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A Test of Uranium Recovery from Seawater with a Packed Bed of Amidoxime Fiber Adsorbent

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ABSTRACT

Uranium in seawater was recovered in this study by adsorption with amidoxime fibers synthesized from commercial PAN fibers. To confirm the stability of the fibers and the applicability of an adsorption bed model, a test was performed in a bay in southwest Japan. The amidoxime fiber was packed in an adsorption bed which was towed for 30 hours at a velocity of 1 $m \cdot s^{-1}$ or moored in the bay for 37 days. The amount of uranium adsorbed agreed well with the simulation model, and the adsorption fiber proved to be resistant to biological erosion.

Key Words. Uranium; Seawater; Adsorption; Amidoxime; Mass transfer

INTRODUCTION

Since the concentration of uranium in seawater is as low as 3 $mg \cdot m^{-3}$, development of highly selective and stable adsorbents is critically important. Recent studies show that amidoxime adsorbent prepared from commercial poly(acrylonitrile) fiber is very useful because of its fine size (1–4). Kato et al. (5) and Kago et al. (6) prepared amidoxime fibers having

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an adsorption rate higher than 250 mg uranium per kilogram of dry fiber per day after the seventh cycle of adsorption and desorption.

To recover a significant quantity of uranium economically, a contacting system between adsorbent and seawater should be developed as well. Since fibrous adsorbents are quite bulky compared with granular adsorbents, the contacting system between fiber and seawater is inherently different from that for particulate adsorbents. Nobukawa et al. (7) proposed a contacting system using entangled amidoxime fiber balls that are packed in cages of 3–5 m diameter with a thickness of 0.2–1 m. The cages are arranged in stacks below sea level, suspended by ropes from a buoy. Seawater around the fibrous balls is exchanged by the flow created by the heaving motion of the buoy and the kinetic force of the ocean current.

Morooka et al. (8) packed the amidoxime fiber in small spherical shells made of plastic nets. The balls were then packed in a column through which water passed. They proposed a model of the packed-bed adsorption unit and showed that the efficiency of uranium adsorption per unit bed volume became optimum at a certain void fraction. Goto et al. (9) improved this model for the case in which the adsorption rate was a function of time. By optimizing configurations and operational conditions of adsorption units, the overall adsorption efficiency was predicted to be higher than 0.5. However, the experiments in an actual sea environment are needed for confirmation of fiber stability and adsorptivity.

In this study a field test of uranium adsorption was carried out in a bay. The amidoxime fiber was packed in honeycomb cells at different void fractions, and the honeycomb block was placed in an adsorption unit towed by a boat at about 1 $m \cdot s^{-1}$. The unit was also moored for a long-duration test. The adsorption efficiency thus determined is compared with the simulation of the model.

PREPARATION OF AMIDOXIME FIBERS

Commercial poly(acrylonitrile) fibers (Mitsubishi Rayon Co.) were treated in a 3.0 wt% methanolic solution of NH_2OH formed by neutralization of $NH_2OH \cdot HCl$, and were then modified in a 0.1 $mol \cdot L^{-1}$ NaOH solution. Details of the treatment are described elsewhere (5, 6). The intrinsic adsorption rate of uranium adsorption, excluding the effect of the liquid-side mass transfer resistance, r_{ad}, was measured at 25°C by using filtrated seawater that was passed through a thin bed packed with dispersed amidoxime fiber (5). r_{ad} is expressed as the mass of uranium adsorbed per unit mass of dry amidoxime fiber per unit time.

The volumetric swelling ratio of the amidoxime fiber, α, was defined as follows:

$$\alpha = \frac{\text{swollen fiber volume in seawater at 25°C}}{\text{dry fiber volume}} \quad (1)$$

TABLE 1
Properties of Amidoxime Fiber

	Keys			
	□	○	△	■
Nominal fiber size, denier	6	6	6	15
Diameter of initial dry fiber, μm	27	27	27	41
Amidoximation time, h	2.75	2.75	2.75	3.0
Alkali treatment time, min	30	45	60	50
Swelling ratio	2.6	3.0	3.4	3.2
Intrinsic adsorption rate, $mg \cdot kg^{-1} \cdot d^{-1}$	250	350	440	320

The swelling ratio and the intrinsic adsorption rate of amidoxime fibers used in the present study are listed in Table 1. The uranium adsorbed was leached with a 1 $mol \cdot L^{-1}$ HCl solution, and the uranium concentration was determined by ICP spectroscopy.

FIELD EXPERIMENTS

The experiments were performed in Imari Bay, in the northern part of Kyushu Island, Japan, from August 6 to September 20, 1991. The average temperature at a depth of 2 m beneath the water's surface was about 25°C in the daytime during the test period.

Structure of Adsorption Bed

A ceramic honeycomb, 150 mm × 150 mm, and having 225 holes, each 8.5 mm × 8.5 mm, was sliced into 10 mm-thick sections. Each stage was backed with a 40-mesh plastic net, and some honeycomb cells in the stages were packed with amidoxime fiber at prescribed void fractions. The other cells were left vacant. Fifteen stages were assembled, and the side faces of the block were sealed with water-resistant tape. The top of the block was covered with the plastic net. Then the block was fixed in a cage 15 cm thick and 100 cm in diameter, as shown in Fig. 1. The space outside the honeycomb block was filled with dummy fibrous balls of ~10 mm diameter.

Towing Experiment

The adsorption unit was suspended from cylindrical buoys with its central axis tilted 30° from the vertical as shown in Fig. 2(a). The buoys were fixed

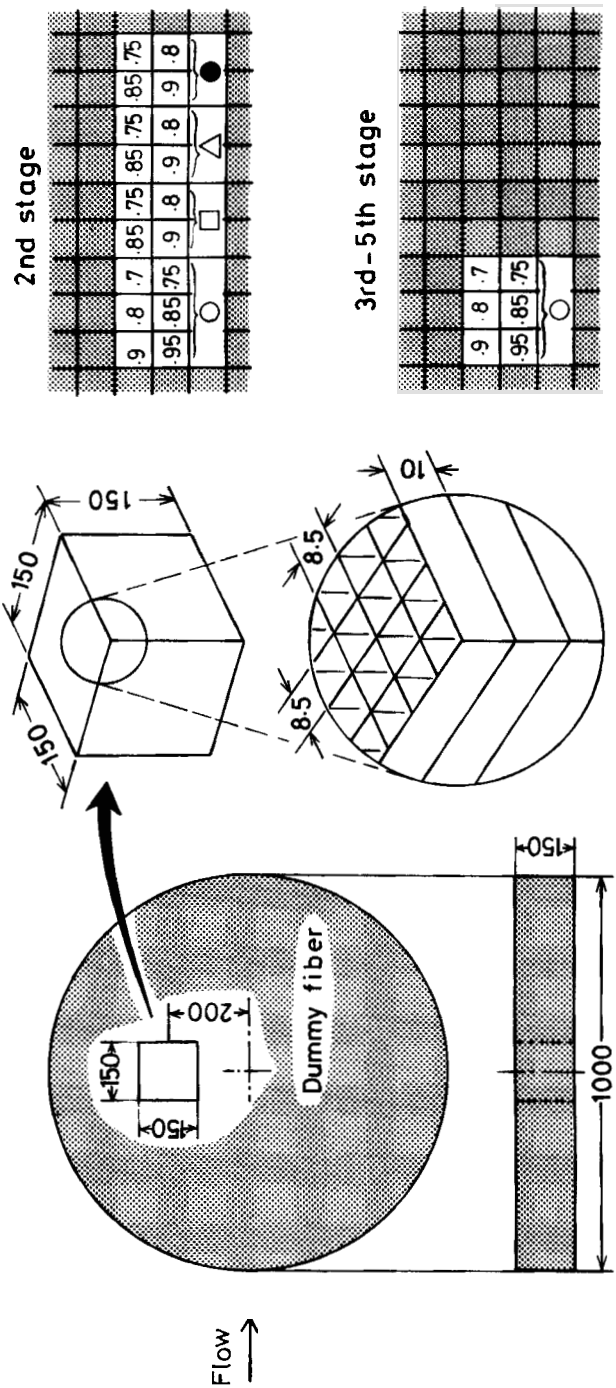

FIG. 1 Structure of adsorption bed. Numbers are in millimeters.

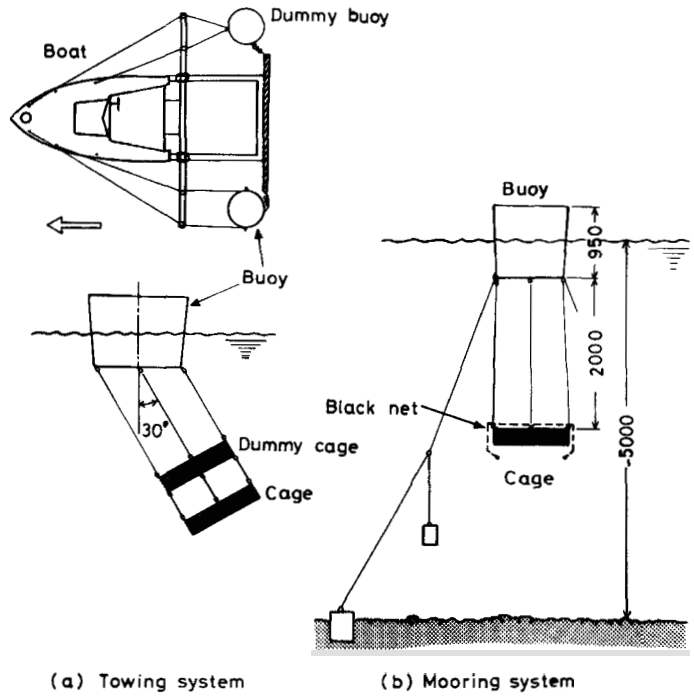

FIG. 2 System of uranium adsorption from seawater. Numbers are in millimeters.

to the stern of a boat and were towed at a speed of 1 $m \cdot s^{-1}$, equivalent to the ocean current near Japan. After 10 hours of towing the adsorption unit was taken ashore for 14 hours and the amidoxime fibers in the prescribed cells were sampled. This operation was performed three times beginning August 6, 1991.

The pressure drop between the top and bottom surfaces of the adsorption unit was measured with piezoelectric pressure transducers. The pressure drop was largest at the front rim and lowest at the rear rim. The average value in the area where the honeycomb block was installed was about 83 Pa, but local values varied widely.

Towing-Mooring Experiment

Figure 2(b) shows the mooring system schematically. The adsorption unit was suspended by ropes from a buoy moored in Imari Bay, and it was allowed to swing with the wave motion. A black 100-mesh net covered the

adsorption unit to prevent the growth of seaweeds. The following consecutive procedures were performed.

(1) 19 days (457 hours) mooring
(2) 10 hours towing
(3) 18 days (432 hours) mooring
(4) 10 hours towing

MODEL OF URANIUM RECOVERY IN FIBROUS ADSORPTION BED

The pressure drop of permeating flow across a fiber layer is expressed by the equation of Kyan et al. (10):

$$\frac{\Delta P}{L} = \frac{\rho_1 u_1^2}{d_f N_e^4 (1 - \epsilon_f)^2} \left\{ \left[62.3 + \frac{107.4}{N_e^2 (1 - \epsilon_f)} \right] \frac{(1 - \epsilon_f)}{d_f u_1 \rho_1} + \frac{c_1 \eta^2}{d_f^2 \eta N_e^6 (1 - \epsilon_f)^{3.5}} \right\} \tag{2}$$

where $N_e = [2\pi/(1 - \epsilon_f)]^{0.5} - 2.5$

c_1 = (constant)/(elasticity modulus of fiber)
= 16–20 $m \cdot s^2 \cdot kg^{-1}$ for normal synthetic fibers

Equation (2) is valid when $\epsilon_f > 0.6$.

Since the intrinsic adsorption rate of uranium from seawater obeys first-order kinetics with respect to uranium concentration (11), the adsorption rate coefficient, q_{ad}, is related to the adsorption rate of amidoxime fiber dispersed completely in seawater, r_{ad}.

$$q_{ad} = r_{ad}(\rho_f/\alpha)/C_b \tag{3}$$

where C_b is about 3×10^{-6} $kg \cdot m^{-3}$. r_{ad} is a function of time because the adsorption is controlled by diffusion of uranyl ion in the fiber (5), and the following relationship is obtained (6):

$$r_{ad} \propto t^{-1/2} d_f^{-1} \tag{4}$$

When the mass transfer between the bulk liquid and the surface of the fiber is not negligible, q_{ad} is expressed as

$$\frac{1}{q_{ad}} = \frac{C_b \alpha}{r_{ad} \rho_f} + \frac{1}{k_m a_f} \tag{5}$$

The mass transfer coefficient in the fiber bed is estimated from the equation for a particulate packed bed (12) by substituting d_f for the particle diameter. When the fiber is packed homogeneously in the cell at a void fraction ϵ_f,

the overall adsorption rate coefficient of the fiber bed, q_{app}, is given as $q_{ad}(1 - \epsilon_f)$. If the packed bed is a plug-flow reactor, the fraction of adsorbed uranium at the bed outlet is expressed by

$$x_U = 1 - \exp(-q_{app}L/U_l) \tag{6}$$

The uranium recovered from seawater per unit volume of the bed at operating time is given as

$$M_V = (C_b U_l / L) \int_0^t x_U dt \tag{7}$$

RESULTS AND DISCUSSION

The amidoxime fibers in Table 1 were packed in the 2nd stage at different void fractions. Figure 3 shows the amount of uranium adsorbed per kilogram of dry amidoxime fiber after the 10-hour towing. The amount adsorbed increased with increasing void fraction. This is due to a higher permeation velocity of seawater through a more loosely packed bed.

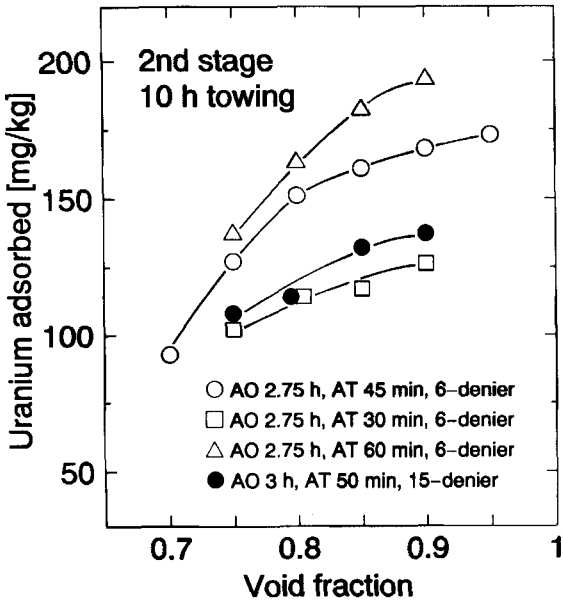

FIG. 3 Effect of void fraction on uranium adsorbed per unit dry fiber mass after 10 h towing.

When the cost of the adsorption unit structure is appreciable, however, the amount of uranium adsorbed per unit bed volume should be considered. Since the mass of packed fiber per unit bed volume is represented as $(1 - \epsilon_f)\rho_f/\alpha$, the amount of uranium adsorbed per unit bed volume is calculated by the following equation:

$$\text{(amount of U-adsorbed per unit bed volume)} = \text{(amount of U-adsorbed per kg-dry fiber)} \times (1 - \epsilon_f)\rho_f/\alpha \quad (8)$$

When the adsorption is compared per unit bed volume, there is an optimum void fraction, as shown in Fig. 4. The effect of the swelling ratio on the amount of uranium adsorbed per unit bed volume becomes smaller than is seen in Fig. 3. The uranium adsorption rate and the swelling ratio should be balanced because the tensile strength of fiber decreases greatly with increasing swelling ratio (6). Accordingly, all the experiments hereafter were carried out by using the fiber denoted by ○ in Table 1.

Figure 5 illustrates the amount of uranium adsorbed with the fiber in the towing–mooring experiment. The fiber was packed in the 2nd stage while the other stages were vacant. In the range of $\epsilon_f = 0.7$–0.8, the amount

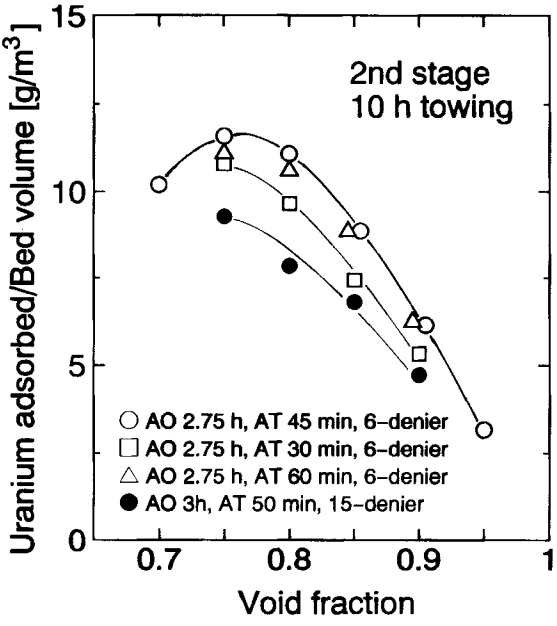

FIG. 4 Uranium adsorbed per unit bed volume in towing experiments.

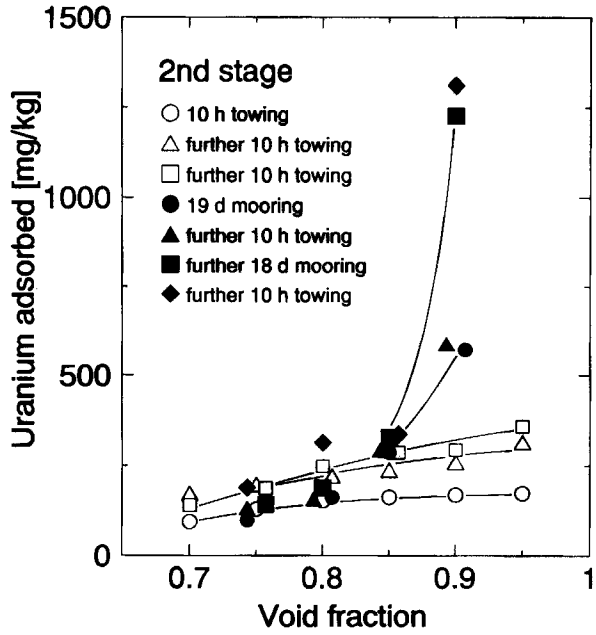

FIG. 5 Uranium adsorbed in towing–mooring experiments.

of uranium adsorbed after the 19–37 day mooring was overlapped with that after the 10–30 hour towing. The permeation flow through the moored adsorption bed was caused by tidal motion in the bay. Contact between seawater and fiber adsorbent was insufficient when the fiber was packed tightly. At a void fraction of 0.9, however, the amount adsorbed increased to 1.3 $g \cdot kg^{-1}$ after the mooring of 37 days. This value is nearly equal to that obtained when the fiber was completely dispersed. The result shows that the amidoxime fiber is resistant to biological erosion for 37 days.

Next, the fiber was packed at different void fractions in the cells of the 2nd to 5th stages. The fiber was sampled after every 10 hours of towing. Figure 6 shows the effects of towing period and void fraction on the amount of uranium recovered. The plots are the average values of the 2nd–5th stages in the adsorption block. Since the average pressure drop between the top and bottom surfaces of the adsorption unit was not precisely known, the calculation was performed for ΔP = 83, 60, and 40 Pa. The experimental data were compatible with the prediction from Eq. (7).

In previous papers (8, 9) we proposed a model of the adsorption unit packed with amidoxime fiber balls. The void space outside the balls is effective for channeling seawater. Thus, seawater from which uranium is

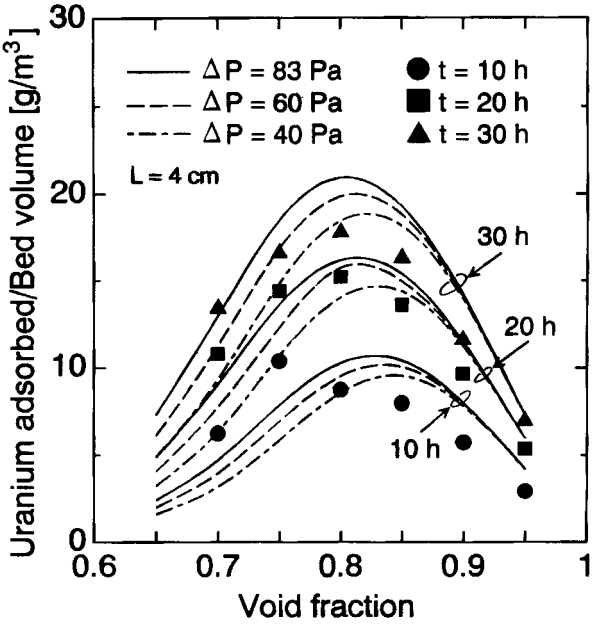

FIG. 6 Effect of towing period on uranium adsorbed.

not exhausted can permeate the fibrous balls. In this bed configuration, the overall adsorption rate coefficient is expressed by

$$q_{\text{app}} = \frac{3(1 - \epsilon_p)u_1}{d_p}\left[\frac{1}{2} - \frac{1 - (1 + N_a)\exp(-N_a)}{N_a^2}\right] \tag{9}$$

N_a is $q_{\text{ad}}(1 - \epsilon_f)d_p/u_l$ and is a function of time. When ϵ_p and d_p are zero, q_{app} becomes identical with q_{app} in Eq. (6).

The amount of uranium adsorbed per unit bed volume is compared between the packed bed of fibrous balls ($\epsilon_p = 0.5$) and the packed bed of fiber ($\epsilon_p = 0$) in Fig. 7. When the bed is thinner than 0.25 m, the bed of fiber is superior to the bed of balls. However, a thin bed is impractical because of its lack of structural strength. An adsorption unit must be designed on the basis of both economic and environmental assessments.

CONCLUSIONS

A field test of uranium recovery from seawater was carried out in Imari Bay to establish a mooring system with an adsorption bed packed with amidoxime fiber. The stability of amidoxime fiber was confirmed by the

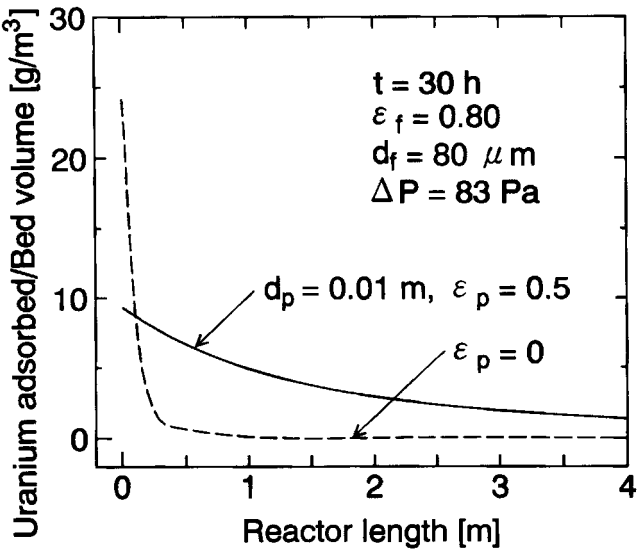

FIG. 7 Effects of void fraction in packed bed and reactor length on uranium recovery.

results of a 37-day test of the mooring system. The adsorption data were in agreement with simulation by the proposed model.

NOTATION

a_f	surface area per unit fiber volume, $a_f = 4/d_f$ (m^{-1})
C_b	uranium concentration in seawater ($kg \cdot m^{-3}$)
c_1	numerical constant defined by Eq. (2) (—)
D	diffusivity ($m^2 \cdot s^{-1}$)
d_f	average diameter of swollen fiber (m)
d_p	ball diameter (m)
k_m	mass transfer coefficient ($m \cdot s^{-1}$)
L	length of packed bed (m)
M_V	amount recovered as defined by Eq. (7) ($kg \cdot m^{-3}$)
N_a	dimensionless number defined by Eq. (9) (—)
N_e	dimensionless number defined by Eq. (2) (—)
ΔP	pressure drop across bed of balls (Pa)
q_{ad}	adsorption rate coefficient of fiber (s^{-1})
q_{app}	overall adsorption rate coefficient of packed bed (s^{-1})
r_{ad}	intrinsic adsorption rate ($kg \cdot kg^{-1} \cdot s^{-1}$)
t	time (s)

U_1 superficial velocity in packed bed of balls ($m \cdot s^{-1}$)
u_l superficial liquid velocity in fiberous bed ($m \cdot s^{-1}$)
V_{ad} volume of adsorption unit (m^3)
x_U recovered fraction of uranium in seawater (—)
α (swollen fiber volume)/(dry fiber volume) (—)
ϵ_f void fraction in ball (—)
ϵ_p void fraction in packed bed of solid balls (—)
η viscosity of liquid (Pa·s)
ρ_f density of dry fiber ($kg \cdot m^{-3}$)
ρ_l density of liquid ($kg \cdot m^{-3}$)
ν kinematic viscosity ($m^2 \cdot s^{-1}$)
AM conditions of amidoximation
AT conditions of alkali treatment

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REFERENCES

1. S. Katoh, K. Sugasaka, K. Sakane, N. Takai, H. Takahashi, Y. Umezawa, and K. Itagaki, *Nippon Kagaku Kaishi*, p. 1455 (1982).
2. N. Takagi, T. Hirotsu, J. Sakakibara, S. Katoh, and K. Sugasaka, *Bull. Soc. Sea Water Sci. Jpn.*, *42*, 279 (1989).
3. Y. Kobuke, T. Aoki, H. Tanaka, I. Tabushi, T. Kamaishi, and I. Hagiwara, *Ind. Eng. Chem. Res.*, *29*, 1662 (1990).
4. T. Takeda, K. Saito, K. Uezu, S. Furusaki, T. Sugo, and J. Okamoto, *Ibid.*, *30*, 185 (1991).
5. T. Kato, T. Kago, K. Kusakabe, S. Morooka, and H. Egawa, *J. Chem. Eng. Jpn.*, *23*, 744 (1990).
6. T. Kago, T. Kato, K. Kusakabe, and S. Morooka, *Ind. Eng. Chem. Res.*, *31*, 204 (1992).
7. H. Nobukawa, M. Tamehiro, M. Kobayashi, H. Nakagawa, J. Sakakibara, and N. Takagi, *J. Shipbuilding Soc. Jpn.*, *165*, 281 (1989).
8. S. Morooka, K. Kusakabe, T. Kago, M. Inada, and H. Egawa, *J. Chem. Eng. Jpn.*, *23*, 18 (1990).

9. A. Goto, T. Kago, K. Kusakabe, and S. Morooka, *Ibid.*, *25*, 195 (1992).
10. C. P. Kyan, D. T. Wasan, and R. C. Kintner, *Ind. Eng. Chem., Fundam.*, *9*, 596 (1970).
11. K. Saito, K. Uezu, T. Hori, S. Furusaki, T. Sugo, and J. Okamoto, *AIChE J.*, *34*, 411 (1988).
12. N. Wakao and T. Funazkri, *Chem. Eng. Sci.*, *33*, 1375 (1978).

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