sub>3</sub>,  $V/m = 200$  ml/g,  $T = 25 \pm 1$  °C

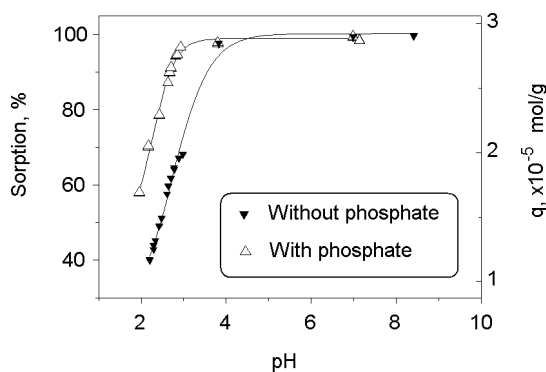


Fig. 2. Sorption percent and solid phase concentration,  $q$  of Th(IV) on TiO<sub>2</sub> as a function of pH in the presence and absence of phosphate;  $C_{Th}^0 = 1.46 \cdot 10^{-4}$  mol/l,  $I = 0.1$  mol/l KNO<sub>3</sub>,  $V/m = 200$  ml/g,  $C_{PO_4}^0 = 3.5 \cdot 10^{-4}$  mol/l,  $T = 25 \pm 1$  °C

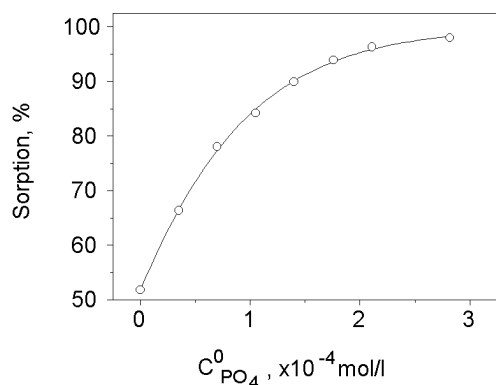


Fig. 3. Sorption percent of Th(IV) on TiO<sub>2</sub> as a function of initial phosphate concentration;  $C_{Th}^0 = 1.46 \cdot 10^{-4}$  mol/l,  $I = 0.1$  mol/l KNO<sub>3</sub>,  $V/m = 200$  ml/g, pH  $2.50 \pm 0.05$ ,  $T = 25 \pm 1$  °C

### The effects of ionic strength and concentration in the absence of phosphate

The sorption isotherms at four different ionic strengths 0.01, 0.05, 0.1 and 0.5 mol/l KNO<sub>3</sub> and four approximately constant pH values  $2.52 \pm 0.05$ ,  $2.44 \pm 0.05$ ,  $2.50 \pm 0.10$  and  $2.48 \pm 0.05$  are shown in Fig. 4. The corresponding  $K_d$  values at four different ionic strengths and four approximately constant pH values are shown in Fig. 5. It is seen from Fig. 4 that these isotherms are roughly in accord with the Freundlich equation and that the concentration of the solid phase is increased with increasing concentration of aqueous solution and with decreasing ionic strength as a whole. A clear plateau at which the surface is saturated was not observed. The Freundlich equation is given by:

$$q = K \cdot C_{aq}^{1/n} \quad (1)$$

The fitted parameters of  $K$  and  $1/n$  at different ionic strengths are listed in Table 1. The sorption isotherms of UO<sub>2</sub><sup>2+</sup> on the same sorbent were linear in the same concentration range of aqueous solution.<sup>18</sup> It is seen from Fig. 5 that the distribution coefficient  $K_d$  is decreased with increasing equilibrium concentration of Th(IV) in aqueous solution, and the maximum  $K_d$  values are of order of  $10^3$  ml/g and the minimum  $K_d$  values are of order of  $10^2$  ml/g. Nevertheless, the comparison of the curves at ionic strengths of 0.05 and 0.1 mol/l indicate the insignificant effect of increase in ionic strength from 0.05 to 0.1 mol/l KNO<sub>3</sub>. On the contrary, the sorption of UO<sub>2</sub><sup>2+</sup> ions onto TiO<sub>2</sub> is increased with increasing ionic strength, the effect of ionic strength on the Th(IV) sorption is opposite that of UO<sub>2</sub><sup>2+</sup> sorption on the same sorbent.<sup>19</sup> While the effects of ionic strength from 0.001 to 0.1 mol/l NaNO<sub>3</sub> on the sorption edges of Th(IV) on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were insensitive.<sup>18</sup>

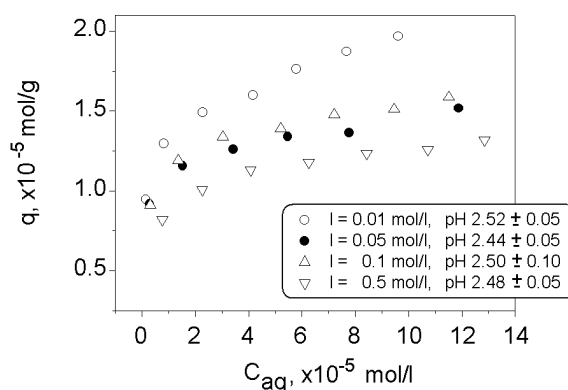


Fig. 4. Sorption isotherms of Th(IV) on TiO<sub>2</sub> at various ionic strengths and approximately constant pH,  $V/m = 200$  ml/g,  $T = 25 \pm 1$  °C

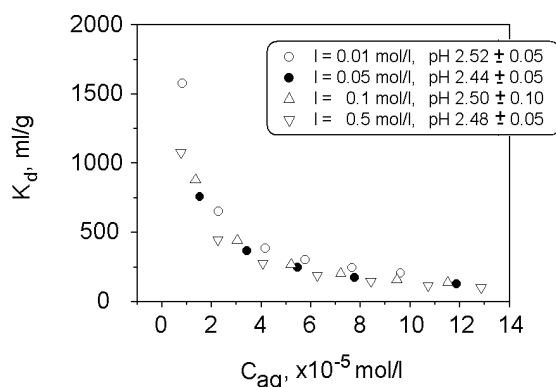


Fig. 5. Distribution coefficients,  $K_d$ , of Th(IV) as a function of the equilibrium aqueous solution concentration of Th(IV) at various ionic strengths and approximately constant pH,  $V/m = 200$  ml/g,  $T = 25 \pm 1$  °C

### Discussion

TiO<sub>2</sub> has very low solubility and has a  $pH_{PZC}$  between the high values of alumina<sup>21</sup> and iron oxides and the low values of oxides of silicon.<sup>22</sup> The current value of  $pH_{PZC}$  of TiO<sub>2</sub> is 6.<sup>7</sup> Thus the surface of TiO<sub>2</sub> carries positive charges at  $pH < 6$  and negative charge at  $pH > 6$ .

Th(IV) is the least hydrolyzed tetrapositive ion, the uncomplexed cation is stable at pH 3 or less.<sup>16,23</sup> CROMIERES et al.<sup>24</sup> calculated the distribution diagram for thorium species at ionic strength 0.1 mol/l from the hydrolysis constants ( $\log \beta_1 = -3.86$ ,  $\log \beta_2 = -8.01$ ,  $\log \beta_3 = -12.99$  and  $\log \beta_4 = -17.16$ ) and found that at  $pH \leq 3$ , Th<sup>4+</sup> is the predominating species ( $\geq 88\%$ ), Th(OH)<sup>3+</sup> is less than 12%; at  $pH \leq 4$ , Th(OH)<sup>3+</sup> is less than 40%, Th(OH)<sub>2</sub><sup>2+</sup> is less than 28%, Th(OH)<sub>3</sub><sup>+</sup> and Th(OH)<sub>4</sub> are less than 12%; at  $pH \leq 4.5$ , Th(OH) is less than 12%, Th(OH)<sub>3</sub><sup>+</sup> is less than 12%, Th(OH)<sub>2</sub><sup>2+</sup> is less than 40% and Th(OH)<sup>3+</sup> is less than 18%. From the continuous titration experiments, ÖSTHOLS et al.<sup>25</sup> found that even if at  $P_{CO_2} = 0.1$  atm, at  $pH \leq 4.5$ , Th(OH)<sub>3</sub>CO<sub>3</sub><sup>-</sup> is less than 3%. Hence, in our experiments at pH range of 2–4.5, Th(OH)<sub>3</sub>CO<sub>3</sub><sup>-</sup> and Th(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup> can be negligible.

JAKOBSSON<sup>9</sup> found that the sorption of Th(IV) increases sharply between pH 1 and 3. As compared with the sorption edge by JAKOBSSON,<sup>9</sup> the sorption edge in this paper was shifted to the right and this must be related to the increase in initial concentration of Th(IV) in the aqueous solution.

In the previous paper,<sup>18</sup> the sorption edges of Th(IV) ions onto the oxides of aluminum and silicon are located in the pH range of 2–4.5. Furthermore, the sorption edges of Th(IV) onto oxides of Fe, Al and Si by CROMIERES et al.,<sup>24</sup> RIGHETTO et al.<sup>26</sup> and ÖSTHOLS,<sup>27</sup> respectively, were located in the pH range of 1–4.5 as well. The common location of sorption edges on different oxides, the sharp increase in sorption of Th(IV) ions onto different oxides must be attributed to the hydrolysis of Th(IV) instead of the surface properties of different oxides. In this pH range ( $pH \leq 4.5$ ), the percent of the total hydrolysis products, Th(OH)<sup>3+</sup>, Th(OH)<sub>2</sub><sup>2+</sup>, Th(OH)<sub>3</sub><sup>+</sup> and Th(OH)<sub>4</sub> in the aqueous solution is increased with increasing pH, and these hydrolysis products become the sorbing species of Th(IV). According to the thermodynamic model for the adsorption by JAMES and HEALY,<sup>28</sup> the Gibbs free energy of adsorption ( $\Delta G_{ads}$ ) involves the Coulomb electrostatic energy ( $\Delta G_{coul}$ ), the hydration energy ( $\Delta G_{hyd}$ ) and chemical bond energy ( $\Delta G_{chem}$ ). Because the Coulomb electrostatic energy for Th(IV) sorption onto TiO<sub>2</sub> at  $pH \leq 4.5$  is deleterious to sorption of the positively charged species of Th(IV), and the hydration energy ( $\Delta G_{hyd}$ ) is always positive and deleterious to sorption, the sole driving force for the positively charged species of Th(IV) onto TiO<sub>2</sub> at  $pH \leq 4.5$  is  $\Delta G_{chem}$ , i.e., the strong chemical bonds between the surface of TiO<sub>2</sub> and the hydrolysis products must be formed at  $pH \leq 4.5$ .

In aqueous solutions of NaCl or NaClO<sub>4</sub>, in the ionic strength ranging from 0.004 to 0.15 mol/l, and at very low concentration of Th(IV) ( $10^{-7}$ – $10^{-8}$  mol/l), JAKOBSSON<sup>9</sup> found that the sorption edge of Th(IV) onto TiO<sub>2</sub> is insensitive to the ionic strength.

CROMIERES et al.<sup>24</sup> also found that the sorption edge of Th(IV) onto hematite is independent on the ionic strength from 0.01 to 0.1 mol/l NaClO<sub>4</sub> and at Th(IV) concentration of  $2.5 \cdot 10^{-10}$  mol/l. In our previous paper<sup>18</sup> and the paper by ÖSTHOLS,<sup>27</sup> insensitivity to ionic strength was also found from the sorption edges of Th(IV) sorption onto SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. It was opposite to the obvious gap between sorption isotherms at ionic strength 0.01 and 0.5 mol/l KNO<sub>3</sub> (Fig. 4). Furthermore, it is also seen from Fig. 4 that the difference between sorptions at ionic strengths 0.05 and 0.1 mol/l KNO<sub>3</sub> is insignificant. Therefore, it may be concluded that the effect of ionic strength on the sorption of a metal onto an oxide is dependent on the concentration of metal, the ionic strength range and the cation and anion of background electrolyte.<sup>29</sup>

Table 1. Values of parameters  $K$  and  $1/n$  of Freundlich equation

Ionic strength, mol/l KNO <sub>3</sub>	pH	$K$ , $\times 10^{-5} \text{ mol}^{1-1/n} \cdot \text{g}^{-1} \cdot \text{l}^{1/n}$	$1/n$	R
0.01	$2.52 \pm 0.05$	$8.8 \pm 0.7$	$0.165 \pm 0.007$	0.99
0.05	$2.44 \pm 0.05$	$4.7 \pm 0.3$	$0.128 \pm 0.007$	0.99
0.1	$2.50 \pm 0.10$	$6.0 \pm 0.4$	$0.147 \pm 0.007$	0.99
0.5	$2.48 \pm 0.05$	$5.7 \pm 0.5$	$0.163 \pm 0.008$	0.99

The addition of phosphate to the sorption system could be expected to have several possible influences. First and foremost, the competition with phosphate for surface site of TiO<sub>2</sub> could decrease Th(IV) sorption. Additionally, non-sorbing aqueous complexes of Th(IV) with phosphate might retain in the aqueous solution, which would also tend to decrease Th(IV) sorption. Therefore, the obvious positive effect of phosphate on the Th(IV) sorption onto TiO<sub>2</sub> only can be attributed to the formation of ternary surface complexes, involving both Th(IV) and phosphate.<sup>16,17</sup>

The difference between sorption rates, pH dependences, sensitivities to ionic strength and types of sorption isotherms of uranyl and Th(IV) onto TiO<sub>2</sub>, in the absence of phosphate or humic substance, are summarized in Table 2 and may be related to the speciations of Th(IV) and U(VI) in aqueous solution. It is well known that in the absence of atmospheric CO<sub>2</sub> at pH≤4, UO<sub>2</sub><sup>2+</sup> is the predominant species (≥90%), UO<sub>2</sub>(OH)<sup>+</sup> is less than 4%; at pH≤5, UO<sub>2</sub><sup>2+</sup> is larger than 69%, UO<sub>2</sub>(OH)<sup>+</sup> is less than 26%, (UO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub><sup>2+</sup> is less than 5%; at pH>5.5, the fraction of UO<sub>2</sub>(OH)<sup>+</sup> and (UO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub><sup>2+</sup> are decreased and the fraction of (UO<sub>2</sub>)<sub>2</sub>(OH)<sub>3</sub><sup>3+</sup> is increased with increasing pH. In the presence of atmospheric CO<sub>2</sub>, the fraction of (UO<sub>2</sub>)<sub>2</sub>(OH)<sub>3</sub>CO<sub>3</sub><sup>-</sup> is negligible at pH<5.5, and at pH>5.5, the fraction of (UO<sub>2</sub>)<sub>2</sub>(OH)<sub>3</sub>CO<sub>3</sub><sup>-</sup> is rapidly increased with increasing pH.<sup>16,18,29</sup> Furthermore, the sorption characteristics of Th(IV) and UO<sub>2</sub><sup>2+</sup> are related to the equilibria among the free ions, the hydrolysis products and the complexes of carbonate, and determined by a number of surface complexations of free ions, hydrolysis products and complexes of carbonate.

The slower sorption rate of Th(IV) onto TiO<sub>2</sub> may be related to the slower shift of equilibria among the Th<sup>4+</sup>, Th(OH)<sup>3+</sup>, Th(OH)<sub>2</sub><sup>2+</sup> and Th(OH)<sub>3</sub><sup>+</sup>. The fact that the sorption rate of Th(IV) onto SiO<sub>2</sub><sup>18</sup> also was obviously slower than that of UO<sub>2</sub><sup>2+</sup> on the same adsorbent, is the base of this explanation. The steep increase in sorption of Th(IV) at pH≤4.5 can be attributed to the very high affinities of these hydrolysis products to the surface of sorbents and to the fact that the total percent of hydrolysis products is rapidly increased with increasing pH at pH<4.5 and attains about 80% at pH 4.5 as mentioned before. In other words, the surface of TiO<sub>2</sub> prefers the hydrolysis products of Th(IV) which form strong chemical bond with the surface, and the preferences of TiO<sub>2</sub> for the hydrolysis products of UO<sub>2</sub><sup>2+</sup> are much less than the preferences for the hydrolysis products of Th(IV). The opposite effects of ionic strength on sorption of UO<sub>2</sub><sup>2+</sup> and Th(IV) result from the difference in the strengths between different chemical bonds of different species on the surface and the difference in the shielding of charged surface species of Th(IV) and UO<sub>2</sub><sup>2+</sup> by the background electrolyte.

It is seen from Fig. 4 in this paper and Fig. 5 in the previous paper<sup>19</sup> that the maximum of *q* values (2·10<sup>-5</sup> mol/g) at aqueous solution concentration (1.0·10<sup>-4</sup> mol/l) of Th(IV), ionic strength 0.01 mol/l and pH 2.5 in this paper is an order of magnitude larger than that of uranyl ions in the previous paper at the same concentration of UO<sub>2</sub><sup>2+</sup>, ionic strength and pH 4.3.<sup>19</sup> Hence, the linearity of sorption isotherms of UO<sub>2</sub><sup>2+</sup> may not be associated with the low degree of saturation of surface. The difference in the types of sorption isotherms of UO<sub>2</sub><sup>2+</sup> and Th(IV) ions onto TiO<sub>2</sub> may be related to the formation of polynuclear surface complexes of UO<sub>2</sub><sup>2+</sup>.<sup>8</sup> It is also seen from Fig. 5 in this paper and Fig. 6 in the previous paper<sup>19</sup> that at the same equilibrium concentration of Th<sup>4+</sup> and UO<sub>2</sub><sup>2+</sup> and the same ionic strength, the *K<sub>d</sub>* values of Th<sup>4+</sup> are constantly and obviously larger than those of UO<sub>2</sub><sup>2+</sup>, in spite the pH of UO<sub>2</sub><sup>2+</sup> solution 3.9 is larger than the pH of Th<sup>4+</sup> solution 2.5.

It is well known that thorium is always associated with uranium in natural phosphates, ores and sands<sup>16</sup> and that both actinides are the potential environmental pollutants from the radwaste repositories. Therefore, the simultaneous investigation of sorptions of uranium and thorium is a subject of current interest.

Based on the experimental results of this paper and our previous paper,<sup>19</sup> TiO<sub>2</sub> is thought to be an important sorbent of UO<sub>2</sub><sup>2+</sup> and Th<sup>4+</sup>. The probable separation of UO<sub>2</sub><sup>2+</sup> and Th<sup>4+</sup> by using TiO<sub>2</sub> as a sorbent, can also be used as a bed for the recovery of UO<sub>2</sub><sup>2+</sup> and Th<sup>4+</sup> having high *K<sub>d</sub>* values from their dilute solution.

Though the results in this paper and our previous paper<sup>19</sup> provided a wealth of information on the nature of sorption process of UO<sub>2</sub><sup>2+</sup> and Th<sup>4+</sup> onto TiO<sub>2</sub>, these macroscopic measurements are fundamentally incapable of providing molecular-level information. The microscopic information is provided by only a few spectroscopic methods.

Table 2. Differences of sorption characteristics of UO<sub>2</sub><sup>2+</sup><sup>19</sup> and Th<sup>4+</sup> onto TiO<sub>2</sub>

Characteristics	UO <sub>2</sub> <sup>2+</sup>	Th <sup>4+</sup>
Sorption rate	Relatively quick	Relatively slow
Equilibrium time	3 hours	10 hours
Sorption edge	Gentle	Steep
pH <sub>90</sub> *	8.6	3.6
pH <sub>50</sub> *	6.2	2.4
pH <sub>10</sub> *	3.0	About 1
ΔpH <sub>90-10</sub> **	5.6	2.6
Effect of ionic strength	Positive	Reduced
Type of sorption isotherm	Linear	Freundlich

\* pH<sub>*x*</sub>, pH at which the *x* percent of total UO<sub>2</sub><sup>2+</sup> or Th<sup>4+</sup> ions was sorbed.

\*\* ΔpH<sub>90-10</sub>, the difference of pH between pH<sub>90</sub> and pH<sub>10</sub>.

### Conclusions

As compared to the sorption rate of U(VI) onto TiO<sub>2</sub>, the sorption of Th(IV) onto the same sorbent is a relatively slow process.

The effect of pH on sorption of Th(IV) onto TiO<sub>2</sub> is greater than that of U(VI) and the sorption is abruptly increased with increasing pH from 2 to 4.

As a whole, the sorption of Th(IV) onto TiO<sub>2</sub> is decreased with increasing ionic strength from 0.01 to 0.5 mol/l KNO<sub>3</sub>, and the reducing effect of ionic strength is opposite to the promoting effect of U(VI) sorption onto the same sorbent.

The sorption isotherm of Th(IV) onto TiO<sub>2</sub> at constant ionic strength, approximately constant pH and moderate concentration range (10<sup>-4</sup>–10<sup>-5</sup> mol/l) can be described by the Freundlich equation, while the sorption isotherm of U(VI) at the same conditions is linear.

The sorption of Th(IV) onto TiO<sub>2</sub> is obviously increased in the presence of phosphate in aqueous solution, as compared to the absence of phosphate.

The affinity of TiO<sub>2</sub> surface for Th(IV) is obviously greater than that for U(VI).

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