The Collection of Uranium from Sea Water with Hydrous Metal Oxide. II. The Mechanism of Uranium Adsorption on Hydrous Titanium(IV) Oxide

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The mechanism of uranium adsorption from sea water by hydrous titanium(IV) oxide was investigated. The uranium adsorption experiments were conducted using a solution containing NaCl, NaHCO$_3$, and uranium. Thermoochemical calculation showed that the tris(carbonato)dioxouranate(VI) ion [UO$_2$(CO$_3$)$_3$]$^{6-}$ found in sea water existed in the solution at pH 8 and 25 °C. The uranium uptake varied with the pH of the solution, exhibiting a minimum value at pH 8. The enthalpy change, $\Delta H$, and the activation energy, $E$, of the uranium adsorption were found to be 23.6 kJ mol$^{-1}$ and 52.7 kJ mol$^{-1}$ respectively. The analysis of carbonate in the adsorbent showed that the carbonate ion in [UO$_2$(CO$_3$)$_3$]$^{6-}$ was released into the solution during the uranium adsorption. On the basis of the present experimental results, the mechanism of uranium adsorption was discussed.

Many studies have been made on extracting uranium from sea water by adsorption on hydrous titanium(IV) oxide.$^{1-9}$ Previous investigations of the uranium adsorption have, however, dealt almost exclusively with the adsorption capacity. Only a few investigations have been carried out on the mechanism of uranium adsorption. Keen$^6$ reported that uranium was adsorbed by hydrous titanium(IV) oxide as the UO$_2^{2+}$ cation. Ogata et al.$^9$ proposed that the uranium was adsorbed by a coordinate bond on hydrous titanium(IV) oxide.

In the present work, the enthalpy change, rate constant, and activation energy of the uranium adsorption by hydrous titanium(IV) oxide were determined, and the adsorption mechanism was discussed.

**Experimental**

Preparation of Hydrous Titanium(IV) Oxide. The hydrous titanium(IV) oxide was prepared in the following manner. Into 200 ml of a 0.6 mol dm$^{-3}$ TiCl$_4$ solution under stirring and heating at 90 °C, a 7% NH$_3$ solution was added at a rate of 3.5 ml/min until the pH of the solution reached 5. After it had then aged for 1 h, the precipitate was filtered, washed several times with water, and dried for about a week at room temperature. The dried samples were crushed and sieved, a portion of 400—600 mesh being used in following experiments. The water content of the dried sample was determined by measuring the ignition loss at 800 °C and found to be 18%, which corresponds to that of TiO(OH)$_2$.

Adsorption Experiment. In the uranium adsorption experiments, 0.04 g of hydrous titanium(IV) oxide was introduced into 1000 ml of a solution containing 0.72 mol dm$^{-3}$ NaCl, 0—5 x 10$^{-3}$ mol dm$^{-3}$ NaHCO$_3$, and 10—500 ppb of uranium. The concentration of NaCl was taken to be 0.72 mol dm$^{-3}$ in order for it to have the same ionic strength as that of sea water. The concentration of NaHCO$_3$ was nearly equal to that of sea water. The solution was stirred vigorously by means of a vertical stirrer. After adsorption equilibrium has been attained, the solution was filtered and the uranium concentration was measured. The uranium uptake by the adsorbent was determined from the change in the uranium concentration in the solution. The pH of the solution was changed from 4 to 12 with an HCl or NaOH solution. The determination of carbonate uptake was carried out by the following procedure. One fifth of a gram of hydrous titanium(IV) oxide was equilibrated with 5000 ml of a 0.72 mol dm$^{-3}$ NaCl + 5 X 10$^{-3}$ mol dm$^{-3}$ NaHCO$_3$ solution containing 40—500 ppb of uranium at pH 8 and 25 °C. After 5 h adsorption, the hydrous titanium(IV) oxide was separated from the solution, and the carbonate adsorbed in the adsorbent was determined.

Analytical Method. The uranium in the solution was determined spectrophotometrically with Arsenazo III as the indicator.$^6$ The determination of carbonate in the adsorbent was carried out by the following procedure. The carbonate was decomposed with an HCl solution, and the carbon dioxide thus produced was measured by coulomatic titration with a Kokusai Denki VK-I-type "Coulomatic C."

**Results and Discussion**

Adsortion Equilibrium. The uranium uptake as a function of the adsorption time with hydrous titanium(IV) oxide of different particle sizes is shown in Fig. 1. The smaller granules showed a faster rate of the uranium uptake than the larger granules. It was found that an adsorption equilibrium was attained within 3 h using the adsorbent smaller than 300 mesh. A portion of 400—600 mesh adsorbent was used, and the adsorption time of 5 h was chosen for the following
experts.

Effect of pH. The effect of the pH on the uranium uptake by the hydrous titanium(IV) oxide is shown in Fig. 2. The uranium uptake is significantly influenced by the pH of the solution, showing a minimum at pH 8. The same adsorption curve as that in Fig. 2 was obtained in the adsorption experiment with sea water in the present work.

The variation in the uranium uptake with the pH is believed to result from the fact that the species of uranium(VI) ions changes with the pH. Under the present experimental conditions, the uranyl(VI) ion may exist in the form of hydroxo-, chloro-, and carbonate-complexes, the stability constants ($K$) of which are summarized in Table 1. The distributions of the uranyl(VI) species in the NaCl-NaHCO$_3$ solution at various pH values, as calculated from the stability constants, are shown in Table 2. Tris(carbonato)dioxouranate(VI) ion which is present in sea water is a predominant species at pH 8—10, while the uranyl and chloro complex ion in an acidic solution and the hydroxo complex ion in an alkaline solution are stable. The uranium uptake reaches its minimum at pH 8, where predominant uranium(VI) species in the solution is [UO$_4$(CO$_3$)$_3$]$^{4-}$.

Effect of Carbonate Ions. In order to investigate the effect of carbonate ions in the solution, the uranium uptake was measured with a solution containing 0.72 mol dm$^{-3}$ NaCl, 60 ppb uranium, and 0—5 x 10$^{-3}$ mol dm$^{-3}$ NaHCO$_3$ at pH 8. The results are shown in Fig. 3. The distribution of uranyl(VI) species in the NaCl-NaHCO$_3$ solution used in the experiments is summarized in Table 3. It may be found from Fig. 3 and Table 3 that the uranium uptake decreases with an increase in [UO$_4$(CO$_3$)$_3$]$^{4-}$. That is, the uranium uptake is larger from the tris(hydroxo)dioxouranate(VI) [UO$_4$(OH)$_3$]$^-\text{solution}$ than from the [UO$_4$(CO$_3$)$_3$]$^{4-}$ solution. It is considered that the

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**Table 1. Stability constants ($K$) of uranyl(VI) complexes**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log $K$</th>
<th>Reaction</th>
<th>log $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_4^{2+}$ + H$_2$O = [UO$_2$(OH)$_2$]$^-$ + H$_2$O</td>
<td>-5.0</td>
<td>2UO$_4^{2+}$ + H$_2$O = [UO$_2$($\text{OH}$)$_3$]$^4+$ + H$^+$</td>
<td>-4.2</td>
</tr>
<tr>
<td>UO$_4^{2+}$ + 2H$_2$O = UO$_2$(OH)$_2$ + 2H$^+$</td>
<td>-11.2</td>
<td>4UO$_4^{2+}$ + 7H$_2$O = [UO$_2$($\text{OH}$)$_3$]$^7+$ + 7H$^+$</td>
<td>-24.9</td>
</tr>
<tr>
<td>UO$_4^{2+}$ + 3H$_2$O = [UO$_2$(OH)$_3$]$^4+$ + 3H$^+$</td>
<td>-17.1</td>
<td>UO$_4^{2+}$ + Cl$^-$ = [UO$_2$Cl]$^-\text{solution}$</td>
<td>-0.1</td>
</tr>
<tr>
<td>2UO$_4^{2+}$ + 2H$_2$O = [(UO$_2$(OH)$_3$)$^2+$ + 2H$^+$</td>
<td>-5.96</td>
<td>UO$_4^{2+}$ + 2Cl$^-\text{solution}$</td>
<td>-0.91</td>
</tr>
<tr>
<td>3UO$_4^{2+}$ + 4H$_2$O = [(UO$_2$(OH)$_3$)$^3+$ + 4H$^+$</td>
<td>-12.8</td>
<td>UO$_4^{2+}$ + 3Cl$^-\text{solution}$</td>
<td>-2.6</td>
</tr>
<tr>
<td>4UO$_4^{2+}$ + 5H$_2$O = [(UO$_2$(OH)$_3$)$^4+$ + 5H$^+$</td>
<td>-12.36</td>
<td>UO$_4^{2+}$ + CO$_3^{2-}\text{solution}$</td>
<td>9.11</td>
</tr>
<tr>
<td>4UO$_4^{2+}$ + 6H$_2$O = [(UO$_2$(OH)$_3$)$^5+$ + 6H$^+$</td>
<td>-20.0</td>
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<td>13.57</td>
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<td>3UO$_4^{2+}$ + 5H$_2$O = [(UO$_2$(OH)$_3$)$^6+$ + 5H$^+$</td>
<td>-16.21</td>
<td>UO$_4^{2+}$ + 3CO$_3^{2-}\text{solution}$</td>
<td>22.8</td>
</tr>
<tr>
<td>5UO$_4^{2+}$ + 8H$_2$O = [(UO$_2$(OH)$_3$)$^8+$ + 8H$^+$</td>
<td>-32.14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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**Table 2. Distribution of uranyl(VI) complexes with various pH values**

<table>
<thead>
<tr>
<th>Species</th>
<th>pH</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_4^{2+}$</td>
<td>57.6</td>
<td>3.9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>[UO$_2$(OH)$_2$]$^+$</td>
<td>5.8</td>
<td>38.6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>UO$_2$(OH)$_2$</td>
<td>0</td>
<td>24.3</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>[UO$_2$(OH)$_3$]$^-\text{solution}$</td>
<td>0</td>
<td>30.7</td>
<td>14.1</td>
<td>39.8</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>[UO$_4$Cl]$^+$</td>
<td>32.9</td>
<td>2.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>UO$_2$Cl$_2$</td>
<td>3.6</td>
<td>0.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>[UO$_2$Cl]$^-\text{solution}$</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>UO$_2$CO$_3$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>[UO$_2$(CO$_3$)$_3$]$^-\text{solution}$</td>
<td>0</td>
<td>0</td>
<td>0.9</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>[UO$_2$(CO$_3$)$_3$]$^4-\text{solution}$</td>
<td>0</td>
<td>0</td>
<td>84.5</td>
<td>60.2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

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**Fig. 2.** Effect of pH on uranium uptake.

Adsorption temperature: 25°C, NaCl: 0.72 mol dm$^{-3}$, NaHCO$_3$: $2.3 \times 10^{-2}$ mol dm$^{-3}$, uranium: 60 ppb.

**Fig. 3.** Effect of carbonate ions on uranium uptake.

Adsorption temperature: 25°C, pH of the solution: 8.0, NaCl: 0.72 mol dm$^{-3}$, uranium: 60 ppb.
Collection of Uranium from Sea Water

Table 3. Distribution of uranyl(VI) complexes with various concentrations of NaHCO₃ (%)

<table>
<thead>
<tr>
<th>Species</th>
<th>[NaHCO₃]/mol dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>[UO₂(OH)₃]⁻</td>
<td>100</td>
</tr>
<tr>
<td>[UO₂(CO₃)₃]⁻</td>
<td>66.7</td>
</tr>
</tbody>
</table>

uranium uptake is reduced by the presence of NaHCO₃ because carbonate ions behave as a masking agent to uranium adsorption. The uranium uptake from a 5×10⁻³ mol dm⁻³ NaHCO₃ solution in which uranyl(VI) species is present in the form of [UO₂(CO₃)₃]⁻ (98.5%) is found to be 0.82 mg g⁻¹ as is shown in Fig. 3. The results indicate that uranium adsorption takes place from the [UO₂(CO₃)₃]⁻ solution by means of hydrous titanium(IV) oxide.

Effect of Temperature. The effect of the temperature on the uranium uptake of hydrous titanium(IV) oxide is shown in Fig. 4. It is shown that the uranium uptake increases with the adsorption temperature. In order to obtain the enthalpy change of the adsorption, ΔH, the distribution coefficient, K₆, was calculated from the data. The distribution coefficient is defined as C₆/C₁, where C₆ is the uranium adsorbed in the adsorbent per gram, and C₁ the uranium in the solution per ml at equilibrium. The enthalpy change of the adsorption can be expressed as follows:

\[
\frac{d \ln K₆}{dT} = \frac{\Delta H}{RT^2}.
\]

By integrating Eq. 1, we obtain

\[
\log K₆ = - \frac{\Delta H}{2.3R} \cdot \frac{1}{T} + \text{const},
\]

Fig. 4. Effect of temperature on uranium uptake.

\[
pH \text{ of the solution: } 8.0, \ NaCl: \ 0.72 \text{ mol dm}^{-3}, \\
NaHCO₃: \ 2.3 \times 10^{-3} \text{ mol dm}^{-3}, \ \text{uranium: } 90 \text{ ppb}.
\]

where T is the adsorption temperature, and R, the gas constant. As is shown in Fig. 4, the distribution coefficient increases markedly with the adsorption temperature. A plot of log K₆ versus 1/T is shown in Fig.

\[\text{Fig. 5. Plot of } \log K₆ \text{ vs. } 1/T.\]

5. The enthalpy change in the adsorption, ΔH, was found to be 23.6 kJ mol⁻¹. This value suggests that the uranium adsorption is neither physical adsorption nor an ion-exchange reaction. The physical adsorption is ordinarily exothermic, and the enthalpy change of the ion-exchange reaction is said to be −8.4−12.6 kJ mol⁻¹.⁷

It may, therefore, be considered that the uranium adsorption proceeds via a certain complex chemical reaction.

Kinetics of Adsorption. The rate constant, k, and the activation energy, E, of the uranium adsorption were also determined. The variation in the uranium uptake with time is shown in Fig. 6. The rate of the uranium adsorption is larger at higher temperatures. The following equation is assumed:

\[
\frac{dv}{dt} = k(v_e - v),
\]

where v is the uranium uptake at time t, vₑ is the equilibrium uptake, and k the rate constant. The activation energy is determined from the Arrhenius equation:

\[
\frac{d \ln k}{dT} = \frac{E}{RT^2}.
\]

By integrating this equation, we obtain

\[
\log k = - \frac{E}{2.3R} \cdot \frac{1}{T} + \text{const},
\]

where T is the adsorption temperature, and R, the gas constant.

\[\text{Fig. 6. Variation of uranium uptake with adsorption time.}\]

\[
pH \text{ of the solution: } 8.0, \ NaCl: \ 0.72 \text{ mol dm}^{-3}, \\
NaHCO₃: \ 2.3 \times 10^{-3} \text{ mol dm}^{-3}, \ \text{uranium: } 60 \text{ ppb}. \\
\text{Adsorption temperature, } O: \ 25^\circ \text{C } \bullet: \ 35^\circ \text{C } \bigcirc: \ 45^\circ \text{C}.
\]

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\text{Adsorption temperature, } O: \ 25^\circ \text{C } \bullet: \ 35^\circ \text{C } \bigcirc: \ 45^\circ \text{C}.
\]
where $v_e$ is the adsorption capacity at equilibrium, and $v$, the adsorption capacity at time $t$. By integrating Eq. 3, Eq. 4 is obtained:

$$\ln \frac{1}{1-\theta} = kt,$$

where $\theta$ is the extent of adsorption ($v/v_e$). A plot of log $1/(1-\theta)$ versus $t$ will give a straight line if the adsorption rate is represented by Eq. 3. As is shown in Fig. 7, the relation between log $1/(1-\theta)$ and $t$ is nearly linear. The rate constants calculated from the slope were 0.0113 min$^{-1}$ at 25°C, 0.0217 min$^{-1}$ at 35°C, and 0.038 min$^{-1}$ at 45°C.

The activation energy, $E$, was determined by using the Arrhenius equation. A plot of log $k$ versus $1/T$ is shown in Fig. 8, which gives an activation energy of 52.7 kJ mol$^{-1}$.

**Mechanism of Adsorption.** The adsorption mechanism of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ found in sea water will now be discussed. Uranium adsorption takes place from the solution containing 0.72 mol dm$^{-3}$ NaCl and $5 \times 10^{-3}$ mol dm$^{-3}$ NaHCO$_3$ by means of the hydrous titanium(IV) oxide mentioned before. In order to investigate the form of uranium adsorbed from the $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ solution on the adsorbent, the uranium and carbonate uptake from the solution containing 0.72 mol dm$^{-3}$ NaCl, $5 \times 10^{-3}$ mol dm$^{-3}$ NaHCO$_3$, and 40–500 ppb uranium are measured. The results are shown in Fig. 9. If the uranium form adsorbed on the adsorbent is $[\text{UO}_2(\text{CO}_3)_3]^{4-}$, the carbonate uptake should increase with the uranium uptake, as is shown by the broken line in Fig. 9. However, the carbonate uptake remains constant regardless of the uranium uptake. It is considered from the results that carbonate in $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ is released into the solution, so that carbonate is not taken up by the adsorbent when uranium adsorption takes place from the tris(carbonato)dioxouranate(VI) solution.

In an alkaline solution, the surface hydroxo group $[-\text{Ti-OH}]$ of hydrous titanium(IV) oxide dissociates into $-\text{Ti-O}^-$, which tends to undergo a cation exchange.$^8$ The amount of $-\text{Ti-OH}$ in hydrous titanium(IV) oxide, as determined by the adsorption of fluoride ions, and that of $-\text{Ti-O}^-$, as determined by the ion-exchange reaction of potassium ions at pH 8, were found to be 1.7 mmol g$^{-1}$ and 0.4 mmol g$^{-1}$ respectively.$^9$ Although $-\text{Ti-OH}$ and $-\text{Ti-O}^-$ are present in the NaCl-NaHCO$_3$ solution at pH 8, it is unlikely that $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ reacts with $-\text{Ti-O}^-$ because they have the same electric charge. Therefore, the adsorption site of hydrous titanium(IV) oxide for the uranium is supposed to be $-\text{Ti-OH}$. Based on the present experimental results, the adsorption mechanism of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ is represented by

$$\text{TiO(OH)}_2 + [\text{UO}_2(\text{CO}_3)_3]^{4-} \rightarrow \text{TiO}_3^{2-} + \text{UO}_2^2+ + 2\text{HCO}_3^- + \text{CO}_3^{2-}.$$  

The decrease in the concentration of NaHCO$_3$ in
the solution raises the uranium uptake, as is shown in Fig. 3. This may be attributable to the increase in [UO$_2$(OH)$_3$]$^{4-}$, which shows a higher adsorbability than [UO$_2$(CO$_3$)$_3$]$^{4-}$. The adsorption mechanism of [UO$_2$(OH)$_3$]$^{4-}$ is deduced to be as follows:

$$\text{TiO(OH)$_2$} + [\text{UO}_2\text{(OH)$_3$}]^{-} = \text{TiO}_3^{-} \cdot \text{UO}_2^{2+} + 2\text{H}_2\text{O} + \text{OH}^{-}. \quad (6)$$

It is considered that the competitive adsorption presented by the reaction of (5) and (6) takes place when [UO$_2$(CO$_3$)$_3$]$^{4-}$ and [UO$_2$(OH)$_3$]$^{4-}$ coexist in the solution. However, with respect to the adsorption mechanism of [UO$_2$(OH)$_3$]$^{4-}$, hydrolysis adsorption has been suggested by Katoh et al. Therefore, further experiments will be made in the future with regard to the adsorption of [UO$_2$(OH)$_3$]$^{4-}$.

In the present work, the mechanism of uranium adsorption from sea water, i.e., a [UO$_2$(CO$_3$)$_3$]$^{4-}$ solution, was investigated. It is important to determine the adsorption mechanisms of all the uranyl(VI) species. However, the data for verifying the assumption of the adsorption mechanism cannot be obtained because various uranyl(VI) species coexist in the solutions of pH 4—8 under the present experimental conditions. Further study is required on this point.

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References