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Desorption of Uranium Recovered with Fibrous Amidoxime Adsorbent Shaped into Balls

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ABSTRACT

Amidoxime fiber synthesized with a commercial PAN fiber was packed in 2 cm-diameter spherical shells made of plastic net. The adsorbent balls were then packed in a cage through which seawater passed. This shape of adsorbent increased the contact efficiency between adsorbent and seawater but might decrease the desorption rate of uranium adsorbed in the balls. The rate of desorption from 2 cm-diameter adsorbent balls packed in a column was nearly equal to the value obtained with completely dispersed amidoxime fiber, however, when the eluent velocity through the balls was higher than 2–4 $cm \cdot s^{-1}$ and the void fraction in the balls was higher than 0.8. Most of the liquid held in the balls was removed with a light centrifugation.

Key Words. Uranium; Adsorption; Desorption; Seawater; Amidoxime fiber adsorbent

INTRODUCTION

To recover a significant quantity of uranium from seawater, adsorbents (1, 2) and adsorption systems (3, 4) should be investigated cocurrently. The desorption process is also one of the key factors that decide the

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structure of a uranium adsorption system. Nobukawa et al. (5) proposed a system consisting of cages packed with fibrous adsorbents. The cages are towed in a flow of seawater. We found that the adsorption efficiency was much improved when amidoxime fiber was packed in small spherical shells made of plastic nets and the balls were then packed in a cage (6, 7).

However, information on uranium desorption from amidoxime adsorbent is insufficient to date. Hirotsu et al. (8) investigated a separative elution of uranium from amidoxime polymer beads packed in a column and reported that the uranium concentration in the eluate was increased by a stepwise elution method, changing the HCl concentration from 0.1 to 1.0 mol·L^{-1}. Goto et al. (9) determined the uranium desorption rate from the amidoxime fiber and found that HCl or HNO_3 solution was superior to alkali carbonate solution as the eluent. With a 0.1 mol·L^{-1} HCl solution, desorption was accomplished completely in 2 hours regardless of the presence of uranium up to 15 ppm in the leaching solution.

In the present study, amidoxime fiber adsorbent was shaped in 2 cm-diameter balls, and the desorption rate of uranium from the ball adsorbent was measured. The balls were packed in a column, and the effects of the flow-through rate of eluent and the void fraction in the balls were determined. Dewatering from the adsorbent balls was also tested by using centrifugation.

EXPERIMENTAL

Adsorption of Uranium

A commercial poly(acrylonitrile) bicomponent fiber of 6 denier (Mitsubishi Rayon Co.) was treated in a 1.5 wt% methanolic solution of NH_2OH at 353 K for 9 hours, then modified in a 0.1 mol·L^{-1} NaOH solution at 353 K for 45 minutes. Details of the treatment are described elsewhere (1, 2). The intrinsic adsorption rate of uranium from seawater, excluding the liquid–solid mass transfer resistance, was about 300 mg per kg of dry fiber per day. The properties of the fiber are listed in Table 1.

TABLE 1
Properties of Amidoxime Fiber Adsorbent Prepared

Outside diameter:	27 μm (in dry state) 48 μm (in seawater)
Elementary analysis:	C: 51.39% H: 6.49% N: 26.93%
Intrinsic adsorption rate:	300 mg U per kg of dry fiber per day

The potassium salt of uranyl tricarbonate ($K_4UO_2(CO_3)_2 \cdot 2H_2O$) was dissolved in seawater at a uranium concentration of 10 ppm. The uranium-loaded fiber used for the desorption test was prepared by immersing the amidoxime fiber in the uranium-enriched solution under agitation. The amount of uranium adsorbed was determined from the difference in uranium concentration measured by ICP spectroscopy before and after the adsorption. The uranium adsorbed initially was 1 g per kg of dry fiber throughout the present study.

Desorption and Dewatering

The eluent used was a hydrochloric acid solution of 0.5 $mol \cdot L^{-1}$ at 298 K. The batch desorption experiment was conducted in a beaker. The uranium-loaded amidoxime fiber (0.05 g) was dispersed in 50 mL of the eluent, and the mixture was shaken in a water bath.

The uranium-loaded amidoxime fiber was packed in a spherical shell made of plastic net at a prescribed void fraction. The diameter of the ball adsorbent was 2 cm, and the mesh size was 0.5 mm. Dummy balls of the same size were also prepared by using PAN fiber and were packed in an acrylic column of 7 cm i.d. and 100 cm height. An active adsorbent ball was placed in the bed as illustrated in Fig. 1. Flow-through desorption,

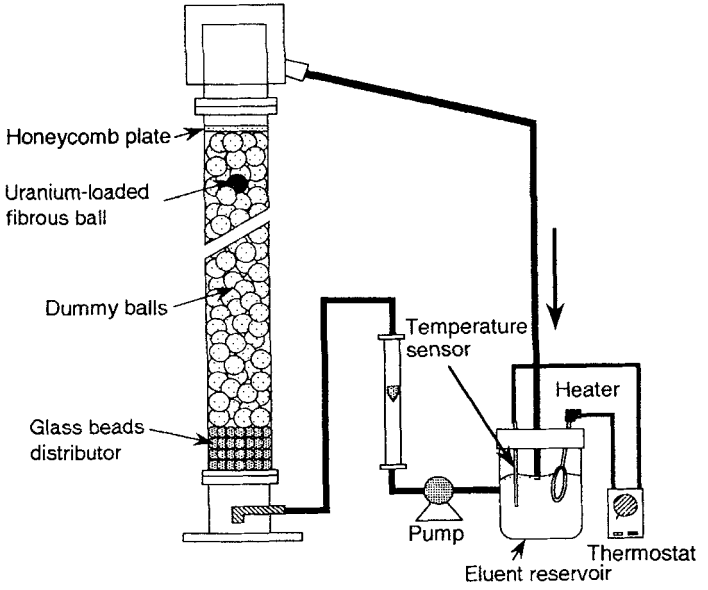

FIG. 1 Schematic diagram of flow-through desorption column.

simulating the actual operation of the adsorption system, was conducted by circulating a 0.5 mol·L^{-1} HCl solution (8 L) at 298 K through the column and by determining the time change in the uranium concentration at the exit of the column by ICP mass spectroscopy. The desorption yield is defined as

$$\text{Desorption yield} = \frac{\text{amount of U desorbed into eluent}}{\text{amount of U initially loaded on fiber}} \quad (1)$$

The dewatering test was performed by using a centrifuge with arms of 23 cm length. The ball adsorbent swollen in the 0.5 mol·L^{-1} HCl solution was centrifuged for a prescribed period at a given rotation speed, and the weight of water removed was measured.

RESULTS AND DISCUSSION

By assuming that the adsorbent ball is a homogeneous body from which uranium diffuses toward the outer liquid phase having a volume V, the amount of uranium leaving the ball after time t, M_t, is expressed by the following equation (10):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1)\exp(-D_e q_n^2 t/r_0^2)}{9 + 9\alpha + q_n^2\alpha^2} \quad (2)$$

where q_n is the nonzero root of

$$\tan q_n = 3q_n/(3 + \alpha q_n^2) \quad (3)$$

The mass transfer resistance in the liquid film outside the ball is neglected, and the adsorption equilibrium between fiber and solution in the ball is considered to be rapidly established in this case. The parameter α, the ratio of volumes of the outer solution and the ball, is equal to $3V/(4\pi r_0^3\epsilon_f)$. The parameter α is expressed in terms of the total amount of uranium in a fibrous ball, M_∞, by

$$\frac{3M_\infty}{4\pi r_0^3 C_0} = \frac{1}{1 + (1/\alpha)} \quad (4)$$

where C_0 is the initial concentration of uranium in the fibrous ball. The initial desorption rate coefficient is defined by $d(1 - M_t/M_\infty)/dt|_{t=0}$, and is calculated from Eqs. (2)–(4). The molecular diffusion coefficient of uranium ion in bulk seawater, D, is 3.4×10^{-6} cm^2·s^{-1} (11), and the effective diffusion coefficient in a fibrous ball, D_e, is given by $\epsilon_f D/\tau$.

The initial desorption coefficient from the completely dispersed fiber is determined by assuming first-order kinetics with respect to the uranium

concentration. The activation energy of intrinsic desorption was 37 $kJ \cdot mol^{-1}$, which was consistent with that of uranium adsorption with the same adsorbent (7).

Figure 2 illustrates the desorption rate from the ball adsorbent in the flow-through packed bed. The desorption rate was faster when the fiber was packed more loosely in the ball. The desorption from the ball packed at the void fraction of 0.85 was not influenced by the superficial velocity of the eluent in the 2.1 to 4.2 $cm \cdot s^{-1}$ range. These velocities were high enough for the liquid to pass through the ball on a time scale much shorter than the desorption period by the molecular diffusion mechanism. This means that the overall desorption rate from the ball is controlled by the desorption from each fiber under these conditions.

Figure 3 shows the effect of the void fraction on the initial desorption coefficient of the ball in the flow-through desorption experiment where the liquid velocity was fixed at 4.2 $cm \cdot s^{-1}$. The coefficient was also determined in the batch operation where the eluent was gently mixed in a beaker. The dotted line is the desorption rate coefficient of the completed dispersed fiber, and it is in agreement with the data for a loosely-packed ball. The heavy line is calculated from the molecular diffusion rate of uranyl ion through the fiber matrix inside the ball, calculated from Eqs. (2)–(4) with $\tau = 1$, and agrees with the initial desorption coefficient at a lower void fraction in the batch operation. Data in the flow-through desorption experiment fall between the two lines.

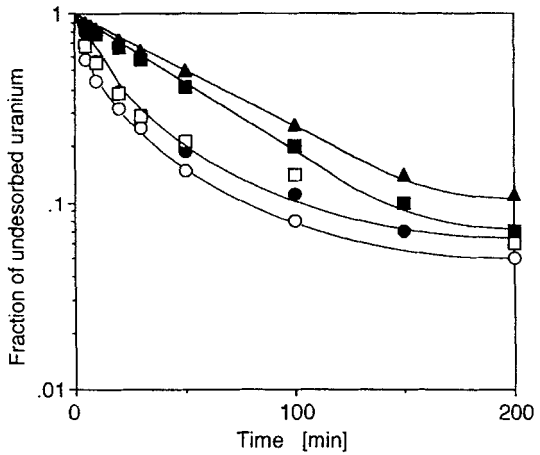

FIG. 2 Desorption of uranium from adsorbent balls packed in flow-through column at a liquid velocity of 4.2 $cm \cdot s^{-1}$. Void fraction in ball: (▲) 0.70, (■) 0.75, (□) 0.80, (●) 0.85, (○) 0.90.

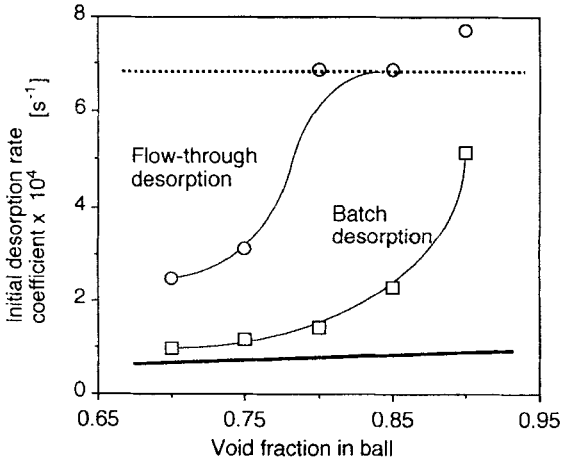

FIG. 3 Effect of void fraction in balls on desorption rate coefficient.

From the adsorption test in an actual sea environment (7), the amount of uranium adsorbed per unit volume of adsorption bed was largest when the void fraction in the balls was about 0.8. Figure 3 indicates that the ball adsorbent under this condition can be easily desorbed at a liquid velocity as low as 4.2 $cm \cdot s^{-1}$.

Figure 4 shows the effect of centrifugal force on the fraction of water content in the ball. The horizontal axis indicates the ratio of centrifugal

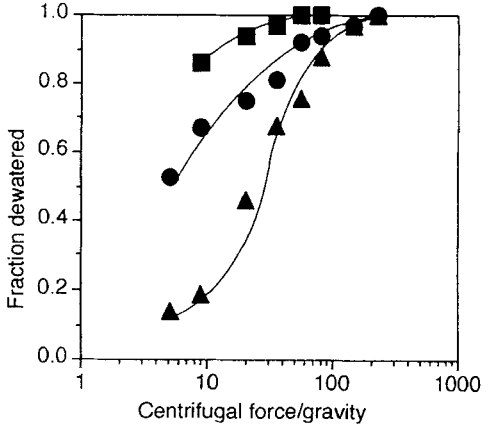

FIG. 4 Effect of dimensionless centrifugal force on fraction dewatered. Centrifugation time = 20 minutes. Void fraction in ball: (■) 0.85, (●) 0.80, (▲) 0.70.

force to gravity, $r_c\omega^2/g$. Ninety percent of the water in 20-mm diameter balls was removed in 20 minutes ar $r_c\omega^2/g$ = 14–56, depending on the void fraction in the balls. Further centrifugation did not change the water content fraction much. Excess centrifugation at $r_c\omega^2/g$ = 1000 caused the escape of fiber from the spherical shell.

CONCLUSION

The overall desorption rate from loosely packed ball adsorbents was controlled by desorption from the inside of the fiber when the eluent velocity was higher than about 4 $cm \cdot s^{-1}$. The molecular diffusion through the fibrous matrix in the ball was not dominant. The solution held in adsorbent balls with a void fraction higher than 0.8 was mostly removed in 20 minutes at a centrifugation of $r_c\omega^2/g > 50$.

NOTATION

C_0	initial uranium concentration in fibrous ball ($mol \cdot m^{-3}$)
D	molecular diffusion coefficient of uranyl ions ($m^2 \cdot s^{-1}$)
D_e	effective diffusion coefficient of uranyl ions in fibrous ball ($m^2 \cdot s^{-1}$)
g	gravitational acceleration ($m \cdot s^{-2}$)
M_t	total amount of uranium leaving fibrous ball after time t (mol)
M_∞	total amount of uranium in fibrous ball (mol)
q_n	parameter defined by Eq. (3)
r	distance from center of sphere (m)
r_0	radius of fibrous ball (m)
r_c	length of centrifuge arm (m)
t	time (s)
V	volume of eluent (m^3)
α	ratio of volumes of solution and sphere (—)
ϵ_f	solid fraction in fibrous ball (—)
τ	tortuosity factor (—)

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