PREPARATION OF AMIDOXIME FIBERS FOR RECOVERY OF URANIUM FROM SEAWATER

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Commercial acrylonitrile fibers of 1.2, 1.5, 3, 8 and 15 denier were separately treated in a 0.38 mol//NH₃OH methanolic solution at 80°C and then in a 0.1 mol//NaOH aqueous solution at 30°C. The treatments were carried out by changing reaction periods to find the optimum conditions. The intrinsic adsorption rate of uranium from seawater with the amidoxime fibers was inversely proportional to fiber diameter, and the capacity was in the range of 120-350 mg per kg of dry fiber per day. The effective diffusivity of uranium in 1.5-denier amidoxime fiber immersed in seawater was 5 × 10⁻⁹ cm²/s. The strength of the fibers was not reduced by the NH₃OH and NaOH treatment.

Introduction

Development of selective adsorbents is essential for economical recovery of uranium from seawater, in which uranium exists at concentrations as low as 3 mg/m³. Screening tests carried out by Astheimer et al.1,19 and Egawa et al.4 revealed that a hydroxylamine derivative of polyacrylonitrile, so called amidoxime resin, is most promising.

Egawa et al.3,4,5 have found that the physical and chemical structure of the adsorbent, especially the pore structure of amidoxime resin, greatly influences its adsorption capacity for uranium. To reduce the intraparticle mass transfer resistance, the amidoxime resin is normally utilized in the form of small beads which are contacted with seawater in a fluidized bed. Those small beads are easy to transport among unit operations in the recovery plant, but the carry-over of solids from the bed must be coped with.21

On the other hand, several authors synthesized fibrous amidoxime adsorbents by treating commercial polyacrylonitrile fibers with hydroxylamine. The adsorption rate of the 15 µm-diameter amidoxime fiber made by Kato et al.9 was nearly 2 g of uranium per kg of dry fiber after 7 days. Omichi et al.14 obtained a 40 µm-diameter amidoxime fiber that adsorbed 5 g per kg of dry fiber after 140 days. The fiber prepared by Sugasaka et al.21 and Takagi et al.22 absorbed 10 g per kg of dry fiber in 80 days. This is the highest adsorption rate to date, but the tensile strength of that fiber is too low for use in a practical plant.

If amidoxime fiber is packed in an adsorption bed, seawater must permeate rapidly through the bed within the pressure drop range induced by the ocean current.12 Since the permeation velocity is inversely proportional to the square of fiber diameter at a given pressure drop, a thicker fiber is preferable. A higher adsorption rate is normally obtained with a thinner fiber, however.14 Thus the total efficiency of a uranium recovery system is strongly influenced by the diameter of adsorption fiber,13 but no detailed investigation has been carried out.

In this work, amidoxime fibers are synthesized under various conditions, and the effect of fiber
Table 1. Properties of amidoxime fibers prepared

<table>
<thead>
<tr>
<th>Fiber diameter (number-average values of traverse size)</th>
<th>Nominal [denier*]</th>
<th>1.2</th>
<th>1.5</th>
<th>3</th>
<th>8</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated fiber [µm]</td>
<td>13</td>
<td>15</td>
<td>20</td>
<td>33</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>Dry amidoxime fiber [µm]</td>
<td>15</td>
<td>18</td>
<td></td>
<td>36</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>Swollen amidoxime fiber [µm]</td>
<td>21</td>
<td>24</td>
<td>30</td>
<td>43</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>Adsorption capacity of Cu(II) [g/kg-DF]</td>
<td>157</td>
<td>163</td>
<td>151</td>
<td>135</td>
<td>116</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Tensile strength</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated fiber [N]</td>
<td>0.046</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.37</td>
</tr>
<tr>
<td>[GPa]</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.27</td>
</tr>
<tr>
<td>Swollen amidoxime fiber [N]</td>
<td>0.037</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.24</td>
</tr>
<tr>
<td>[GPa]</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.10</td>
</tr>
</tbody>
</table>

Amidoxime fibers were prepared with 6-h NH₂ON and 20-h NaOH treatment.
* Weight in g of 9 km-long fiber.

diameter on the adsorption rate is studied.

1. Preparation of Fibers

Commercial acrylonitrile fibers containing 6.9% vinyl acetate were obtained from Mitsubishi Rayon Co. (nominal size = 1.2, 1.5, 3, 8 and 15-denier). The cross section of the fiber was heart-shaped, and the average diameters of the original fibers were 13, 15, 20, 33 and 41 µm, respectively. The fiber was treated with a 0.38 mol/l methanolic solution of NH₂OH produced by neutralization of NH₂OH·HCl at 80°C. The reaction was carried out for a prescribed period in a glass autoclave of 200 ml with stirring. The pressure was kept constant in the range of 0.23–0.7 MPa. After rinsing with water, the fiber was modified in a 0.1 mol/l NaOH solution at 30°C for a certain period.

The density of the original fiber was 1.14 kg/l, that of the dry amidoxime fiber 1.2 kg/l and that of the swollen amidoxime fiber 1.14 kg/l. The major properties of fibers prepared are listed in Table 1.

The intrinsic adsorption rate of uranium excluding the liquid-side mass transfer resistance was determined by the following procedures:

1. 90 mg of amidoxime fiber was packed in a framed space, 15-mm square and 2-mm thick, sandwiched with plastic nets (packing density =0.2 kg/l). The frame was connected to a 15-mm square duct, and seawater at 25°C was passed through the fiber bed. Then the desorption of uranium adsorbed was performed by contacting the adsorbent with a 0.5 mol/l HCl solution for 1 h at 30°C. The adsorption rate became constant when the liquid velocity was higher than 0.5 cm/s.\(^{11}\)

2. A small amount of amidoxime fiber (normally 20 mg) was sandwiched with 40-mesh polyester nets in the shape of a 20-mm square mattress whose periphery was welded with an ultrasonic plastic welder. Two or three mattresses were suspended for prescribed days at 25°C in a seawater tank with vigorous stirring.

These methods gave the same result, and the latter was mostly used for testing adsorptivity in the present work because of its simplicity.

The uranium concentration in seawater was determined as 2.9–3.1 mg/m³ (average 3 mg/m³) by the Arsenazo III method.\(^{13}\) That in extract solutions was determined by ICP spectrometry at 385.96 nm.

2. Results and Discussion

2.1 Properties of Amidoxime Fibers

Figure 1 shows the effect of NH₂OH and NaOH treatment time on the adsorption rate of seawater uranium. The optimum reaction time for the 15-denier fiber was 6 h for NH₂OH treatment and 40 h for NaOH treatment. Because no effect of pressure on
adsorptivity was observed, the reaction was mainly carried out at 0.23 MPa. When the effect of fiber size
on the adsorption rate was compared, the fibers were synthesized with a 6-h NH₃OH treatment and a 20-h
NaOH treatment. The NaOH treatment time was so fixed as to avoid excess treatment of the thinnest fiber.

Figure 2 indicates the change in the atomic ratio of nitrogen to carbon in the 15-denier amidoxime fiber.
The nitrogen content increased with increasing NH₃OH treatment time, and monotonously decreased
with NaOH treatment time. When the 3-denier fiber was used, the value of N/C was much influenced by
the preparation conditions. The highest adsorption rate, however, was always observed in the range of
N/C = 0.37–0.40.

The swollen diameter of the 15-denier fiber after NH₃OH treatment became maximum at 6 h and then
decreased with increasing treatment time. The swollen diameter of the fiber prepared with a 6-h NH₃OH
treatment increased with NaOH treatment period as shown in Fig. 3. SEM pictures show that the fiber
surface became a little uneven after long NaOH treatment.

Figure 4 shows the changes in the XRD pattern due to NH₃OH and NaOH treatment. The peak at
2θ = 16.8° is characteristic of polyacrylonitrile. The presence of acrylonitrile-vinyl acetate copolymer
does not change the diffraction angle. The disappearance of the 16.8° peak means that the crystal-
line structure of the fiber was transformed to an amorphous structure by the NH₃OH and NaOH
treatment. Nevertheless, the tensile strength of the swollen amidoxime fibers was not much changed, as
shown in Table 1.

To evaluate the amount of effective amidoxime group in the fiber, the adsorption capacity for Cu(II)
ion was determined. A small amount of the fiber (0.05–0.1 g) was immersed in 10 ml of a 0.05 mol/l
CuCl₂ solution which was maintained at pH 4.5 with an acetic acid-sodium acetate buffer, and was shaken
for 2 days at 25°C. After filtration, the concentration of copper in the solution was measured by ICP
spectrometry. The relationship between fiber diameter and Cu(II) adsorption capacity are also listed in Table 1.
Typical radial distribution profiles of Cu are shown in Fig. 5. The Cu concentration was constant in the
core of the 1.2-, 1.5-, and 3-denier fibers, but the concentration in the central region for the 8- and
15-denier fibers was a little lower than that in the peripheral region.

Amidoxime forms 1:1 and 1:2 complexes with Cu(II) and U(VI)O₂ ions in seawater. Since the
chelating capacity of the 1.5-denier fiber for Cu(II) ion is 2.5 mol/kg-DF from Table 1, that for uranium
is given as (2.5/2) mol/kg-DF = 300 g/kg-DF. To verify the calculation, the 1.5-denier fiber was immersed for
30 days in a carbonate-free 1 g/m³ uranium solution which was controlled at pH 8.1 with NaOH. Uranium
exists mostly as [(UO₂)₂(OH)₂]²⁺ in this solution. The flask was sealed under nitrogen atmosphere to minimize contamination with carbonate ion. The adsorption capacity was determined as 254 g/kg-DF, which was close to the calculated value.

The adsorption capacity experiment for uranium from seawater took a very long time, and the adsor-
sorption equilibrium was not confirmed in the present experiment. Yamawaki et al. determined the adsorption isotherm for seawater uranium using a 0.1-denier amidoxime fiber. Their data were corre-
lated by

\[ Q_0 = 2.06C_0^{0.57} \]

where the units of \( Q_0 \) and \( C_0 \) are g/kg-DF and mg/m³, respectively. The adsorption capacity for Ag(I) ion
was given as 5.8 mol/kg-DF, and the adsorption capacity for uranium from seawater was ca. 3.5
g/kg-DF. It can be assumed that the adsorption capacity for seawater uranium is proportional to that for Cu(II) or Ag(I), both of which form a 1:1 chelate with amidoxime group. Since the 1.5-denier fiber prepared in the present study adsorbs Cu(II) ion up to 2.5 mol/kg-DF, its adsorption capacity for seawater uranium is estimated as $(2.5/5.8) \times 3.5 = 1.5$ g/kg-DF.

### 2.2 Adsorption Rate

Figure 6 reveals that the adsorption rate of uranium is inversely proportional to the diameter of swollen fiber diameter. The mass transfer resistance in the liquid film is negligible, as noted in the experimental section. The adsorption rate for fibers synthesized under optimized conditions are shown in the same figure. Figure 7 illustrates that the adsorption of uranium from seawater is proportional to $\sqrt{t}$ in the smaller time range (Curve C). The same tendency was observed in the carbonate-free $1$ g/m$^3$ uranium solution (Curve A). This exponent value and the EPMA pictures in Fig. 8 suggest that the adsorption is controlled by the diffusion rate of uranyl ions in the fiber. However, the exponent for the $1$ g/m$^3$ uranium solution containing $0.05$ mol/l of Na$_2$CO$_3$ (Curve B of Fig. 7) was a little larger than $1/2$. The
amount of uranium adsorbed at equilibrium was much smaller than for the carbonate-free system at the same uranium concentration. As shown in Fig. 9, uranium adsorbed on the fiber is nearly constant at any radial position and increases with time. The adsorption rate is presumably affected by the reaction rate between the amidoxime group and $\text{UO}_2\text{(CO}_3\text{)}_3^{2-}$.

If the mass transfer resistance in the outer liquid side is neglected, the mass balance of uranyl ions in the fiber is expressed by

$$
\frac{\partial q}{\partial t} + (1-\varepsilon_o) \frac{\partial C}{\partial t} = D_e \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right)
$$

where the chelating reaction is assumed to proceed very quickly. Then the fiber is regarded as a homogeneous gel in which the uranium concentration is $\{\varepsilon_o q + (1-\varepsilon_o) C\}$. The initial and boundary conditions are

$$
\begin{align*}
& t=0; \quad r=R; \quad C=C_0, \quad q=0 \\
& r<R; \quad C=q=0 \\
& t>0; \quad r=0; \quad \frac{\partial C}{\partial r}=0
\end{align*}
$$

The amount of uranium in the fiber is calculated by

$$
M(t) = \int_0^R \{\varepsilon_o q + (1-\varepsilon_o) C\} r dr / \int_0^R r dr
$$

The uranium concentrations, $q$ and $C$, are defined on the swollen fiber volume and are related to the uranium concentration based on the mass of dry fiber, $Q$, as follows:

$$
\{\varepsilon_o q + (1-\varepsilon_o) C\} = \rho f_\text{U} Q / \alpha
$$

The equilibrium is given by

$$
Q / Q_0 = a(C/C_0)^n
$$

The value of $n$ in Eq. (8) is smaller than unity. Equation (6) can be solved analytically when $n=0$ and 1.

\[ n=1; \quad \frac{M(t)}{M_0} = 4 \frac{m}{\sqrt{\pi}} \]  
\[ n=0; \quad \frac{M(t)}{M_0} = \frac{m}{4} + \frac{1-m}{4} \ln(1-m) \]

where $m = D_e \pi C_0 / (R^2 \rho f_\text{U})$. The effective diffusivity of uranium in the 1.5-denier amidoxime fiber is obtained by comparing the experimental data in Fig. 7 with Eq. (6), which falls between Eqs. (9) and (10). The value for seawater (Curve C) was $5 \times 10^{-8}$ cm$^2$/s and that for the carbonate-free 1 g/m$^3$ uranium solution (Curve A) was $6 \times 10^{-8}$ cm$^2$/s. These values are smaller than that obtained by Yamawaki et al.$^{24}$

$$
D_e = 1.23 \times 10^{-7} \text{cm}^2/\text{s}, \text{for uranium in seawater using a 0.1-denier amidoxime fiber, but are in the same order of magnitude.}
$$

Hirotzu et al.$^7$ measured transient radial distributions of uranium in porous amidoxime particles, and found the value of $D_e$ for uranium in seawater to be $3.3 \times 10^{-7}$ cm$^2$/s. The diffusivity in bulk seawater at 25°C is $3.4 \times 10^{-6}$ cm$^2$/s.$^{15}$

On the other hand, $D_e$ for the 1 g/m$^3$ uranium solution containing 0.05 mol/l carbonate ions was calculated as $2 \times 10^{-9}$ cm$^2$/s. This is comparable with the value of $5 \times 10^{-10}$ cm$^2$/s given by Hirotzu et al.$^{20}$ using 3μm-diameter amidoxime fiber immersed in an artificial seawater containing nearly 1 g/m$^3$ uranium. The small diffusivities are probably caused by the assumption that the reaction rate is very fast, which is not the case, as illustrated in Fig. 9. However, further research is needed on this problem.

Figure 10 shows the adsorption of metal ions by the amidoxime fibers. The adsorption rate is roughly inverse to the fiber diameter except for magnesium, which exists abundantly in seawater.

Figure 11 indicates the effect of the number of cycles on adsorption performance. The adsorption rate of
the fiber prepared was decreased by 50–60% after the first cycle of adsorption and desorption, the 15-denier fiber was stable after the fifth run.

**Conclusion**

Amidoxime fibers were prepared with commercial acrylonitrile fibers of 1.2, 1.5, 3, 8 and 15 denier. The intrinsic adsorption rate of uranium from seawater with the amidoxime fibers was inversely proportional to fiber diameter. The adsorption rate of other metals in seawater showed the same tendency. The effective diffusivity of uranium in 1.5-denier amidoxime fiber immersed in seawater was $5 \times 10^{-8}$ cm$^2$/s. The adsorption rate of uranium from seawater was 120–350 mg/kg-DF per day for the fibers prepared. The strength of the fibers was not much decreased by NH$_2$OH and NaOH treatment.

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**Nomenclature**

- $a$ = constant used in Eq. (8) [—]
- $C_m$ = uranium concentration in pore phase [kg/m$^3$]
- $C_s$ = uranium concentration in seawater [kg/m$^3$]
- $D_e$ = effective diffusivity of uranyl ion in swollen fiber [m$^2$/s]
- $M(t)$ = amount of uranium adsorbed in fiber at time $t$ [kg/m$^3$]
- $M_0$ = amount of uranium adsorbed in equilibrium with $C_s$ [kg/m$^3$]
- $n$ = exponent defined by Eq. (8) [—]
- $Q$ = uranium concentration based on mass of dry fiber [kg/kg-DF]
- $Q_0$ = uranium concentration based on mass of dry fiber in equilibrium with $C_s$ [kg/kg-DF]
- $q$ = uranium concentration in solid phase in swollen fiber [kg/m$^3$]
- $q_0$ = uranium concentration in solid phase in swollen fiber in equilibrium with $C_s$ [kg/m$^3$]
- $R$ = radius of swollen fiber [m]
- $r$ = radial coordinate of swollen fiber [m]
- $t$ = time [s]
- $x$ = volumetric swelling ratio, (swollen fiber volume)/(dry fiber volume) [—]
- $e_s$ = volume fraction of solid phase in swollen fiber [—]
- $p_{DF}$ = density of dry amidoxime fiber [kg/m$^3$]

―DF‖ = refers to dry amidoxime fiber

**Literature Cited**