

Optimum Preparation Conditions of Amidoxime Hollow Fiber Synthesized by Radiation-Induced Grafting

KYOICHI SAITO,* TAKEO YAMAGUCHI, KAZUYA UEZU, and SHINTARO FURUSAKI, *Department of Chemical Engineering, Faculty of Engineering, University of Tokyo, 113, Japan*, and TAKANOBU SUGO, and JIRO OKAMOTO, *Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, Gunma 370-12, Japan*

Synopsis

The preparation process of amidoxime hollow fiber consists of three steps: (1) radiation-induced graft polymerization of acrylonitrile (AN) onto porous hollow fiber (AN grafting), (2) chemical conversion of the cyano group into an amidoxime group (amidoximation), and (3) conditioning of the hollow fiber with alkaline solution (alkaline treatment). Systematic optimization of this preparation process was found to improve the adsorption rate. For the AN-grafted hollow fiber having 130% degree of grafting, the optimum reaction was 1 h each for amidoximation and alkaline treatment, respectively. Also the change in the structure of the amidoxime hollow fiber with alkaline treatment was discussed based on measurements of water content, swelling and pore volume distribution, and observation of morphology of cross section by SEM.

INTRODUCTION

Among the various adsorbents for recovery of uranium from seawater, a chelate-forming resin containing an amidoxime group has been selected because of its ease of synthesis, better adsorption characteristics, and feasible cost.^{1,2} Since the concentration of uranium in seawater is extremely low, 3.3 mg U/m³, a tremendous volume of seawater must be contacted with the adsorbent to produce an artificial uranium ore from seawater. Recently, we have suggested the utilization of porous hollow fiber having an amidoxime group (amidoxime hollow fiber) as an adsorbent.²⁻⁴ The adsorption bed charged with the bundle of amidoxime hollow fibers has the following advantages: (1) It provides a high surface area to bed volume ratio; (2) it permits a lower pressure loss in comparison with a bed charged with spherical adsorbents.

A novel method for the synthesis of amidoxime resin has been developed by Okamoto and co-workers.⁵⁻⁹ The amidoxime hollow fiber could be prepared by applying this method. The preparation process of amidoxime hollow fiber is shown in Figure 1. This process consists of three steps: (1) radiation-induced

*Department of Chemical Engineering, Faculty of Engineering, University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan.

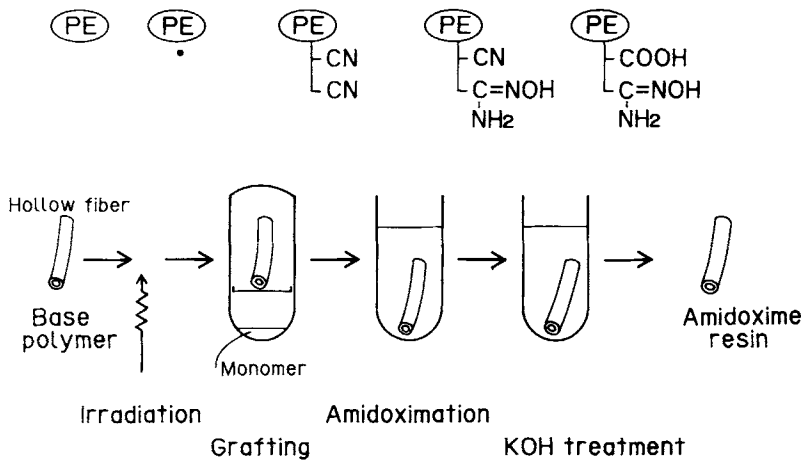


Fig. 1. Preparation process of amidoxime hollow fiber.

graft polymerization of acrylonitrile (AN) onto porous hollow fiber (AN grafting), (2) chemical conversion of the cyano group into an amidoxime group (amidoximation), and (3) conditioning of the hollow fiber with alkaline solution (alkaline treatment). Systematic optimization of this preparation process is effective to improve the adsorption characteristics of uranium from seawater, such as adsorption rate, adsorption capacity, and durability.

The objectives of our study were twofold: (1) to optimize amidoximation and alkaline treatment of AN-grafted hollow fiber and (2) to discuss the physical properties of the resulting amidoxime hollow fiber, such as swelling and morphology in correlation to uranium adsorption.

EXPERIMENTAL

Preparation of Amidoxime Hollow Fibers

After the trunk polymer was preirradiated in a nitrogen atmosphere, acrylonitrile was grafted onto it from the vapor phase. Porous polyethylene hollow fiber (Mitsubishi Rayon Co., Ltd., Japan) was used as the trunk polymer for grafting. This trunk polymer has been commercially used for microfiltration membranes having the following physical properties in the dry state: inner diameter 0.27 mm; outer diameter 0.38 mm; pore size 0.04 μm ; porosity 60%. Next, the cyano group was converted into an amidoxime group by soaking the AN-grafted hollow fiber in neutral hydroxylamine solution. Then the resulting amidoxime hollow fiber was conditioned with potassium hydroxide solution prior to adsorption experiment. Reaction conditions at each step are summarized in Table I. The degree of grafting was defined as follows:

$$\text{degree of grafting} = [(W_1 - W_0)/W_0] 100$$

where W_0 and W_1 are the weights of the starting hollow fiber and AN-grafted hollow fiber. The conversion in amidoximation was calculated from the follow-

TABLE I
Preparation Conditions of AO-H Fiber

AN Grafting		
Irradiation dose		20 Mrad
Reaction temp		308 K
Degree of grafting		130%
Amidoximation		
Conc. of NH ₂ OH HCl		3%
Solvent		H ₂ O/CH ₃ OH = 1/1
Molar ratio ^a		3.71
Reaction temp		350 K
Reaction time		0.67-4 h
Alkaline treatment		
Conc. of KOH		2.5%
Reaction temp		353 K
Reaction time		0-24 h

^aMolar ratio = (mol NH₂OH in solution)/(mol CN group in AN-grafted fiber).

ing equation:

$$\text{conversion in amidoximation} = \frac{\text{(amount of HCl adsorbed per kg of trunk polymer)}}{\text{(amount of CN group per kg of trunk polymer)}}$$

Performance of Recovery of Uranium from Seawater

The resin optimized in amidoximation was reported to exhibit relatively high resistance to adsorption-elution cycles.¹⁰ Therefore, with use of the amidoxime hollow fiber which provided a maximum amount of HCl adsorbed, the time conditioned with 2.5% KOH solution at 353 K, which will be hereafter referred to as the KOH-conditioning time, was increased to 24 h. The amidoxime hollow fiber conditioned with KOH solution for 8 h will be designated AO-H8 fiber.

The experimental apparatus and procedure for recovery of uranium from seawater were detailed in our previous report.² A bundle of 1000 AO-H fibers, 3 cm in length, was charged in a 1.5 cm ID column 3 cm in height. Seawater was passed upward through the column. The superficial velocity was controlled precisely at 1 cm/s. After the fibers were taken from the column after 5-day contact with seawater, the uranium adsorbed on the fibers could be quantitatively stripped with 1N HCl solution. The content of uranium in the eluate was determined by colorimetry.¹¹ Also, both magnesium and calcium were analyzed using an atomic absorption spectrophotometer.

Properties of Amidoxime Hollow Fibers

Measurements of swelling, water content, IR spectra, and pore size distribution of the resulting AO-H fibers were made, and the cross sections of these hollow fibers were also observed using scanning electron micrography (SEM).

The swelling ratio was defined to be the ratio of the volume of AO-H fiber (AO-H2, etc.) conditioned with KOH solution to that of AO-H fiber untreated (AO-H0). The volume of AO-H fiber was determined from the measurement of inner and outer diameters with a microscope and length with

a scale. Water content was calculated from the following equation:

$$\text{water content} = [(W_w - W_d)/W_w] 100$$

where W_w and W_d are the weights of AO-H fiber in the wet and dry states, respectively. IR spectra were determined by the KBr method. After the AO-H fiber was freeze-dried, the pore size distribution was measured by the mercury intrusion method.

RESULTS

Conversions in Amidoximation

The AN-grafted hollow fiber having 130% degree of grafting was examined to optimize amidoximation and alkaline treatment. Figure 2 shows the conversion in amidoximation as a function of reaction time. The reaction time of 1 h provided the maximum conversion of cyano groups into amidoxime groups, 47%. This value corresponded to the amount of amidoxime groups, 11.6 mol/kg of trunk polymer, which is a little higher than that of a commercial chelate-forming resin of a bead form.

Uranium Adsorption

Figure 3 shows the amount of uranium recovered from seawater over 5 days as a function of KOH-conditioning time. A relatively large difference was observed between AO-H0 fiber and AO-H fibers conditioned with alkaline solution. Conditioning times between 1 and 2 h provided the maximum uranium adsorption rate per volume of the adsorbent of hollow fiber form.

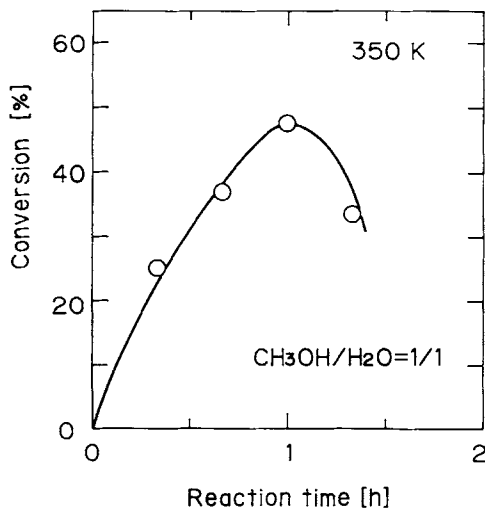


Fig. 2. Conversion in amidoximation.

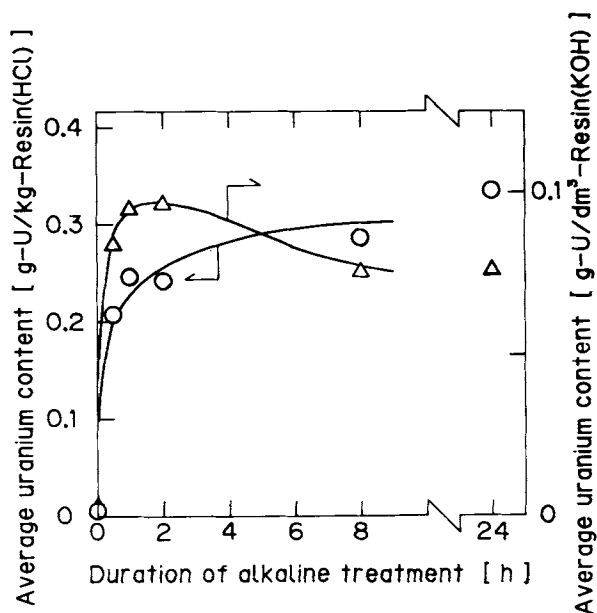


Fig. 3. Uranium adsorption.

Figure 4 shows the amount of magnesium and calcium adsorbed on the AO-H fibers. Measurement of IR spectra indicates that the longer KOH-conditioning time caused the partial hydrolysis of the remaining cyano groups into carboxyl groups and that the amidoxime groups remained. Since the cationic functional groups such as carboxyl groups adsorb magnesium and calcium, the Mg and Ca adsorbed increased with an increase in KOH-conditioning time. To evaluate the selectivity of the AO-H fibers, concentration

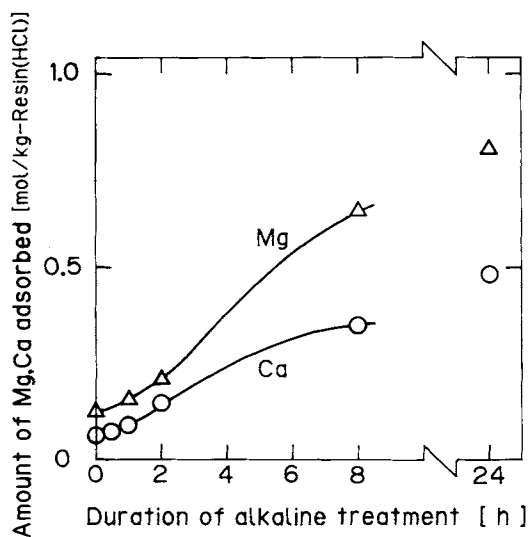


Fig. 4. Mg and Ca adsorption.

TABLE II
Concentration Factor and Recovery Ratio^a

Metal	Concn. in seawater (g/L)	Concn. adsorbed (g/kg)	Concn. factor (L/Kg)	Recovery ratio (%)
U	0.000033	0.246	75,000	6.5
Mg	1.4	3.66	2.6	0.00023
Ca	0.40	3.92	9.8	0.00085

^aAdsorbent = AO-H1; 5-day contact.

TABLE III
Comparison of Adsorption Rate

Ref.	Adsorbent ^a	Adsorption Rate ^b			Bulk density (kg resin/L bed)
		(g U/Kg resin)	(g U/L resin)	(g U/L bed)	
14	Sp	0.098			
8	F	0.10			
15	Sp	0.16	0.060		
16	F	0.71	0.071		
4	CF	0.06	0.024	0.013	0.22
2	HF	0.15	0.071	0.024	0.16
This study	HF	0.24	0.097	0.035	0.15

^aSp = spherical bead; F = fibrous adsorbent; CF = capillary fiber; HF = hollow fiber.

^b5-day contact.

factor and recovery yield were calculated as follows and listed in Table II:

$$\text{concentration factor} = \frac{(\text{concentration adsorbed on the adsorbent})}{(\text{concentration in seawater})}$$

$$\text{recovery yield} = \frac{(\text{total amount adsorbed in the column})}{(\text{total amount in seawater flowing in the column})}$$

With regard to feasibility of the adsorbent, the adsorption rate based on the adsorbent volume or the adsorption column is an important value for the design of the contactor. Comparison of the adsorption rate of the adsorbent optimized in this study to that of previous studies is summarized in Table III. The adsorption rate per volume of the adsorbent was 0.097 kg/m³ resin for 5-day contact at a superficial velocity of 1 cm/s. This value can be converted into 0.035 kg/m³ of bed volume by multiplying the volume fraction of the adsorbent in the bed, 0.37.

DISCUSSION

Figure 5 shows a plot of swelling ratio and water content vs. KOH-conditioning time. With increased KOH-conditioning time, both swelling ratio and water content increased. Micrographs of a section of the AO-H0, -H2, and

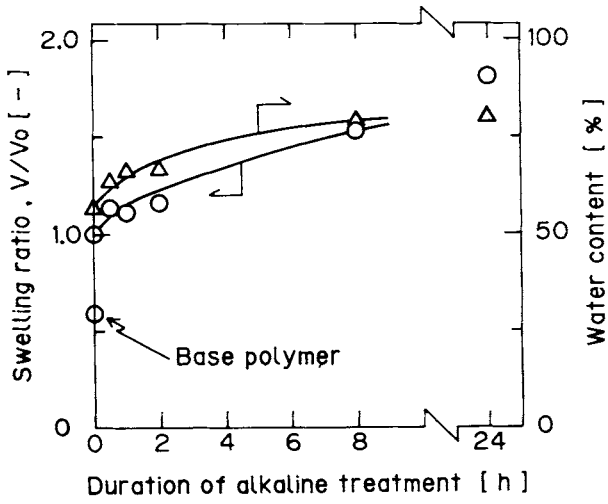


Fig. 5. Swelling with alkaline treatment.

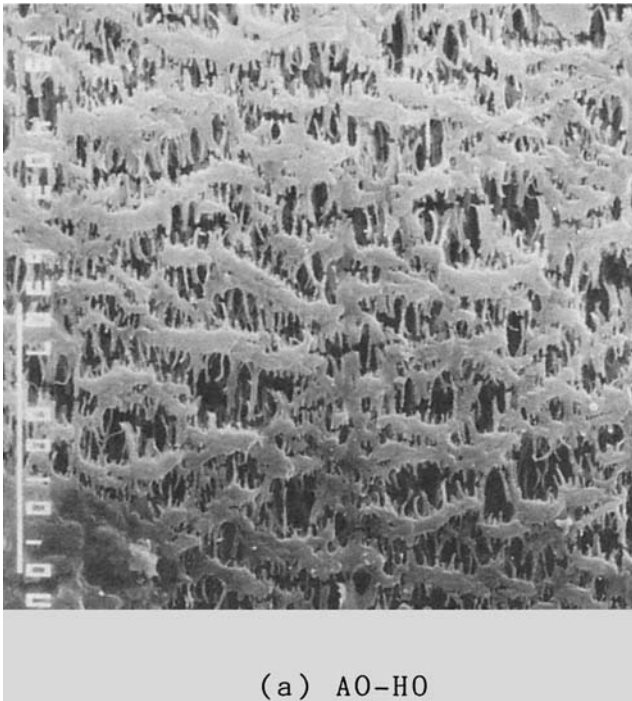
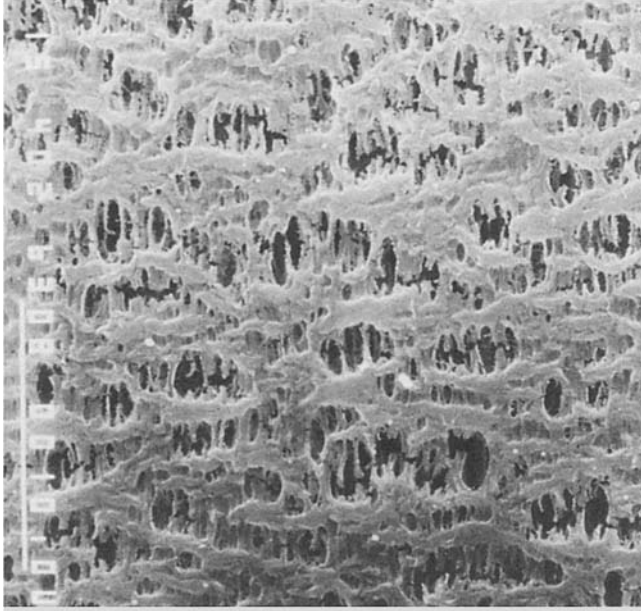
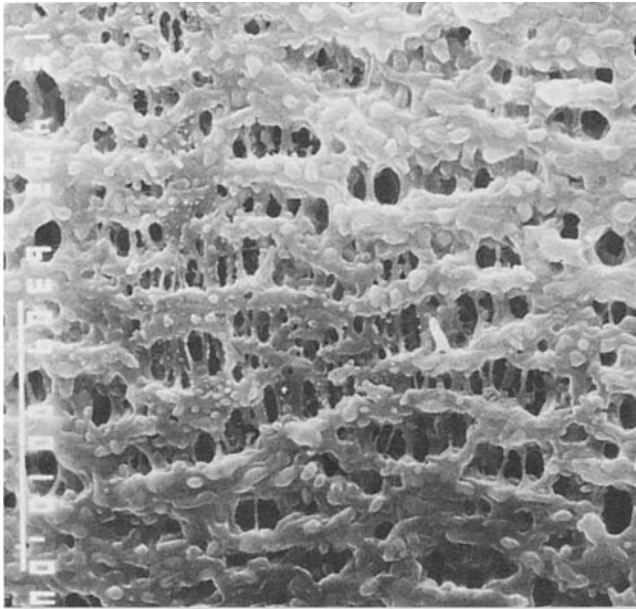


Fig. 6. SEM pictures of outer surfaces (marker = 10 μ m).



(b) AO-H2



(c) AO-H8

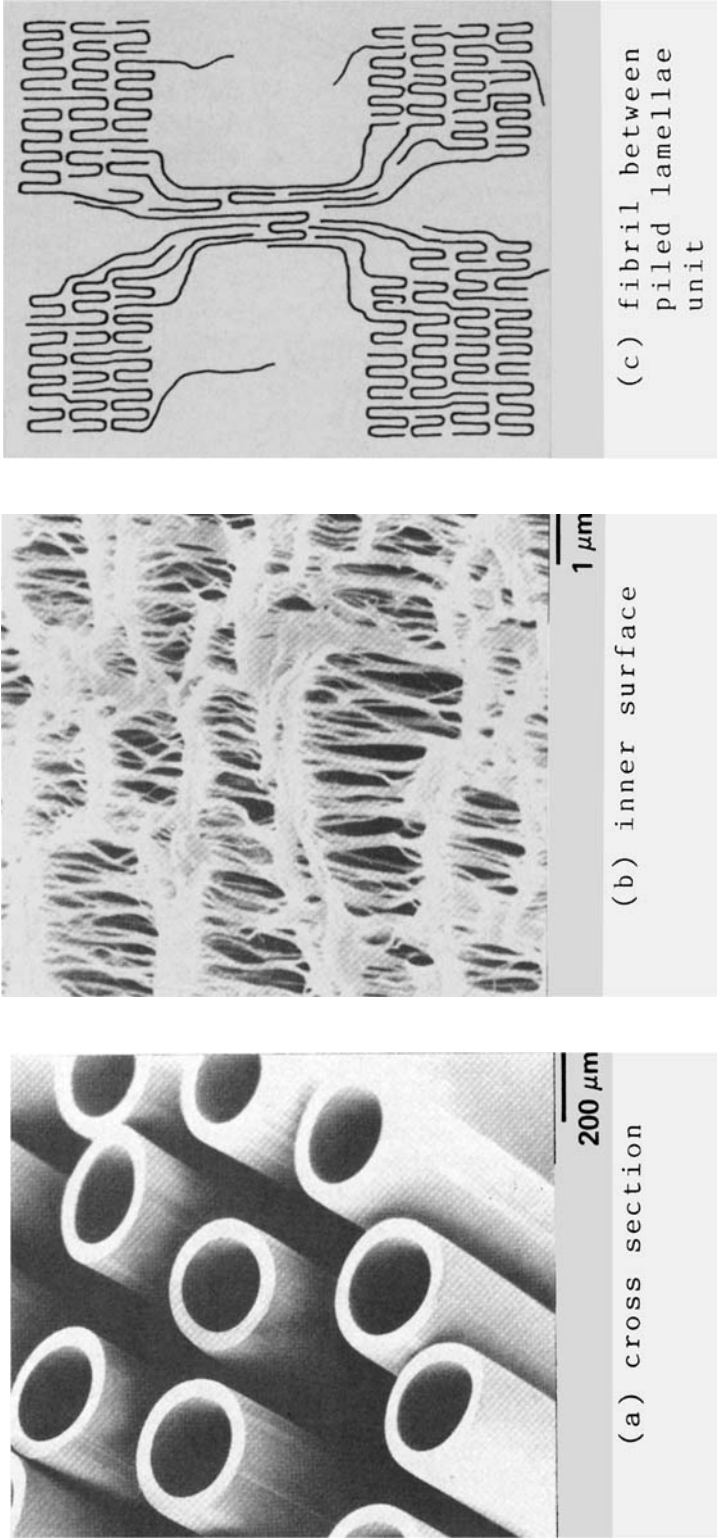


Fig. 7. Structure of porous hollow fiber.

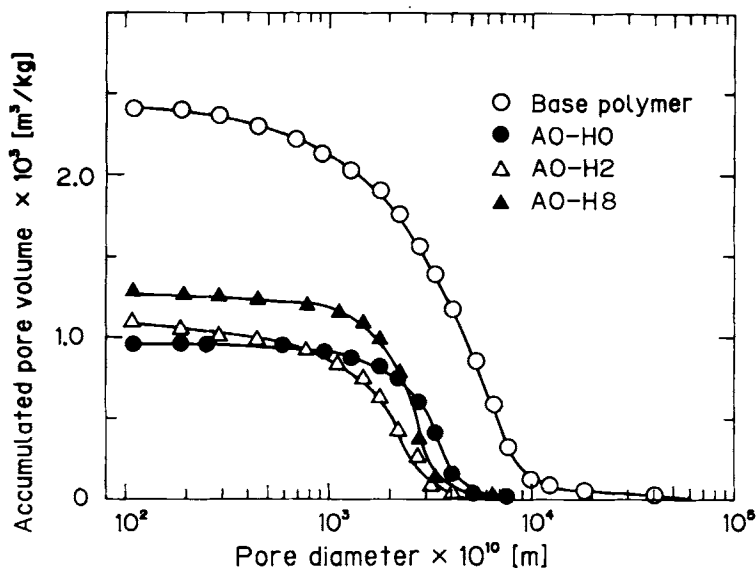


Fig. 8. Pore volume distribution.

-H8 fibers are shown in Figure 6, where the dark and grey regions are pores and resin phase, respectively. Greater enlargement and swelling of the resin phase was observed with increased KOH-conditioning time.

The porous hollow fiber used as trunk polymer is manufactured by the stretching technique.¹² The drawing of the amorphous polymer between the piled lamellae causes the formation of microfibrils, resulting in creation of slitlike pores,¹³ as illustrated schematically in Figure 7. In the preirradiation grafting employed, the radicals are mainly trapped on the surface of the undrawn crystalline lamellae. The vapor of acrylonitrile monomer, therefore, can react with them and form the graft chains both on the surface of the pores and in the region between individual folded-chain lamellae. The amidoximation converts the produced cyano groups into amidoxime groups and byproduct groups such as cyclic compounds. The alkaline treatment induces the hydrolysis of the remaining cyano groups and byproduct groups into cation exchange groups such as hydroxamic and carboxyl groups. In addition, the ion exchange reaction between these cation exchange groups and potassium ion hydrated with water molecules resulted in the swelling of the resin phase and the formation of micropores within it. The micropores facilitate the diffusion of uranyl ion species in seawater, $\text{UO}_2(\text{CO}_3)_3^{4-}$, into the graft chains containing amidoxime groups. Figure 8 shows the comparison of cumulative pore volume distribution between the trunk polymer and AO-H fibers. The trunk polymer has a relatively broader pore volume distribution ranging from 0.05 to 1×10^{-6} m pore diameter. On the other hand, the narrower distribution between 0.1 and 0.5×10^{-6} m was observed in AO-H fibers. Also, the pore volume of the AO-H0 fiber, 0.96×10^{-3} m³/kg, decreased by about 40% from that of the trunk polymer, 2.42×10^{-3} m³/kg. When we define pores larger than 0.01×10^{-6} m in diameter as macropores, there is no significant difference in

pore volume distribution for different KOH-conditioning times. In other words, the alkaline treatment exhibited almost no effect on macropore diameter.

The authors thank Takeji Ohtani of the Membrane and Medical Dept., Mitsubishi Rayon Co., Ltd., for his help in providing the starting polymer. This work was supported by Grants-in-Aid for Energy Research No. 63603006 from the Ministry of Education, Science and Culture.

References

1. H. Egawa, M. Nakayama, T. Nonaka, and E. Sugihara, *J. Appl. Polym. Sci.*, **33**, 1993 (1987).
2. K. Saito, K. Uezu, T. Hori, S. Furusaki, T. Sugo, and J. Okamoto, *AIChE J.*, **34**, 411 (1988).
3. T. Hori, K. Saito, S. Furusaki, T. Sugo, and J. Okamoto, *Nippon Kagaku Kaishi*, 1792 (1986).
4. K. Uezu, K. Saito, T. Hori, S. Furusaki, T. Sugo, and J. Okamoto, *J. At. Energy Soc. Jpn.*, **30**, 359 (1988).
5. J. Okamoto, T. Sugo, A. Katakai, and H. Omichi, *J. Appl. Polym. Sci.*, **30**, 2967 (1985).
6. H. Omichi, A. Katakai, T. Sugo, and J. Okamoto, *Sep. Sci. Technol.*, **20**, 163 (1985).
7. H. Omichi, A. Katakai, T. Sugo, and J. Okamoto, *Sep. Sci. Technol.*, **21**, 299 (1986).
8. H. Omichi, A. Katakai, T. Sugo, and J. Okamoto, *Sep. Sci. Technol.*, **21**, 563 (1986).
9. H. Omichi, A. Katakai, T. Sugo, J. Okamoto, S. Katoh, K. Sakane, K. Sugasaka, and T. Itagaki, *Sep. Sci. Technol.*, **22**, 1313 (1987).
10. T. Hori, S. Furusaki, T. Sugo, and J. Okamoto, *Nippon Kagaku Kaishi*, 1071 (1987).
11. K. Motojima, T. Yamamoto, and Y. Kato, *Bunseki Kagaku*, **18**, 208 (1969).
12. K. Yoshida, *Kobunshi*, **37**, 142 (1988).
13. T. Tagawa and K. Ogura, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 971 (1980).
14. L. Astheimer, H. J. Schenk, E. G. Witte, and K. Schwochau, *Sep. Sci. Technol.*, **18**, 307 (1983).
15. H. Egawa, M. Nakayama, T. Nonaka, H. Yamamoto, and K. Uemura, *J. Appl. Polym. Sci.*, **34**, 1557 (1987).
16. S. Katoh and K. Sugasaka, *Bull. Soc. Seawater Sci. Jpn.*, **40**, 265 (1987).

Received December 12, 1988

Accepted June 9, 1989