Bull. Chem. Soc. Jpn., ***53***, *1331—1334 (1980)*

The Collection of Uranium from Sea Water with Hydrous Metal Oxide. III. The Effects of Diverse Ions in Sea Water on Uranium Adsorption by Hydrous Titanium(IV) Oxide

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

(Received April 2, 1979)

The effect of diverse ions present in sea water on the uranium adsorption is elucidated in the present paper. The uranium-adsorption experiments were conducted using sea water and a solution containing 0.72 mol dm^{-3} NaCl and 2.3×10^{-3} mol dm^{-3} $NaHCO_3$. The uranium uptake was about ten times larger from the NaCl–$NaHCO_3$ solution than from sea water. The ions which depressed the uranium uptake were the calcium, magnesium, and fluoride present in sea water. Among these ions, calcium had the largest effect on the uranium uptake. The analysis of calcium and carbonate in the adsorbent after the adsorption experiment has revealed that the molar ratio between calcium and carbonate was about one. It was considered that calcium carbonate was deposited on the adsorbent during the uranium adsorption. The specific surface area and the pore volume decreased after the deposition of calcium carbonate. It was supposed that the decrease in the uranium uptake was caused by the coverage of the surface of hydrous titanium(IV) oxide with calcium carbonate. Magnesium ions depressed the uranium uptake in the same manner as calcium ions. The effect of the magnesium ions, however, was relatively small compared with that of the calcium ions.

For the purpose of collecting uranium from sea water, several methods have been proposed; adsorption,[1—2] coprecipitation,[3] ion exchange,[4] ion floatation,[5] and solvent extraction.[4] The adsorption method has been thought to be most feasible. In the adsorption method, an adsorbent with a high adsorption capacity and selectivity is prerequisite, because the uranium concentration is very low (3 ppb), and a large amount of diverse ions are present in sea water. A large number of adsorbents have been examined.

It has been reported that hydrous titanium(IV) oxide is the most suitable as a uranium adsorbent.[1—2]

More than sixty ions are present in sea water. Since hydrous titanium(IV) oxide serves as a cation exchanger in sea water, cations present in sea water may affect the uranium adsorption. Ogata *et al.*[6] reported that the uranium uptake decreased slightly in the presence of phosphate, fluoride, and copper. Kanno *et al.*[7] described that carbonate ions present in sea water had a negative effect on the uranium adsorption. However, these results can not satisfactorily account for the effect of diverse ions on uranium adsorption.

In the present work, the effect of diverse ions present in sea water on the uranium adsorption by hydrous titanium(IV) oxide is described.

Experimental

Preparation of Hydrous Titanium(IV) Oxide. Hydrous titanium(IV) oxide was prepared by adding 7% aqueous ammonia to a solution of 0.6 mol dm^{-3} titanium(IV) chloride at 90 °C. The precipitate was filtered off, washed with water, and dried at room temperature for about 10 d. The dried samples were crushed and sieved, a portion of 300—400 mesh being used in the experiments. The water content was determined by measuring the ignition loss at 800 °C; it was found to be 18%, which corresponded to $TiO_2\cdot H_2O$. X-Ray powder diffraction analysis showed the crystal form of anatase, with an apparent crystal size of 38 Å.

Adsorption Experiments. Sea water and a NaCl–$NaHCO_3$ solution were used in the adsorption experiments. The molar concentrations of uranium and the major constituents of sea water used in the present work are shown in Table 1. In the case of a NaCl–$NaHCO_3$ solution, the concentration of NaCl was taken to be 0.72 mol dm^{-3} in order for it to be the same ionic strength as that of sea water while that of $NaHCO_3$ was ordinarily chosen to be 2.3×10^{-3} mol dm^{-3}, equal to that of sea water. The concentration of uranium in the solution was taken to be 3—60 ppb by adding a uranyl(VI) chloride solution. In the uranium-adsorption experiments, 40 mg of the adsorbent were introduced into 1000 ml of the solution. The solution was stirred by means of a vertical stirrer at 25 °C. Within 5 h, the adsorption equilibrium was achieved under the present experimental conditions. The adsorbent was separated from the solution, and the change of the uranium concentration in the solution was measured.

TABLE 1. MOLAR CONCENTRATIONS OF URANIUM AND MAJOR IONS IN SEA WATER SAMPLED AT THE HITACHI SEASHORE

	Concentration/mol dm^{-3}
U	1.3×10^{-8}
Cl	5.4×10^{-1}
Na^+	4.6×10^{-1}
Mg^{2+}	5.2×10^{-2}
SO_4^{2-}	2.7×10^{-2}
Ca^{2+}	9.9×10^{-3}
K^+	9.7×10^{-3}
$HCO_3^-+CO_3^{2-}$	2.3×10^{-3}
pH	8.0—8.1

The carbonate, calcium, and magnesium uptake was measured by the following procedure; one-fifth gram of the adsorbent was introduced into 5000 ml of the solution, after which the solution was stirred for 5 h at 25 °C. The contents of calcium, magnesium, and carbonate in the adsorbent were then determined.

Analytical Method. The uranium in the solution was determined spectrophotometrically, with Arsenazo III as the indicator.[8] The determination of the carbonate in the adsorbent was carried out by the following procedure. The adsorbent after the adsorption experiment was washed with distilled water and dried at room temperature. The dried samples were placed in a flask, where N_2 as carrier gas was passed through continuously, about 10 ml of 0.1 mol dm^{-3} HCl solution were then added to the flask at 50 °C. The carbon dioxide thus produced was introduced into the carbon analyzer, Kokusai Denki VK-1-type "Coulomatic C," and was determined by the coulometric titration. The limit of detection was 4.2×10^{-5} mmol as carbon, and the coefficient of variation was found to be 3.5% when 5 mg of calcium carbonate was analyzed by this procedure.

The determination of the calcium and magnesium adsorbed in the adsorbent was carried out by the following procedure; after the adsorption experiment, the dried samples were fused with sodium carbonate and boric acid and dissolved in an HCl solution. The concentration of calcium or magnesium in the HCl solution was then determined by atomic absorption spectrophotometry using a Hitachi 207 Atomic-absorption spectrophotometer.

The specific surface area and pore volume of the adsorbent were determined by means of the N_2 adsorption at −195 °C using a Carlo Erba Sorptomatic Series 1800.

Results and Discussion

Adsorption Isotherm of Uranium. The adsorption isotherm of uranium in sea water or a NaCl–$NaHCO_3$ solution is shown in Fig. 1. Kanno *et al.*[7] reported that the uranium adsorption from sea water gave a Freundlich-type isotherm. As is shown in Fig. 1, the same results were obtained in both sea water and the NaCl–$NaHCO_3$ solution.

The value of n in the Freundlich equation ($v = k\,C^{1/n}$) was found to be 1.4 and 1.3 for sea water and for the NaCl–$NaHCO_3$ solution respectively.

It is known that uranium in sea water exists in the form of tris(carbonato)dioxouranate(VI) ion $[UO_2(CO_3)_3]^{4-}$. The distributions of uranyl(VI) species in the NaCl–$NaHCO_3$ solution used in the present work were calculated from the stability constants;[9] they are summarized in Table 2. The tris(carbonato)dioxouranate(VI) ion, which is the major uranyl(VI) species in sea water, is a predominant species in the NaCl–$NaHCO_3$ solution. Although the uranyl(VI) species and the type of adsorption are the same in sea water and in the NaCl–$NaHCO_3$ solution, the uranium uptake is found to be quite different. The difference in the uranium uptake is thought to be attributable to the diverse ions in sea water.

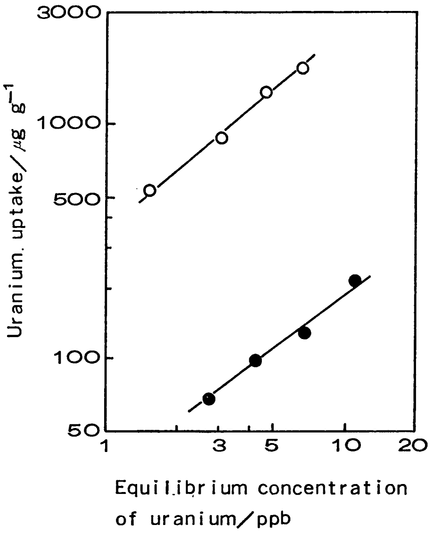

Fig. 1. Adsorption isotherm of uranium on hydrous titanium(IV) oxide.
Adsorption temperature: 25 °C, ○: NaCl-$NaHCO_3$ solution, ●: sea water.

Table 2. Distribution of uranyl complexes in the NaCl-$NaHCO_3$ solution at pH 8

Species	Ratio/%
UO_2^{2+}	0
$UO_2(OH)^+$	0.1
$UO_2(OH)_3^-$	14.1
UO_2Cl^+	0
$UO_2Cl_3^-$	0
$UO_2(CO_3)_2^{2-}$	0.9
$UO_2(CO_3)_3^{4-}$	84.9

Effect of Diverse Ions in Sea Water. In order to investigate the effect of diverse ions in sea water on uranium adsorption, the uranium uptake was measured with NaCl–$NaHCO_3$ solutions containing 20 ppb uranium and a diverse ion at the concentration equal to that of sea water. The ion species examined are magnesium, calcium, strontium, potassium, borate, sulfate, fluoride, and bromide ions. The results are summarized in Table 3. The uranium uptake from an NaCl–$NaHCO_3$ containing K^+, Sr^{2+}, SO_4^{2-}, Br^-, or BO_3^{3-} was nearly equal to that from the NaCl–$NaHCO_3$ solution. The obtained results show that these ions have no effect on the uranium uptake. On the other hand, the uranium uptake was reduced by the presence of calcium, magnesium, and fluoride ions. Particularly, the presence of calcium ions hindered the uranium adsorption.

The uranium uptake from the solution containing all the ions together (No. 10 in Table 3) agreed well with that from sea water. The effects of calcium, magnesium, and fluoride ions on the uranium uptake

Table 3. Uranium uptake with a NaCl-$NaHCO_3$ solution containing 20 ppb of uranium and various ions at pH 8

Sample No.	Salt added	Concentration mol dm^{-3}	Uranium uptake μg g^{-1}
1	Not added	—	460
2	$MgCl_2$	5×10^{-2}	428
3	Na_2SO_4	3×10^{-2}	458
4	$CaCl_2$	1×10^{-2}	273
5	KCl	9×10^{-3}	462
6	KBr	8×10^{-4}	460
7	H_3BO_3	4×10^{-4}	460
8	$SrCl_2$	2×10^{-4}	457
9	NaF	7×10^{-5}	435
10	No. 2 to No. 9 added		223
11	Sea water		220

are discussed below.

It was reported in our previous paper[10] that the adsorption site of hydrous titanium(IV) oxide for $[UO_2(CO_3)_3]^{4-}$ may be supposed to be the surface hydroxo group [Ti–OH]. The fluoride ion reacts with Ti–OH to form Ti–F. The reaction is useful for the determination of the surface hydroxo group.[11] It may, therefore, be considered that fluoride ions reduce the uranium adsorption site by forming Ti–F. Since the concentration of fluoride ions in sea water is low, the effect of fluoride ions on the uranium uptake is small.

Figure 2 shows the variation in the uranium uptake with the concentration of calcium ions in $NaCl$–$NaHCO_3$ solutions containing 20 ppb of uranium. The uranium uptake decreases with an increase in the concentration of calcium ions. Since the deposition of the calcium compound was expected to take place on the adsorbent, the calcium uptake and carbonate uptake were measured in various solutions. The results are shown in Table 4. The calcium uptake was 0.56 mmol g^{-1} from the $NaCl$–$NaHCO_3$–$CaCl_2$ solution (No. 2 in Table 4) and 0.34 mmol g^{-1} from the $NaCl$–$CaCl_2$ solution (No. 3 in Table 4). Since hydrous titanium(IV) oxide behaves as a cation exchanger in an alkaline solution,[12] the calcium ion is thought to be adsorbed from the $NaCl$–$CaCl_2$ solution by means of an ion-exchange reaction. It is deduced that 0.34 mmol g^{-1} of the 0.56 mmol g^{-1} calcium uptake from the $NaCl$–$NaHCO_3$–$CaCl_2$ solution is attributable to the ion-exchange reaction, and 0.22 mmol g^{-1} (=0.56 mmol g^{-1}—0.34 mmol g^{-1}) to an other adsorption process. The carbonate uptake from the $NaCl$–$NaHCO_3$–$CaCl_2$ solution is found to be about 0.20 mmol g^{-1} (No. 2 in Table 4), while it is very small without calcium ions (No. 1 in Table 4).

The calcium uptake attributed to the adsorption process other than ion-exchange (0.22 mmol g^{-1}) is nearly equal to the carbonate uptake (0.20 mmol g^{-1}), indicating that calcium carbonate is deposited on the surface of the adsorbent. In the case of sea water, the calcium uptake and the carbonate uptake are in good agreement with those from the $NaCl$–$NaHCO_3$–$CaCl_2$ solution (No. 2 and No. 6 in Table 4).

The variation in the uranium, calcium, and carbonate uptake with the concentration of $NaHCO_3$ in the $NaCl$–$CaCl_2$ solution is shown in Fig. 3. The increase in the concentration of $NaHCO_3$ raises the calcium and carbonate uptakes while the uranium uptake markedly decreases. Regardless of the $NaHCO_3$ concentration, the difference between calcium and carbonate

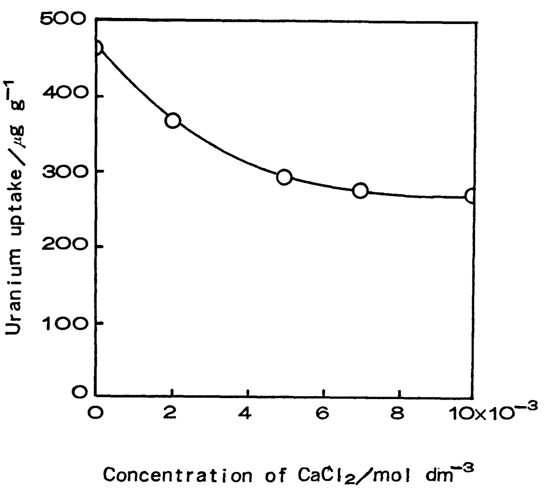

Fig. 2. Variation of uranium uptake with concentration of $CaCl_2$.
pH of the solution: 8.0, NaCl: 0.72 mol dm^{-3}, $NaHCO_3$: 2.3×10^{-3} mol dm^{-3}, uranium: 20 ppb.

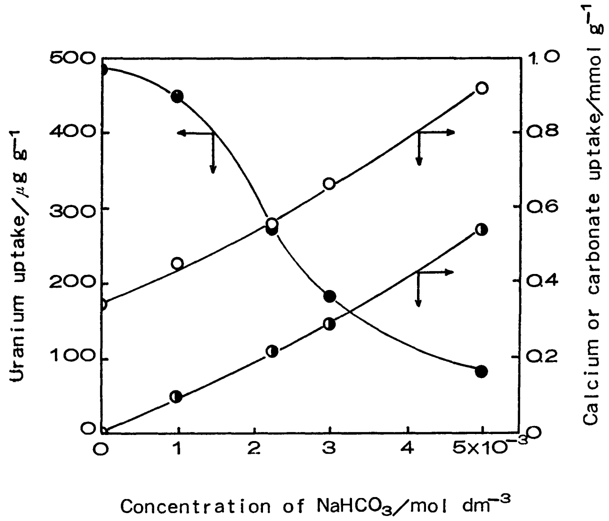

Fig. 3. Variation of uranium, calcium and carbonate uptake with concentration of $NaHCO_3$.
pH of the solution: 8.0, NaCl: 0.72 mol dm^{-3}, $CaCl_2$: 10^{-2} mol dm^{-3}, uranium: 20 ppb, ●: uranium uptake, ○: calcium uptake, ◑: carbonate uptake.

Table 4. Uptake of calcium, magnesium, and carbonate by hydrous titanium(IV) oxide with various solutions at pH 8

Sample No.	Solution[a]	Uptake/mmol g^{-1}		
		Calcium	Magnesium	Carbonate
1	$NaCl$-$NaHCO_3$	—	—	0.003
2	$NaCl$-$NaHCO_3$-$CaCl_2$	0.56	—	0.20
3	$NaCl$-$CaCl_2$	0.34	—	—
4	$NaCl$-$NaHCO_3$-$MgCl_2$	—	0.25	0.04
5	$NaCl$-$MgCl_2$	—	0.20	—
6	Sea water	0.51	0.18	0.22

a) NaCl: 0.72 mol dm^{-3}, $NaHCO_3$: 2.3×10^{-3} mol dm^{-3}, $CaCl_2$: 10^{-2} mol dm^{-3}, $MgCl_2$: 5×10^{-2} mol dm^{-3}.

TABLE 5. SPECIFIC SURFACE AREA(S) AND PORE VOLUME(V) OF HYDROUS TITANIUM(IV) OXIDE BEFORE AND AFTER URANIUM ADSORPTION

	Before adsorption	After adsorption		
		NaCl-$NaHCO_3$	NaCl-$NaHCO_3$-$CaCl_2$	Sea water
$S/m^2\ g^{-1}$	261	250	177	168
$V/cm^3\ g^{-1}$	0.34	0.33	0.26	0.24

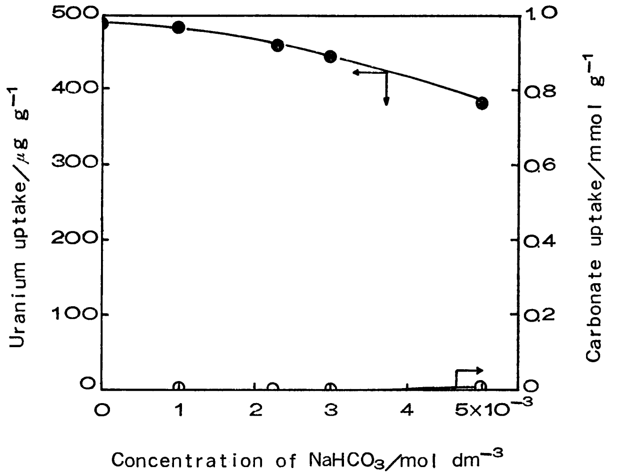

Fig. 4. Variation of uranium and carbonate uptake with concentration of $NaHCO_3$.
pH of the solution: 8.0, NaCl: 0.72 mol dm^{-3}, uranium: 20 ppb, ●: uranium uptake, ○: carbonate uptake.

uptakes remained constant (about 0.35 mmol g^{-1}); this value corresponds to the calcium uptake by the ion-exchange reaction. The variation in the uranium and carbonate uptakes with the $NaHCO_3$ concentration in the NaCl solution is shown in Fig. 4. In the absence of calcium ions, the carbonate uptake is very small, and the uranium uptake is slightly decreased with the concentration of $NaHCO_3$. It may be supposed that the decrease in the uranium uptake is due to the deposition of calcium carbonate on the adsorbent.

The magnesium uptake by the adsorbent is also shown in Table 4. The magnesium uptake in the presence and in the absence of $NaHCO_3$ were 0.25 mmol g^{-1} (No. 4 in Table 4) and 0.20 mmol g^{-1} (No. 5 in Table 4) respectively. Thus, the effect of carbonate ions on the magnesium uptake is rather small compared with that on the calcium uptake. It is considered that the deposition of magnesium carbonate is more difficult on the adsorbent than that of calcium carbonate. The specific surface area and pore volume of the adsorbent before and after the adsorption experiment are presented in Table 5. With the NaCl–$NaHCO_3$ solution, the changes in the surface area and the pore volume are very small.

On the other hand, with the NaCl–$NaHCO_3$–$CaCl_2$ solution and sea water, the decreases in the specific surface area and the pore volume are large. These results indicate that the decreases in the specific surface area and pore volume are due to the deposition of calcium carbonate on the adsorbent.

The present experimental results make it possible to conclude that the uranium uptake from sea water by hydrous titanium(IV) oxide is reduced mainly because of the calcium carbonate deposition.

The authors wish to thank Professor Shosuke Imoto of Osaka University for his many helpful discussions and suggestions.

References

1) N. J. Keen, *J. Brit. Nucl. Energy. Soc.*, **7**, 178 (1968).
2) N. Ogata and H. Kakihana, *J. At. Energy. Soc. Jpn.*, **11**, 82 (1969).
3) M. Ishibashi, T. Fujinaga, T. Kuwamoto, and Y. Ogino, *Nippon Kagaku Kaishi*, **88**, 73 (1967).
4) R. V. Davies, J. Kennedy, R. W. McIlroy, R. Spence, and K. M. Hill, *Nature*, **203**, 1110 (1964).
5) Y. S. Kim and H. Zeitlin, *Anal. Chem.*, **43**, 1390 (1971).
6) N. Ogata, N. Inoue, and H. Kakihana, *Nippon Kaisui Gakkai Shi*, **24**, 68 (1970).
7) M. Kanno, Y. Ozawa, and T. Mukaibo, *J. At. Energy. Soc. Jpn.*, **12**, 708 (1970).
8) Y. Miyake, Y. Sugimura, and T. Uchida, *Recod. Oceanog. Works. Jpn.*, **11**, 53 (1972).
9) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chem. Soc., London (1964), p. 138.
10) H. Yamashita, Y. Ozawa, F. Nakajima, and T. Murata, *Bull. Chem. Soc. Jpn.*, **53**, 1 (1980).
11) H. P. Boehm, *Adv. Catal.*, **16**, 179 (1966).
12) M. Abe, *Bunseki Kagaku*, **23**, 1254 (1974).