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Simulation of Adsorption of Uranium from Seawater Using Liquid Film Mass Transfer Controlling Model

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Abstract

A liquid film mass transfer control model was applied to the batch adsorption of uranium from seawater with an amidoxime-group-containing polymeric adsorbent made by the radiation-induced grafting method. The adsorption amount was calculated by changing two parameters, equilibrium adsorption amount q_0 and liquid film mass transfer coefficient k, to obtain the best fit between the observed and calculated values. The index of a Freundlich-type isotherm was obtained as 1.6, which is similar to the previously observed value with hydrous titanium oxide adsorbent. The plot of k vs $1/T$ provided the activation energy as 10.0 kcal/mol. Both q_0 and k showed an approximately first-order dependency on the amidoxime group content in the adsorbent. The simulation made it clear that the increase in k brought about by mixing amidoxime groups with carboxyl groups was due to a synergistic effect of these groups.

INTRODUCTION

Among various organic adsorbents for separating uranium from seawater, polymeric adsorbents containing amidoxime groups have been noted as promising because of the rapid adsorption rate and the high capacity for uranium (*1–7*). In our previous studies (*8–11*), this type of adsorbent was synthesized by the radiation-induced grafting method. The polyacrylonitrile chains which were grafted to polymeric raw materials were reacted with hydroxylamine to produce amidoxime groups. This synthetic procedure has such merits as the controllability of both the concentration and the distribution of active sites for adsorption, and the availability of various kinds of polymeric raw materials as base substrates for adsorbents. The first characteristic extends the possibility of designing an improved adsorbent because the adsorbent will require a precisely controlled location of amidoxime groups in order to obtain maximum adsorption efficiency. The second characteristic is useful from a practical point of view because it is possible to make adsorbents with sufficient mechanical strength by using such tough polymers as polypropylene as a raw material. In the future the amidoxime-group-containing adsorbent fiber, which is thought to be the most effective shape for uranium recovery (*12*), will be developed in such practical shapes as nets and fabrics. Therefore, the availability of adsorbents in different shapes with enough mechanical strength by the present synthetic method is of great value.

The saturated amount of adsorption and the adsorption rate are usually treated as two factors for the evaluation of adsorbents. However, these values are affected by such experimental conditions as amounts of seawater and adsorbents, etc. Therefore, a theoretical treatment is desirable in order to estimate the adsorption efficiency universally. In this paper a simulation of adsorption using liquid film mass transfer control was employed to elucidate the adsorptive characteristics of the present adsorbents.

EXPERIMENTAL

Details of the synthetic procedure have been reported in previous papers (*8-11*). In this study a fibrous adsorbent, made by grafting acrylonitrile onto polypropylene fiber followed by amidoximating the nitrile groups of the grafted chains, was used for the adsorption experiments. The concentration of amidoxime groups introduced in the adsorbents was estimated by elemental analysis. The average diameter of the adsorbent obtained was 0.01 cm and the density was 1.6 g/cm^3.

A batch process was used for adsorbing uranium from seawater. About 40 mg of the adsorbent was agitated in 2–5 L seawater at 25°C. The amount of uranium desorbed with 1 *N* hydrochloric acid and complexed with Arsenazo III was measured optically at 665 nm by means of a Shimadzu spectrophotometer, model UV 100-02.

The water uptake was obtained by immersing the adsorbents in water for 24 h followed by blotting the surface of the adsorbents and weighing on a microbalance. The exchange rate of adsorbed water with the water outside the adsorbent was carried out as follows (*13*): the wet adsorbent was dipped in D_2O for a prescribed time interval, and the content of H_2O in D_2O was followed with a JEOL proton-NMR apparatus, model JNM-PET-100.

RESULTS AND DISCUSSION

When the liquid film mass transfer control model is applied to batch adsorption, the following equations of mass balance are available (*14*, *15*):

$$W dq/dt = kS(c - c_i) \tag{1}$$

$$c_0 V = cV + Wq \tag{2}$$

If a Freundlich-type isotherm is applied, then

$$q/q_0 = (c_i/c_0)^{1/n} \tag{3}$$

From Eqs. (1)–(3),

$$dq/dt = (kS/W)(c_0 - qW/V - c_0(q/q_0)^n) \tag{4}$$

$$\text{at } t = 0\text{: } c = c_0 \text{ and } q = 0 \tag{5}$$

where S/W is equal to $2/R\rho$ because of the cylindrical shape of the fibrous adsorbent. This differential equation can be numerically integrated by changing parameters n, q_0, and k in order to obtain the best fit between the observed and calculated adsorption vs time curves.

Several adsorption runs were carried out by changing the adsorbent/seawater ratio. Figure 1 shows the relation between the amount of uranium in adsorbent q and the concentration of uranium remaining in the seawater at equilibrium adsorption c^* which was obtained by seven days' adsorption. Every data point scatters around a straight line, which indicates that the adsorption isotherm is of the Freundlich type. From the slope of the straight line, the parameter n in Eq. (3) was obtained as 1.6. This value is close to 1.5 which was previously observed in the adsorption of uranium from seawater with hydrous titanium oxide adsorbent (*14*). The integration of Eq. (4) is possible by changing q_0 and k.

In the recovery of uranium from seawater, adsorption depends on the temperature of seawater. When the adsorption is carried out for several

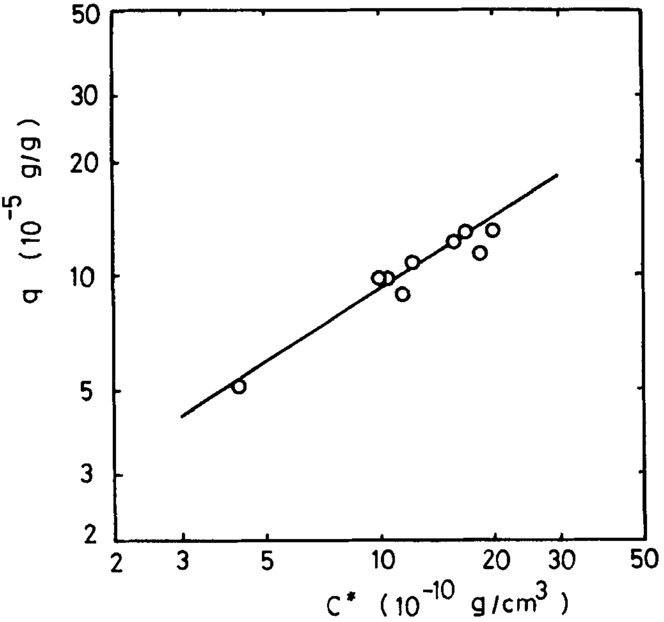


FIG. 1. Relation between the amount of uranium in adsorbent and the concentration of uranium remaining in seawater at equilibrium.

months, for example, the difference in seawater temperature is more than 10°C in the sea around Japan. Therefore, it is important to elucidate the temperature effect on adsorption efficiency. The adsorption was carried out with the adsorbent containing 5 mmol/g-Ad of amidoxime groups at the prescribed temperature in the range of 15 to 35°C. As shown in Fig. 2, the adsorption rate was enhanced by raising the temperature. The equilibrium adsorption amount, on the other hand, was less affected by the temperature. When the temperature was 35°C, equilibrium was obtained in less than 3 d. On the other hand, it took 7 d at 15°C.

The values q_0 and k needed to provide the best fit between the observed and the calculated adsorption were plotted against $1/T$. As shown in Fig. 3, the dependency of q_0 on temperature in much smaller than that of k. In other words, an increase in seawater temperature mainly facilitates the movement of metal ions through the liquid-solid boundary phase. The activation energy was obtained as 10.0 kcal/mol from the slope of the plot of k vs $1/T$.

The result that the solid lines calculated by Eq. (4) are in good

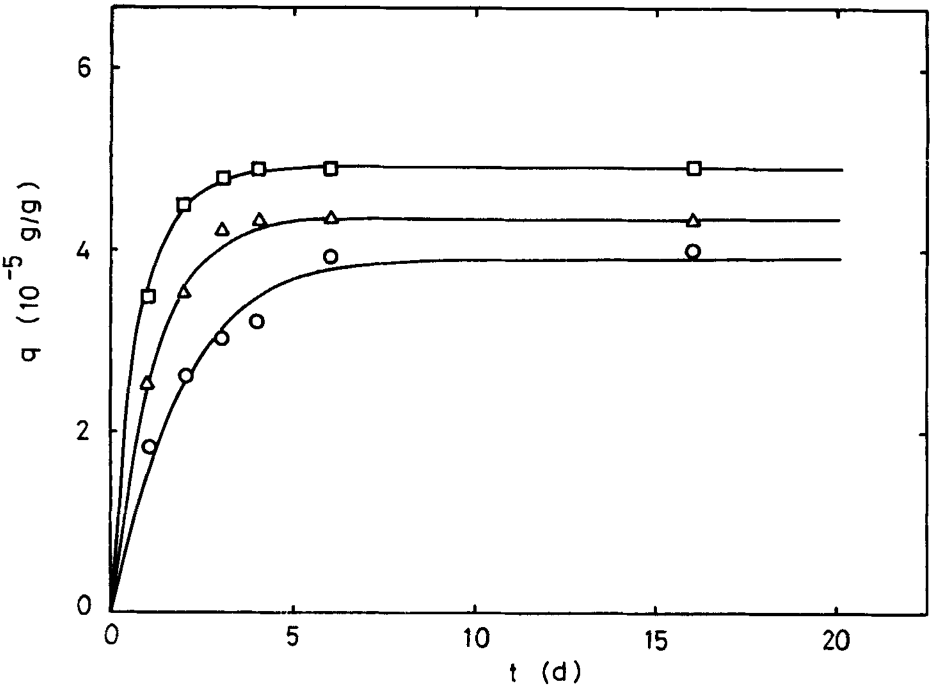


FIG. 2. Effect of seawater temperature on adsorption of uranium: (○) 15°C, (△) 25, (□) 35.

agreement with the observed adsorption in Fig. 2 indicates that the simulation using liquid film mass transfer control is effective for describing the present adsorption process. In this case the product B_im ($B_im = kR/D_e$, $m = c_0/q_0$) should be smaller than unity (*15*). D_e should be larger than 3×10^{-11} cm^2/s under the present condition: $k = 1 \times 10^{-3}$ cm/s, $R = 0.005$ cm, $c_0 = 3 \times 10^{-9}$ g/cm^3, and $q_0 = 0.06$ g/g. This is plausible because the value is only $1/10^5$ that observed in seawater (3×10^{-6} cm^2/s) (*14*).

As mentioned above, one of the characteristics of the present method for synthesizing adsorbents is the controllability of the amount of amidoxime groups introduced. The first controlling step is the production of active sites for polymerization through irradiation. The amount of active sites is a simple function of irradiation dose. The second one is the polymerization in which monomer concentration, temperature, and reaction time are the main factors for controlling the amount of nitrile groups which are changed to amidoxime groups. The amount of amidoxime is also controlled by the reaction conditions of amidoximation.

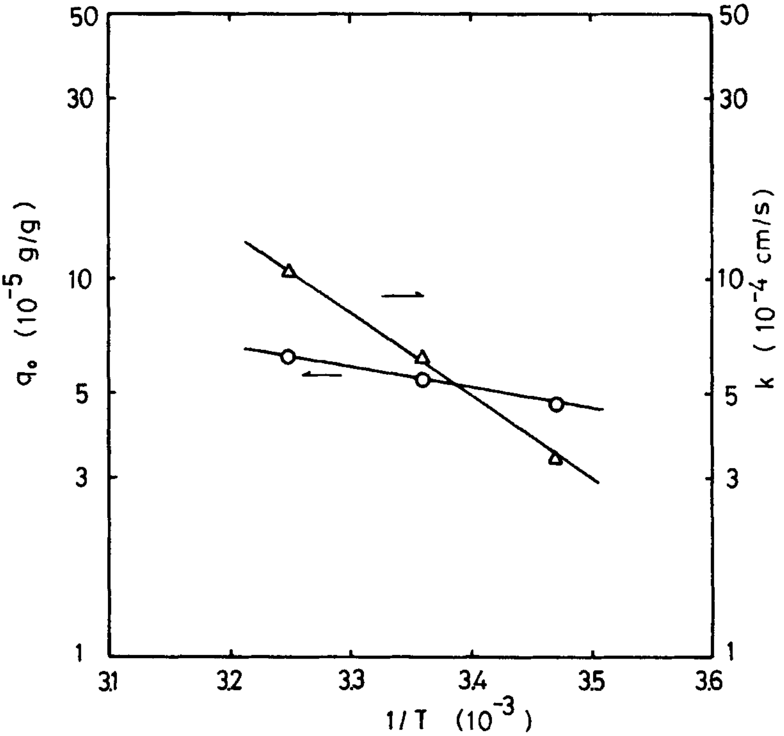


FIG. 3. Plots of q_0 and k against $1/T$.

In the present study the amount of amidoxime groups was changed by changing the reaction time of graft polymerization. Figure 4 shows the relation between the adsorption q and contact time t obtained by these adsorbents. Both the rate and the capacity of adsorption increase with an increase in the amidoxime content in the adsorbent. The calculated values, represented by solid lines, are in good agreement with the observed values.

The values of q_0 and k that provide the best fit between the observed and calculated adsorption are plotted against the content of amidoxime functional groups in the adsorbent [F.G.] in Fig. 5. The almost first-order dependencies of q_0 and k on [F.G.] obtained from the slopes of the straight lines ($q_0 \propto [\text{F.G.}]^{0.8}$ and $k \propto [\text{F.G.}]^{0.9}$) indicate that increases in both adsorption capacity and mass transfer coefficient through the liquid film are in proportion to the increase in [F.G.]. Because the metal ions are dissolved in water, their mobility is reduced to the movement of water in

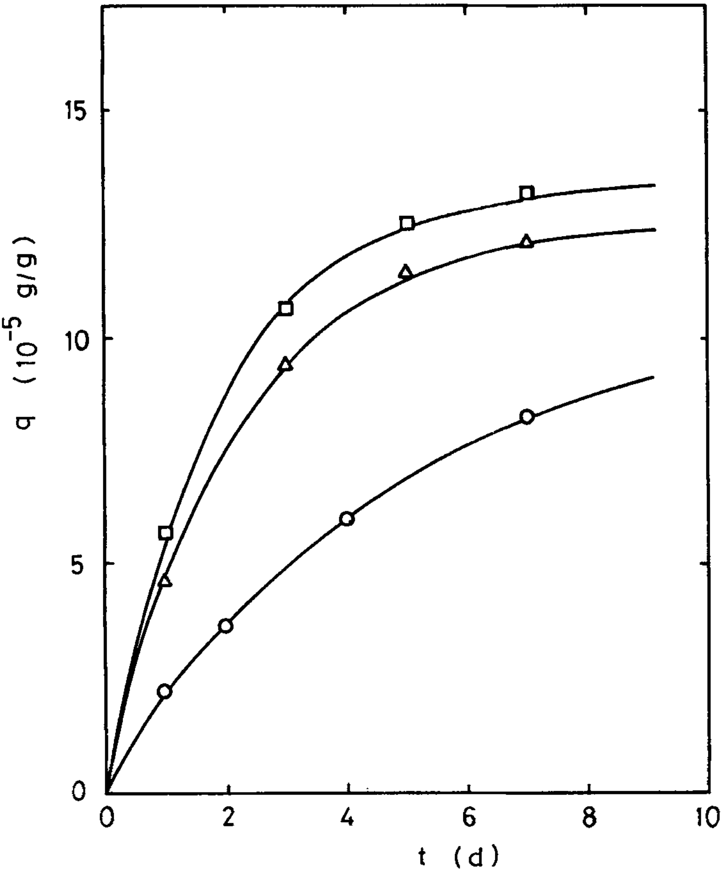


FIG. 4. Adsorption of uranium obtained by adsorbents with various amidoxime contents: (○) 2.3 meq/g, (△) 5.4, (□) 8.4.

the adsorbents. As shown in Fig. 6(a), the water uptake was 0.37 g/g-Ad at [F.G.] = 3.5 meq/g while it was 0.99 g/g-Ad at [F.G.] = 6.6 meq/g. Figure 6(b) shows that the exchange rate of adsorbed water in the water surrounding the adsorbent is enhanced by increasing [F.G.]. These results indicate that the higher the amidoxime content, the easier is the movement of metal ions. The previous study with titanium oxide adsorbents pointed out that increases in both q_0 and k are important for increasing the efficiency of adsorption and economizing the recovery process (*16*). Therefore, the present synthetic procedure appears to be a

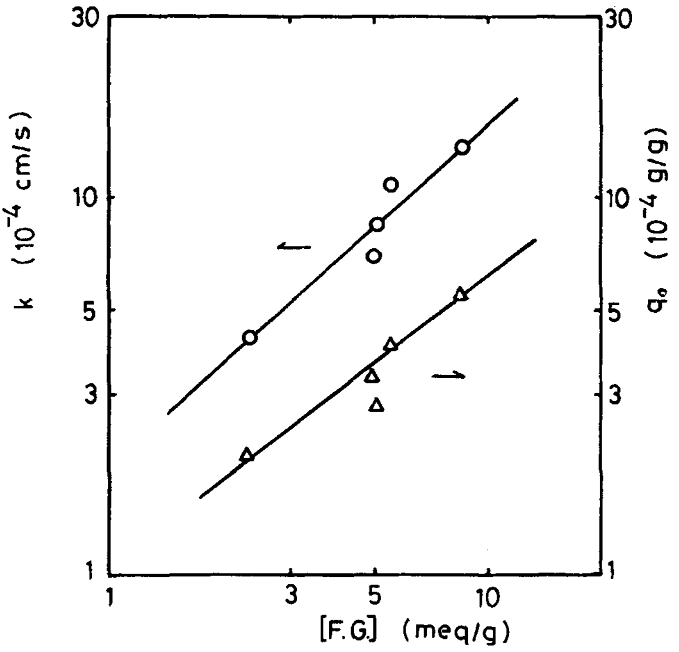
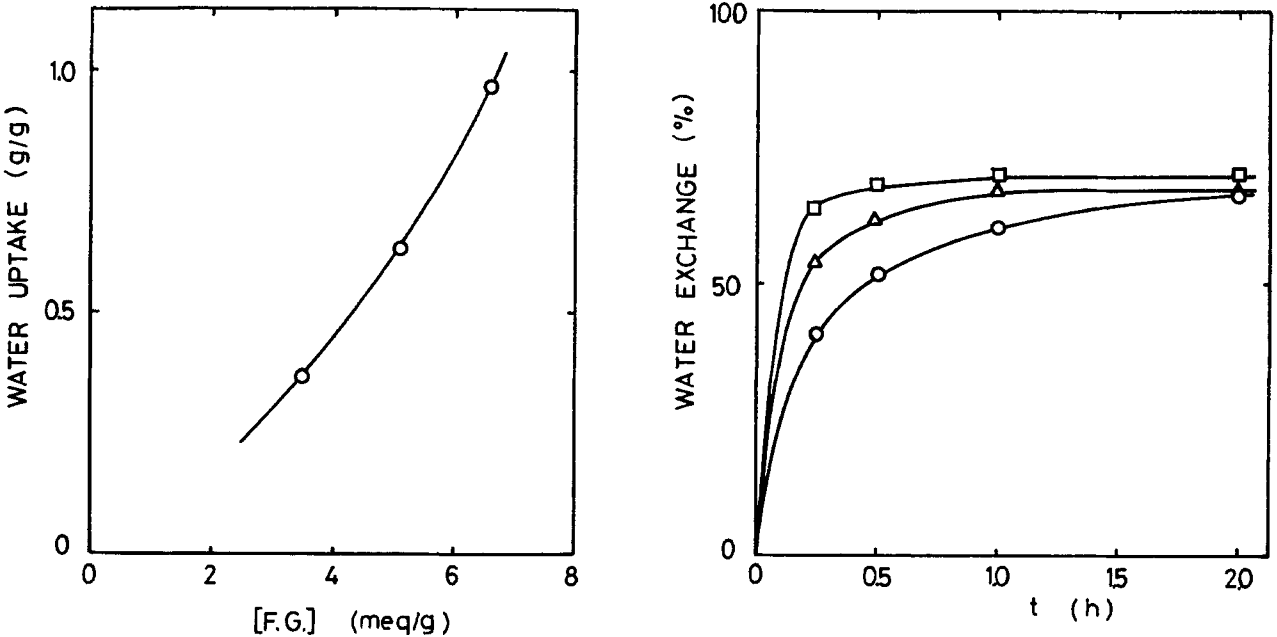


FIG. 5. Plots of q_0 and k against [F.G.].

hopeful approach to attaining an adsorbent with high efficiency by increasing both q_0 and k.

This type of improvement was more clearly observed when two kinds of functional groups, amidoxime and carboxyl, were mixed by the stepwise graft polymerization technique (*17*). The adsorption of uranium was compared between the adsorbent AOF containing only amidoxime groups at 2.5 meq/g-Ad and the adsorbent AOF-CA containing amidoxime groups at 2.6 meq/g-Ad with a small amount of carboxyl groups (less than 0.5 meq/g-Ad). As shown in Table 1, the difference in q_0 between AOF and AOF-CA is small. On the other hand, k for AOF-CA is 3.6 times that for AOF. Here, the carboxyl group does not work as an adsorption site for uranium from seawater (*9*). The increase in k by the combination of amidoxime and carboxyl is, therefore, thought to be due to a special synergistic effect which enhances the chelate formation between uranyl ions and amidoxime groups by the help of carboxyl groups. The present theoretical treatment of adsorption is useful in quantitatively elucidating such an effect.



(a) (b)

FIG. 6. Effect of [F.G.] on the mobility of adsorbed water: (a) water uptake of the adsorbents, (b) exchange of adsorbed water with the water outside the adsorbents: (○) [F.G.] = 3.5 meq/g, (△) 5.1, (□) 6.6.

TABLE 1
Effect of Mixing Different Functional Groups on Adsorption

Adsorbent	[F.G.] (meq/g)	q_0 (mg/g)	k (10^{-4} cm/s)
AOF	2.5	0.20	4.0
AOF-CA	2.6	0.25	14.5

NOMENCLATURE

B_i	Biot number kR/D_e
c	concentration of uranium in seawater (g/cm^3)
c_i	concentration of uranium at liquid-solid interface (g/cm^3)
c_0	initial concentration of uranium in seawater (g/cm^3)
D_e	diffusion coefficient through the adsorbent (cm^2/s)
k	liquid film mass transfer coefficient (cm/s)
n	Freundlich exponent
q	amount of adsorption (g/g)
q_0	amount of adsorption in equillibrium with c_0 (g/g)
R	radius of cylindrical adsorbent (cm)
S	surface area of adsorbent (cm^2)
t	contact time (s)
V	volume of seawater (cm^3)
W	weight of adsorbent (g)
ρ	density of adsorbent (g/cm^3)

REFERENCES

1. N. Jaffrezic, M. H. Andrade, and D. H. Trang, *J. Chromatogr.*, *201*, 187 (1980).
2. I. Tabushi, Y. Kobuke, and T. Nishiya, *Nature*, *280*, 665 (1979).
3. K. Sugasaka, S. Katoh, N. Takai, H. Takahashi, and Y. Umezawa, *Sep. Sci. Technol.*, *16*, 971 (1981).
4. M. B. Collela, S. Siggia, and R. M. Barnes, *Anal. Chem.*, *52*, 967 (1980).
5. S. Fried, A. M. Friedeman, and J. C. Sullivan, *Environ. Sci. Technol.*, *15*, 834 (1981).
6. J. Borzekowski, M. J. Driscoll, and F. R. Best, *Trans. Am. Nucl. Soc.*, p. 44 (1983).
7. L. Astheimer, H. J. Schenk, E. G. Witte, and K. Schwochau, *Sep. Sci. Technol.*, *18*, 307 (1983).
8. H. Omichi, A. Katakai, T. Sugo, and J. Okamoto, *Ibid.*, *20*, 163 (1985).
9. H. Omichi, A. Katakai, T. Sugo, and J. Okamoto, *Ibid.*, *21*, 299 (1986).
10. H. Omichi, A. Katakai, T. Sugo, and J. Okamoto, *Ibid.*, *21*, 563 (1986).
11. H. Omichi, A. Katakai, T. Sugo, J. Okamoto, S. Katoh, K. Sakane, K. Sugasaka, and T. Itagaki, *Ibid.*, *22*, 1313 (1987).

12. M. J. Driscoll, *Proceedings of the International Meeting for the Recovery of Uranium from Seawater,* Tokyo, 1983, p. 1.
13. T. Maekawa, H. Nishide, E. Tsuchida, H. Omichi, and J. Okamoto, *J. Appl. Polym. Sci., 29,* 3795 (1984).
14. M. Yamawaki, S. Otsuka, T. Hori, and M. Kanno, *Proceedings of the International Meeting for the Recovery of Uranium from Seawater,* Tokyo, 1983, p. 252.
15. K. Saito and S. Furusaki, *J. Nucl. Sci. Technol., 20,* 352 (1983).
16. S. Nakamura, Y. Ito, and M. Kanno, *Bull. Soc. Sea Water Sci. Jpn., 41,* 38 (1987).
17. H. Omichi and J. Okamoto, *J. Polym. Sci., Polym. Chem. Ed., 20,* 521 (1982).

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