NOTES *Bull. Chem. Soc. Jpn.*, ***60***, *4443—4444 (1987)*

Adsorption of Uranium from Nitric Acid Solutions Using Crystalline Hydrous Titanium Dioxide Fibers

Yū Komatsu,* Yoshinori Fujiki, and Takayoshi Sasaki
National Institute for Research in Inorganic Materials, 1-1 Namiki, Sakura-mura, Niihari-gun, Ibaraki 305
(Received May 2, 1987)

Synopsis. The adsorption of uranium on an ion exchanger of crystalline hydrous titanium dioxide fibers from nitric acid solutions has been studied. The rate of the adsorption of uranium was much higher than that of alkaline earth metal ions. The adsorption behavior of uranium was well explained by their ion exchange with hydrogen ions in the fibers.

Hydrous titanium dioxides have been mentioned for use in the extraction of uranium from seawater.[1,2] However, conventional hydrous titanium dioxide has been prepared of a fine particle powder and is not very suitable for column operations. Recently, Ohta and Fujiki have reported[3] a new type of hydrous titanium dioxide, crystalline hydrous titanium dioxide fibers, which is a derivative of potassium tetratitanate ($K_2Ti_4O_9$) fibers. The adsorption of alkali metal ions,[4,5] alkaline earth metal ions,[6-9] and bivalent transition metal ions[10] from weakly acidic solutions on the fibers has been studied by the authors. In the present work, the adsorption properties of crystalline hydrous titanium dioxide fibers for uranium are studied in order to obtain further information on the fibers.

Experimental

The titanium dioxide used was of 99.9% purity. Potassium tetratitanate fibers, $K_2Ti_4O_9$, were grown by the slow-cooling method in a K_2MoO_4 flux melt.[3] The fiber of about 10 g was filled in a glass column and converted to the protonated form, $H_2Ti_4O_9 \cdot nH_2O$, by passing 1 mol dm^{-3} hydrochloric acid until detection limit of potassium ion in the effluent by an atomic absorption method(Hitachi Polarized Zeeman Atomic Absorption Spectrophotometer 180-80). The weight of uranyl nitrate was measured as unhydrated state. All the other reagents used were of analytical grade. The measurements of the ion-exchange equilibria were made in a similar way to that in the previous study,[7] except that the fiber and the aqueous solution were agitated 50 times a day by hand.

The distribution coefficient K_d of uranium was obtained by mixing 0.1 g of the fiber with 10 cm^3 of the aqueous solution containing various concentrations of uranium and calculated as:

$$K_d = (\text{amount of uranium of sorbed per 1 g of the fiber}) / (\text{amount of uranium per 1 cm}^3 \text{ of solution}) \qquad (1)$$

Here, the weight of the solid was measured in the air-dried state.

The pH values of the solutions were controlled with nitric acid and were measured by a TOA pH meter(model HM-20E). The uranium contents in the supernatant solution was determined with a Daini Seikosha Inductively Coupled Plasma Optical Emission Spectrophotometer(model SPS-1100).

Results and Discussion

Figure 1 gives the percent adsorption values for uranium between fibers and aqueous solution as a function of the contact time. Although 10—14 days were required to attain equilibrium for alkaline earth metal ions[7] and bivalent transition metal ions,[10] the equilibrium of uranium was attained within three days.

Crystalline hydrous titanium dioxide fibers have two exchangeable protons in the chemical formula. When alkali metal ions are incorporated in the hydrated fibers, one of these protons may be replaced with an alkali metal ion by ion exchange. An alkaline earth metal ion or a bivalent transition metal ion can replace the two protons in the fiber. As can be seen in Fig. 2, the distribution coefficient of uranium is first-

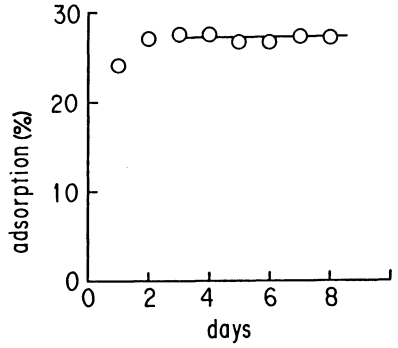

Fig. 1. The percent absorption of the uranium as a function of contact time at 298 K. Ion exchanger: $H_2Ti_4O_9 \cdot nH_2O$ (0.1 g). Aqueous phase: nitric acid containing 1×10^{-4} mol dm^{-3} uranyl nitrate at initial time (10 cm^3).

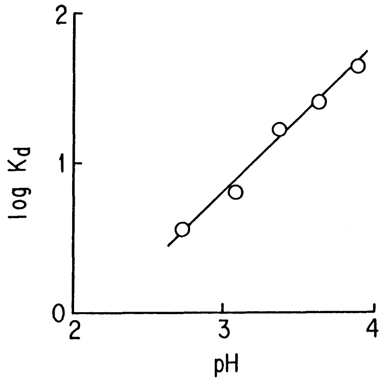

Fig. 2. The distribution coefficient of the uranium as a function of pH in the aqueous solution at 298 K. Ion exchanger: $H_2Ti_4O_9 \cdot nH_2O$ (0.1 g). Aqueous phase: nitric acid containing 1×10^{-4} mol dm^{-3} uranyl nitrate at initial time (10 cm^3).

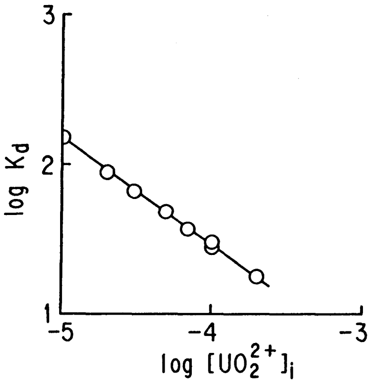

Fig. 3. The distribution coefficient of the uranium as a function of initial uranium concentration in the aqueous phase at 298 K. Ion exchanger: $H_2Ti_4O_9 \cdot nH_2O$ (0.1 g). Aqueous phase: uranyl nitrate solution of various concentrations (10 cm^3).

order with respect to pH value under the substantially constant concentration of the hydrogen ion in the solid. Furthermore, the rate of ion-exchange reaction for uranium is as fast as that for alkali metal ions.[5] These facts may indicate that uranium acts as a univalent metal complex ion on adsorption. The two kinds of univalent uranium complex ions exist in the solution as $[UO_2NO_3]^+$[11] or $[UO_2OH]^+$.[12] However, since the stability constant for $[UO_2NO_3]^+$($\log K_{(\mathrm{UO_2NO_3^+})}$ $=-0.3$)[11] is extremely larger than that for $[UO_2OH]^+$ ($\log K_{(\mathrm{UO_2OH^+})}=-5.0$)[12] in the aqueous solution, the adsorption reaction of uranium in this system can be written as

$$m[\mathrm{UO_2NO_3}]^+\,(\mathrm{aq}) + \mathrm{H_2Ti_4O_9}\cdot n\mathrm{H_2O}\,(\mathrm{s}) \longrightarrow [\mathrm{UO_2NO_3}]_m\mathrm{H}_{(2-m)}\mathrm{Ti_4O_9}\cdot n\mathrm{H_2O}\,(\mathrm{s}) + m\mathrm{H}^+\,(\mathrm{aq}) \quad (0<m<2), \qquad (2)$$

where the subscripts "aq" and "s" denote the aqueous and solid phase.

Figure 3 gives the log K_d values as a function of the initial uranium concentration in the aqueous solution. The K_d increases with a decrease of the uranium concentration. Accordingly, this result is to be expected for the recovery of uranium in seawater since these ions are contained only about 3 ppb in sea water.

The authors are very grateful to Professor Tatsuya Sekine and Mr.Kazuho Inaba of Science University of Tokyo for their valuable discussions during the work, and to Professor Mitsuo Abe of Tokyo Institute of Technology who encouraged us during this work.

References

1) N. J. Keen, *J. Br. Nucl. Energy Soc.*, **7**, 178 (1968).

2) N. Ogata, *Nippon Genshiryoku Gakkai Shi*, **13**, 121 (1971).

3) N. Ohta and Y. Fujiki, *Yogyo Kyokai Shi*, **89**, 134 (1981).

4) Y. Komatsu and Y. Fujiki, *Chem. Lett.*, **1980**, 1525.

5) Y. Komatsu, Y. Fujiki, and T. Sasaki, *Bunseki Kagaku*, **31**, E225 (1982).

6) T. Sasaki, Y. Komatsu, and Y. Fujiki, *Chem. Lett.*, **1981**, 957.

7) Y. Komatsu, Y. Fujiki, and T. Sasaki, *Bunseki Kagaku*, **32**, E33 (1983).

8) Y. Komatsu, Y. Fujiki, and T. Sasaki, *Bunseki Kagaku*, **33**, E159 (1984).

9) Y. Komatsu, Y. Fujiki, and T. Sasaki, *Yogyo Kyokai Shi*, **92**, 665 (1984).

10) T. Sasaki, Y. Komatsu, and Y. Fujiki, *Sep. Sci. Technol.*, **18**, 49 (1983).

11) L. G. Sillen and A. E. Martel, "Stability Constants," the Chemical Society, Spec, Pub. (1964), p. 17.

12) J. Stary, *Collect. Czech. Chem. Commun.*, **25**, 890 (1960).