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The Collection of Uranium from Sea Water with Hydrous Metal Oxide. IV. Physical Properties and Uranium Adsorption of Hydrous Titanium(IV) Oxide

Hisao YAMASHITA,* Yoshihiro OZAWA,** Fumito NAKAJIMA, and Toshifumi MURATA**
Hitachi Research Laboratory, Hitachi, Ltd., Kujimachi, Hitachi 319-12
*** Energy Research Laboratory, Hitachi, Ltd., Moriyama-cho, Hitachi 316*

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The adsorption of uranium from sea water with hydrous titanium(IV) oxide(HTO) was studied. HTO was prepared by mixing titanium(IV) chloride and aqueous ammonia at different pHs and temperatures. The fundamental property of HTO was investigated for apparent crystal size, specific surface area, and pore size. The uranium uptake of HTO was found to depend more strongly on the temperature than on the pH in the preparation. HTO prepared at higher temperatures exhibited larger pores and a higher uranium uptake. A kinetic study of the uranium adsorption revealed that the rate of adsorption was controlled by the particle diffusion. The diffusion coefficients were calculated.

There are a large number of elements dissolved in sea water. Though the concentration of uranium in sea water is very low (3 ppb), the total amount of uranium is estimated to be about 4×10^9 t. The recovery of uranium from sea water has been studied, and several techniques for the extraction have been proposed.[1–4] Among these techniques, the adsorption method has been considered most feasible.

Hydrous titanium(IV) oxide (HTO) may be the most suitable uranium adsorbent because of its higher selectivity and adsorption capacity. Ogata[5] has shown that the uranium uptake depends strongly on the method of the preparation of HTO. However, no systematic study has been reported of the relation between the physical properties and uranium adsorption of HTO.

In the present work, the relationship between the uranium adsorption and the physical properties of HTO, such as the apparent crystal size, the specific surface area, and the pore size, is investigated.

Experimental

Preparation of HTO. HTO was prepared by the addition of 7% aqueous ammonia to a solution of 0.6 mol dm^{-3} titanium(IV) chloride at different temperatures. The pH values at the end of precipitation was controlled between 3 and 9. The precipitate was filtered off, washed with distilled water, and finally dried at room temperature for about 10 d. The dried samples were crushed and sieved, a fraction of 150—200 mesh size being used in the following experiments.

Sample Solution. The sea water used in the present work was obtained at the seashore of Hitachi city. The uranium concentration was found to be 3.1 ppb, and the pH value, 8.1. In the adsorption experiments, the initial concentration of uranium was set as 10—30 ppb by the addition of uranyl(VI) chloride solution to the sea water.

Adsorption Experiment. The HTO samples of 0.04 g were introduced into 1000 ml of sea water at 25 °C. The solution was stirred by means of a vertical stirrer. The adsorption equilibrium was attained within 8 h under the present experimental conditions. The solution was filtered to separate the adsorbents, and the uranium in the solution was determined spectrophotometrically, with Arsenazo III as an indicator.[6]

Measurement of X-Ray Diffraction. The X-ray diffraction pattern of HTO was measured with a Rigaku Denki Geiger Flex X-Ray Diffractometer, filtered Cu $K\alpha$ being used. The apparent crystal size was calculated by the Sheller equation from a peak corresponding to the (101) plane of anatase.

Measurement of Specific Surface Area and Mean Pore Radius. The specific surface area and pore volume of HTO were measured by means of the N_2 adsorption at -195 °C. The mean pore radius, r, was calculated from the $r=2V/S$ equation, where V is the pore volume and S the specific surface area.

Results and Discussion

Uranium Uptakes of HTO Prepared at Different pHs, and Temperatures. The effects of the final preparation pH of HTO on the specific surface area and the uranium uptake are shown in Fig. 1. The specific surface area (about 400 $m^2\ g^{-1}$) of HTO is independent of the pH values of the preparation. It can be seen that uranium uptakes also do not depend on the pH values of the preparation.

The effect of the preparation of HTO on the uranium uptake was investigated as well. The uranium uptake

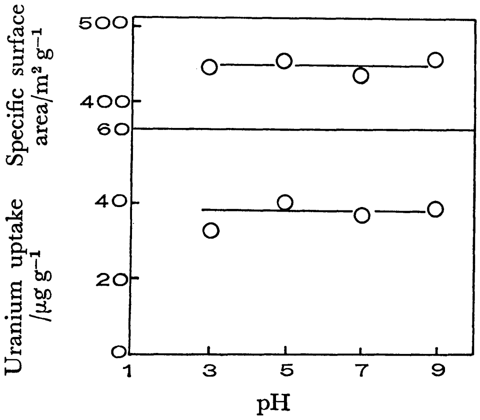

Fig. 1. Effect of preparation pH on uranium uptake and specific surface area.
Uranium adsorption;
concentration of uranium: 10 ppb, temperature: 25 °C, stirring time: 8 h.
Preparation of hydrous titanium(IV) oxide;
temperature: 25 °C, particle size: 150—200 mesh.

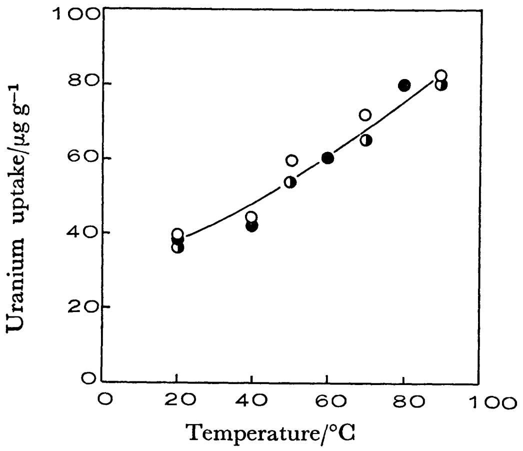

Fig. 2. Effect of preparation temperature on uranium uptake.
Uranium adsorpttion; same as Fig. 1.
Preparation of hydrous titanium(IV) oxide; pH: ○: 5, ●: 7, ◑: 9, particle size: 150—200 mesh.

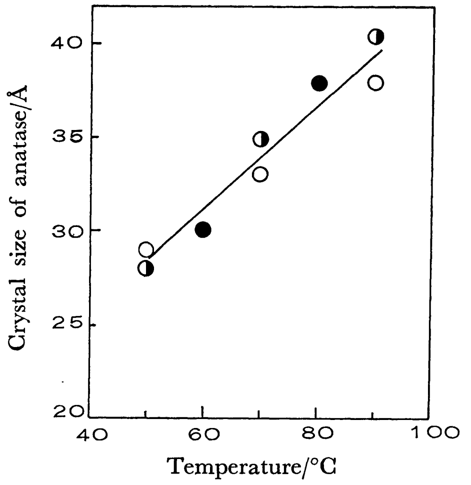

Fig. 3. Effect of preparation temperature on apparent crystal size of hydrous titanium(IV) oxide.
Preparation pH, ○, ●, ◑: same as Fig. 2.

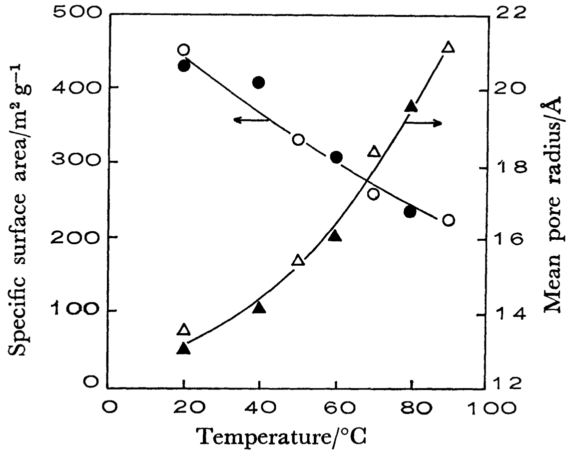

Fig. 4. Effect of preparation temperature on specific surface area and mean pore radius of hydrous titanium(IV) oxide.
Preparation pH, ○, △: 5, ●, ▲: 9.

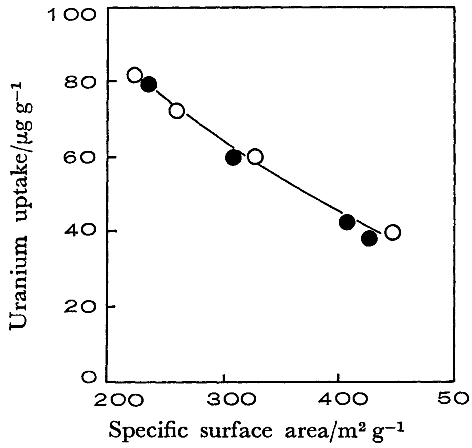

Fig. 5. Relation between uranium uptake and specific surface area of hydrous titanium(IV) oxide.
Preparation pH, ○: 5, ●: 9.

by HTO increased with an increase in the temperature of the preparation (Fig. 2). That is, HTO prepared at 20 °C and pH 5 had the uranium uptake of 40 μg g^{-1}; at 50 °C, 60 μg g^{-1}; at 70 °C, 73 μg g^{-1}, and at 90 °C, 82 μg g^{-1}. It is thus found that the uranium uptake depends strongly on the preparation temperature.

Physical Properties and Uranium Adsorption. In order to investigate the effect of the preparation temperature on the uranium uptake, the apparent crystal size, the specific surface area, and the mean pore radius of HTO were measured.

HTO prepared at 20 °C was found to be an amorphous structure, while that prepared above 50 °C showed some weak diffraction lines, indicating a crystal growth of an anatase type. The apparent crystal size of the anatase type is plotted against the temperature in Fig. 3. The crystal size of anatase increased with the temperature from about 28 Å at 50 °C to about 40 Å at 90 °C. The uranium uptake increased with the crystal growth of HTO under the present experimental conditions.

The specific surface area of HTO shows an inverse relationship with the pore radius and the crystal size (Fig. 3 and Fig. 4). The specific surface area decreased with the increase in the temperature from about 450 m^2 g^{-1} at 20 °C to about 220 m^2 g^{-1} at 90 °C. At the same time, the mean pore radius increased with the preparation temperature, *i.e.*, the values of the mean pore radius of the samples prepared at pH 5 were found to be 13.5 Å at 20 °C, 15.3 Å at 50 °C, 18.2 Å at 70 °C, and 21 Å at 90 °C. The preparation temperature thus had a large effect on the specific surface area and the mean pore radius of HTO.

The relation between the specific surface area and the uranium uptake of HTO is shown in Fig. 5. The uranium uptake decreased with the increase in the specific surface area, while it increased with the mean pore radius, as is shown in Fig. 6. The results show that the uranium uptake is low when the mean pore radius is small, despite the high specific surface area.

In consequence of the relatively high carbonate

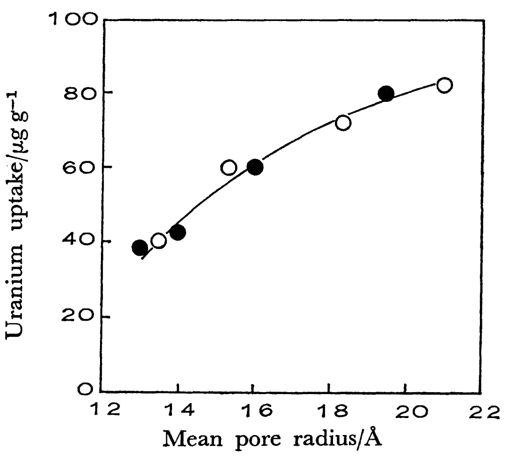

Fig. 6. Relation between uranium uptake and mean pore radius of hydrous titanium(IV) oxide.
○, ●: Same as Fig. 5.

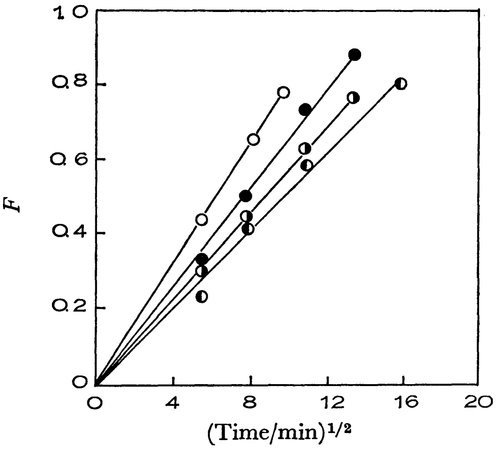

Fig. 7. Plot of F *vs.* $t^{1/2}$.
Uranium adsorption; concentration of uranium: 30 ppb, temperature: 25 °C.
Preparation of hydrous titanium(IV) oxide; particle size: 150—200 mesh, temperature: ○ 90 °C, ● 70 °C, ◑ 50 °C, ◐ 20 °C.

concentration in sea water (2.3×10^{-3} mol dm^{-3}), uranium exists in the form of tris(carbonato)dioxouranate(VI) $[UO_2(CO_3)_3]^{4-}$.[7] The ionic radius of the ion is estimated to be more than 4.7 Å.[8] It is supposed that $[UO_2(CO_3)_3]^{4-}$ can easily enter the pores with a larger diameter of HTO. However, in the case of HTO prepared at a lower temperature, the entrance of $[UO_2(CO_3)_3]^{4-}$ into the small pores is difficult. Therefore, it is considered that HTO prepared at a higher temperature exhibits a higher uranium uptake.

Kinetic Studies. Kinetic measurements were made of the uranium adsorption by HTO. When the adsorption is controlled by the particle diffusion, the following equation holds:[9]

$$F = \frac{Q_t}{Q_\infty} = \frac{6}{R}\sqrt{\frac{D_i t}{\pi}},$$

where F is the extent of adsorption, Q_t the uranium uptake in time t and Q_∞ the uranium uptake at equilibrium. R is the radius of the adsorbent, and D_i the diffusion coefficient. A plot of F *versus* $t^{1/2}$ will be a straight line if the adsorption is controlled by the particle diffusion, and the diffusion coefficient can be obtained from the slope of the line.

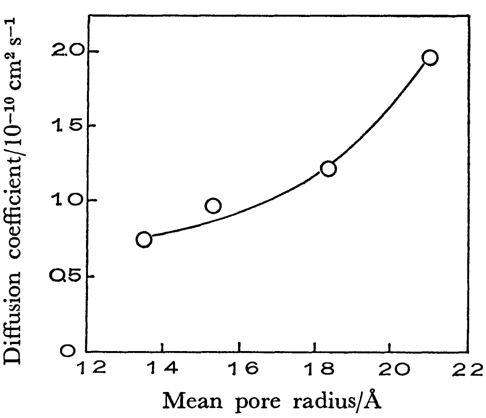

Fig. 8. Relation between diffusion coefficient and mean pore radius.

The rate of the uranium adsorption with HTO prepared at pH 5 and at 20—90 °C is shown in Fig. 7, which gives a linear relationship of F with $t^{1/2}$. The calculated diffusion coefficients are found to be 0.73×10^{-10} cm^2 s^{-1} for HTO prepared at 20 °C, 0.95×10^{-10} cm^2 s^{-1} at 50 °C, 1.24×10^{-10} cm^2 s^{-1} at 70 °C, and 1.98×10^{-10} cm^2 s^{-1} at 90 °C.

Figure 8 shows the relation between the diffusion coefficient and the mean pore radius of HTO prepared at 20—90 °C. It can be seen that the diffusion coefficients increase with the mean pore radius, *i.e.*, HTO prepared at a high temperature has larger pores and exhibits a higher uranium adsorption rate than that prepared at a low temperature. The diffusion coefficients in the present work are of the same magnitude as for the adsorption of methylene blue (with an ionic radius of about 4.5 Å) on the activated carbon (pore radius 10—30 Å, $D_i = 1.1 \times 10^{-10}$ cm^2 s^{-1}).[10]

The rate of the uranium adsorption increased with the temperature of the solution. The diffusion coefficient for HTO prepared at 90 °C was found to be 2.53×10^{-10} cm^2 s^{-1} at 40 °C of the solution in the adsorption experiment shown in Fig. 7. The activation energy was calculated to be 12.6 kJ mol^{-1}. The relatively small activation energy indicates that the adsorption rate is controlled by the particle diffusion.

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