Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

A New Type of Amidoxime-Group-Containing Adsorbent for the Recovery of Uranium from Seawater. II. Effect of Grafting of Hydrophilic Monomers

H. Omichi[a]; A. Katakai[a]; T. Sugo[a]; J. Okamoto[a]
[a] Japan Atomic Energy Research Institute Takasaki Radiation Chemistry Research Establishment Takasaki, Gunma, Japan

To cite this Article Omichi, H. , Katakai, A. , Sugo, T. and Okamoto, J.(1986) 'A New Type of Amidoxime-Group-Containing Adsorbent for the Recovery of Uranium from Seawater. II. Effect of Grafting of Hydrophilic Monomers', Separation Science and Technology, 21: 3, 299 — 313

To link to this Article: DOI: 10.1080/01496398608058379

URL: http://dx.doi.org/10.1080/01496398608058379

SEPARATION SCIENCE AND TECHNOLOGY, 21(3), pp. 299-313, 1986

A New Type of Amidoxime-Group-Containing Adsorbent for the Recovery of Uranium from Seawater. II. Effect of Grafting of Hydrophilic Monomers

---

H. OMICHI, A. KATAKAI, T. SUGO, and J. OKAMOTO

JAPAN ATOMIC ENERGY RESEARCH INSTITUTE
TAKASAKI RADIATION CHEMISTRY RESEARCH ESTABLISHMENT
TAKASAKI, GUNMA 370-12, JAPAN

Abstract

A fibrous adsorbent containing amidoxime groups (AOF) for recovering uranium from seawater was synthesized by the radiation-induced grafting of acrylonitrile (AN) to a fiber followed by the amidoximation of cyano groups of poly(AN) graft chains. When such hydrophilic monomers as *N,N*-dimethylacrylamide (DMAAm) and acrylic acid (AAc) were preliminarily grafted, both the water uptake and the mobility of the sorbed water in AOF were improved in the order: AOF-containing poly-(DMAAm) graft chains (AOF-DMAAm) > AOF-containing poly(AAc) graft chains (AOF-AAc) > AOF without hydrophilic graft chains. The uranium uptake with these adsorbents was, on the other hand, in the order: AOF-AAc > AOF-DMAAm > AOF. The adsorption of alkaline earths was related to the distribution pattern of poly(AAc) graft chains inside the fiber. The adsorbed alkaline earths were eliminated from the adsorbent fiber by introducing a solution of heavy metal ions such as Cu^{2+}.

INTRODUCTION

Many types of adsorbents have been tested for the recovery of uranium from seawater (*1–16*). Amidoxime-group-containing fibrous adsorbents (AOF) have been especially noted because of a larger uranium uptake when compared with hydrous titanium oxide (*14*).

In our previous papers (*17, 18*) we reported the characteristics of AOF which was synthesized by the radiation-induced grafting technique. First, the amount of amidoxime groups and their distribution in the fiber are

0149-6395/86/2103-0299$3.50/0

precisely controlled by the irradiation conditions (dose, dose rate) and the grafting conditions (reaction time, temperature, etc.). Second, it is possible to synthesize an adsorbent with high stability to contact with seawater and treatment with alkaline solution because such inert synthetic polymers as poly(tetrafluoroethylene-*co*-ethylene) and polypropylene can be used as trunk polymers for making adsorbents. This enables the repeated use of the adsorbent. Third, the mixing of different kinds of functional groups is possible by co-grafting of different monomers. The introduction of plural functional groups is expected to provide a much higher uranium uptake through a "synergistic effect."

Adsorbents containing both amidoxime groups and carboxyl groups (AOF-AAc) were synthesized by grafting acrylic acid in the first step and acrylonitrile in the second step (*18*). The uranium uptake with these adsorbents was found to be much higher than with an adsorbent containing only amidoxime groups. In the present paper the effect of hydrophilic properties of AOF on uranium uptake from seawater as well as the adsorption of such metals as alkaline earths was investigated in connection with the distribution of poly(AAc) graft chains in the adsorbent fiber.

EXPERIMENTAL

AOF were synthesized by the radiation-induced grafting of acrylonitrile (AN) followed by the conversion of cyano groups to amidoxime groups (AO) with hydroxylamine. The details of the procedure were reported in our previous papers (*17*, *18*). Tetrafluoroethylene-ethylene copolymer poly(TFE-E) fiber (40 μmϕ) was used as a trunk polymer for grafting. The monomers acrylic acid (AAc), *N,N*-dimethylacrylamide (DMAAm), and AN were purified by the usual methods.

The water uptake of AOF was measured as follows: The weighed amount of AOF which was preliminarily immersed in water for 24 h at 25°C was wiped with filter papers and was kept in a vessel containing saturated water vapor at 25°C for 24 h. Then the vessel was evacuated to dryness. The water uptake was calculated as the difference between the weight under wet conditions and that under dry conditions.

The exchange rate of water sorbed in AOF with the water outside AOF was measured as follows: About 0.1 g of AOF containing a saturated amount of H_2O was immersed in 5 mL of D_2O (purity = 99.8%) for the prescribed periods and the change in composition of D_2O was followed by means of a JEOL high resolution proton NMR, model JNM-PFT-100.

The adsorption of uranium from natural seawater was carried out with a batch process (the volume of the vessel = 2 L, with vigorous agitation) at 25 ± 1°C or with a semi-batch process (the volume of the vessel = 2 L, with agitation, and the intermittent exchange of seawater at the rate of 2 L/d).

The desorption of uranium was accomplished by contacting 0.1 g of AOF with 25 mL sulfuric acid (1 *N*) for 1 h at 25°C. The amount of uranium complexed with arsenazo III was measured optically at 665 nm by means of a Shimadzu spectrophotometer, model UV-100-02. The amounts of alkaline earths were determined by means of a Jarrell-Ash atomic absorption and flame emission spectrophotometer, model AA-8200.

The distribution of carboxyl groups in the cross section of AOF was measured as follows: AOF-AAc was boiled in 2.5% KOH solution for 24 h, followed by contact with fresh water at room temperature for 72 h to eliminate excess KOH. The specimen for electron microscopy was made by placing AOF in liquid nitrogen. The line profiles of potassium combined with carboxyl groups was measured by means of a JEOL electron probe x-ray microanalyzer, model JXA 733.

The change in diameter of AOF after contact with a 2.5% KOH solution at 80°C for 10 min and with seawater at 30°C for 24 h was followed optically.

RESULTS AND DISCUSSION

The graft polymer composed of hydrophobic poly(TFE-E) and poly(AN) graft chains does not sorb water until the cyano groups of the graft chains are converted to amidoxime groups. The poly(TFE-E) grafted with such hydrophilic monomers as DMAAm and AAc, on the other hand, can sorb water without any modification. Figure 1 shows the relationship between the water uptake and the amount of these functional groups in the graft polymers. The polymers were preliminarily treated with 2.5% KOH solution at 80°C for 10 min in order to obtain as high water uptake as possible (*19*). The water uptake increases in proportion to the amount of functional groups. The slopes of the lines differ from one another depending on the kind of functional groups. The magnitude of the slope with different functional groups is in the order: amide > carboxyl > amidoxime. The result that the amidoxime group is less hydrophilic is consistent with previous results (*16*). Figure 1 also shows that the water uptake of graft polymer containing mixed functional groups depends on the content of these groups.

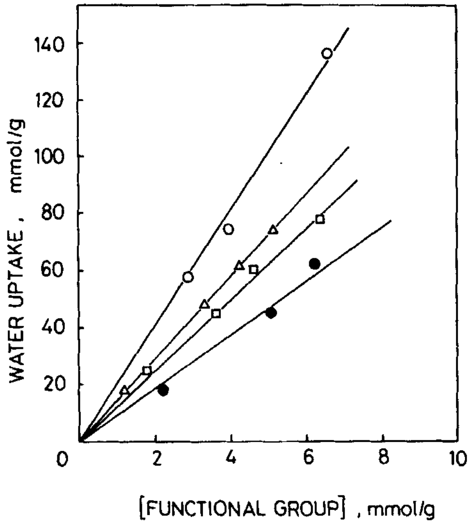


FIG. 1. Relationship between the water uptake and the amount of hydrophilic groups in graft polymers: (○) hydrophilic group = amide, (△) carboxyl, (●) amidoxime, (□) amidoxime/carboxyl = 1/1.

From Fig. 1 the numbers of the water molecules sorbed per unit functional group were obtained as 8 for amidoxime, 13 for carboxyl, and 18 for amide. These values are 2 to 3 times as large as those obtained with the same graft polymer without KOH treatment (*18*). This is due to the fact that the KOH treatment of graft polymers at high temperature changes the polymer structure in such a way as to enlarge the spaces between crystallites and facilitates the sorption of water.

It is expected that the diffusion of aqueous solution in more hydrophilic polymers will be faster than in less hydrophilic polymers. In order to obtain a relationship between the diffusion of water and the hydrophilic property of AOF, the mobility of the water in AOF was studied by measuring the exchange rate of the water in AOF with the water outside AOF. Figure 2 shows the ratio of the exchanged water at different periods. About 80% of the initially sorbed water in AOF-DMAAm was exchanged with the water outside AOF-DMAAm within 2 h. The increase of exchange in the following 10 h, however, was less than 10%. Although the exchange in the initial stage was small in the case of AOF-AAc, the equilibrium exchange in 24 h was equal to that with AOF-DMAAm. On the other hand, the equilibrium exchange with AOF without hydrophilic groups was about one-half those observed with

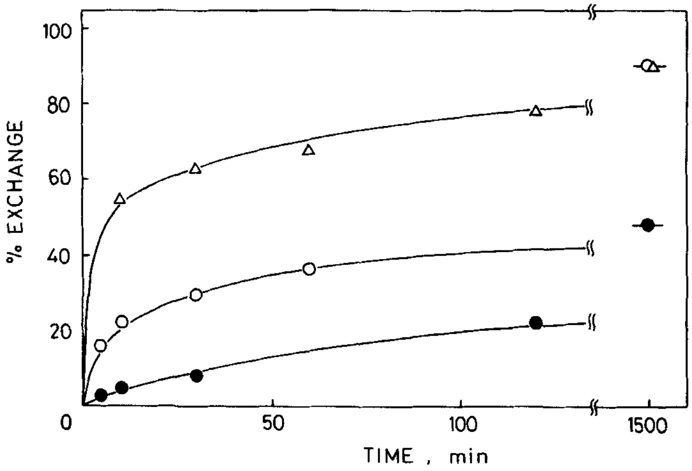


FIG. 2. Ratio of the water in AOF exchanged with the water outside AOF: (●) AOF, (○) AOF-AAc, (□) AOF-DMAAm.

AOF-AAc. When it is considered that the equilibrium amount of exchange water corresponds to the content of "mobile water" (free water) in the total sorbed water (mobile + immobile) (*19*), the results in Fig. 2 indicate that ~90% of the sorbed water in both AOF-DMAAm and AOF-AAc is mobile, while the content of the mobile water in AOF is less than 50%.

These differences in water uptake (as shown in Fig. 1) and the mobile water content (Fig. 2) among the adsorbents affect the uranium uptake from seawater because the diffusion of seawater in the adsorbents is a rate-determining step for adsorption (*17*). The adsorbents AOF, AOF-AAc, and AOF-DMAAm, as well as poly(TFE-E) containing poly(AAc) graft chains P-*g*-AAc and that containing poly(DMAAm) graft chains P-*g*-DMAAm, were contacted with seawater in the semibatch process. Figure 3 shows that P-*g*-AAC and P-*g*-DMAAm, which do not have amidoxime groups, have no ability to adsorb uranium from seawater. On the other hand, AOF showed an increase in adsorption with an increase in the amount of seawater. The uranium uptake with AOF-AAc is about twice that with AOF and 20–30% higher than that with AOF-DMAAm. This result indicates that an acidic hydrophilic group (carboxyl) is superior to a nonionic hydrophilic group (amido) for facilitating uranium uptake from seawater with AOF. In the following experiments, therefore, AOF-AAc was mainly used as the adsorbent.

Figure 4 shows the relationship between the uranium uptake and the

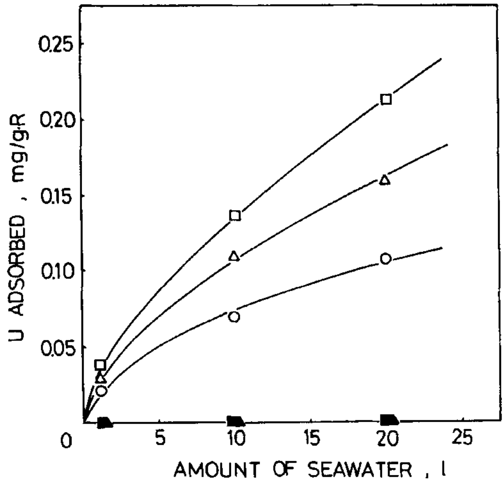


FIG. 3. Uranium adsorption from seawater with (□) AOF-AAc, (△) AOF-DMAAm, (○) AOF, (■) P-*g*-AAc, (▲) P-*g*-DMAAm. A semibatch process containing 0.1 g of adsorbent with the exchange of seawater at 2 L/d for 5 d.

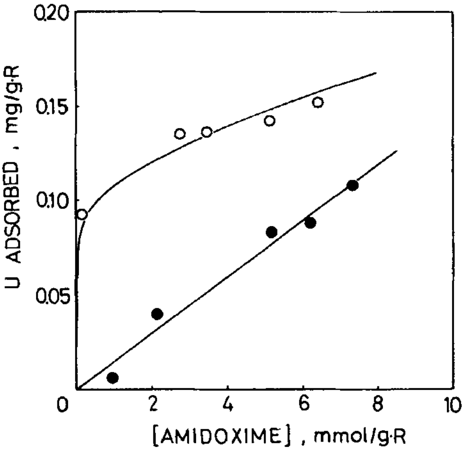


FIG. 4. Relationship between the uranium uptake and the amount of amidoxime groups in (●) AOF and (○) AOF-AAc for the semibatch process under the same conditions as shown in Fig. 3.

amount of amidoxime groups in AOF and AOF-AAc. The amount of carboxyl groups in AOF-AAc was maintained at a constant value ([COOH] = 1 mmol/g). The uranium uptake increased almost in proportion to the amount of amidoxime groups in AOF. On the other hand, in the case of AOF-AAc, the uranium uptake with 0.1 mmol/g of amidoxime groups reached about 0.1 mg/g. Although the further introduction of amidoxime groups increased the uranium uptake in proportion to the amount of amidoxime groups, the increment was about one-third that observed with AOF.

The higher uranium uptake observed with AOF-AAc may be partly due to the hydrophilic properties of AOF introduced by poly(AAc) graft chains. Comparison of the results in Figs. 2 and 3, however, indicates that there is another factor in facilitating uranium uptake with AOF-AAc, because a higher uranium uptake was observed with AOF-AAc compared to AOF-DMAAm which was more hydrophilic than AOF-DMAAm. This promoting factor for uranium uptake is probably due to the effect of carboxyl groups which provide a local acidic atmosphere around amidoxime groups. Uranium in seawater exists in the form of a uranyl tricarbonate complex. A decrease in pH changes the equilibrium by converting the tricarbonate-type complex to the bicarbonate-type complex (*14*). Accordingly, the exchange reaction between amidoxime groups and carbonate ligands in the uranyl tricarbonate chelate complex is facilitated by the acidic atmosphere.

On the other hand, the use of AOF-AAc has the possibility of increasing the adsorption of undesirable metal ions, such as alkaline earths, because poly(AAc) has an affinity for these metals. The adsorption of alkaline earths (magnesium and calcium) was compared with that of uranium during contact of AOF and AOF-AAc with seawater in the batch process. The results are shown in Fig. 5. Several features about the amount of adsorption should be pointed out. First, the adsorption of uranium is much slower than that of alkaline earths. For example, equilibrium of uranium adsorption was not reached until after 7 days, while the adsorption of alkaline earths reached equilibrium in 2 days. One reason for the slow adsorption of uranium is the low concentration of uranium in seawater (3×10^{-3} mg/L) when compared with that of alkaline earths (Mg, 1.4×10^3 mg/L; Ca, 4.0×10^2 mg/L, respectively) because the diffusion rate of metals into the adsorption sites is a first-order function of the concentration of the metals. The other reason is the difference in the size of the ions. The uranium in seawater, in the form of a bulky uranyl tricarbonate chelate complex (the size is ~10 Å), needs a much larger space for diffusing into the adsorbent compared with the

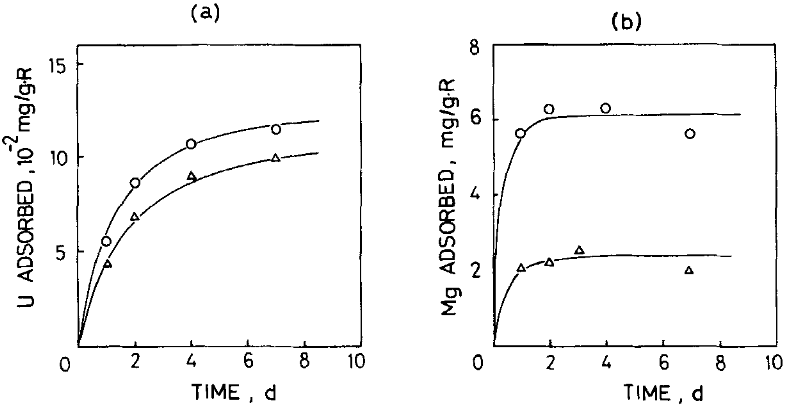


FIG. 5. Adsorption of (a) uranium and (b) magnesium from seawater with (△) AOF and (○) AOF-AAc in the batch process: adsorbent 0.1 g, amount of seawater 5 L.

smaller alkaline earths. The hard polymer structure of poly(TFE-E) prevents the free movement of such bulky ions in the adsorbent.

Second, the presence of poly(AAc) graft chains has a different effect on the adsorption of uranium and alkaline earths. The increase in the adsorption of alkaline earths through the introduction of poly(AAc) graft chains is about five times that for uranium. This large increase for alkaline earths adsorption is due to the high affinity of alkaline earths for the carboxyl groups of poly(AAc) graft chains. On the other hand, uranium in seawater has little affinity for poly(AAc), as shown in Fig. 3.

The difference in the effect of carboxyl groups on the adsorption between uranium and alkaline earths is more evident as indicated when the adsorption amounts are plotted against the amounts of carboxyl groups in the adsorbents as shown in Fig. 6. In the case of uranium, the amount of adsorption increases abruptly by introducing a small amount (~0.5 mmol/g) of carboxyl groups. A further increase in the amount of carboxyl groups, however, has no effect on adsorption. On the other hand, an increase in the amount of adsorbed alkaline earths has a linear relationship with the amount of carboxyl groups. These results show that the adsorption of alkaline earths is mainly due to carboxyl groups.

Because metals are adsorbed from the surface region of adsorbents (*14*), adsorption is affected by the distribution pattern of functional groups inside the adsorbent. Figure 7 shows EPMA line profiles of different amounts of carboxyl groups in the cross section of fibers. The

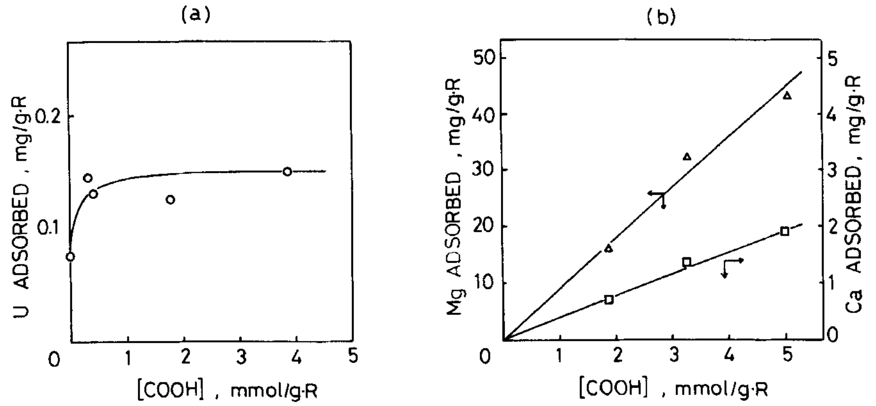


FIG. 6. Relationship between the amount of carboxyl groups and (a) the adsorption amount of uranium (○) and (b) the adsorption amounts of magnesium (△) and calcium (□) for the semibatch process under the same conditions as shown in Fig. 3.

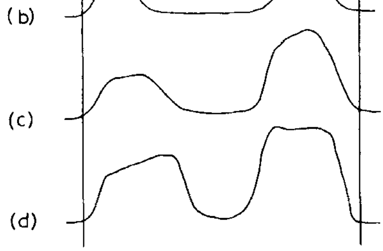


FIG. 7. EPMA line profiles of carboxyl groups in the cross section of AOF-AAc: (a) [COOH] = 1.2 mmol/g, (b) 1.9, (c) 3.3, (d) 4.2.

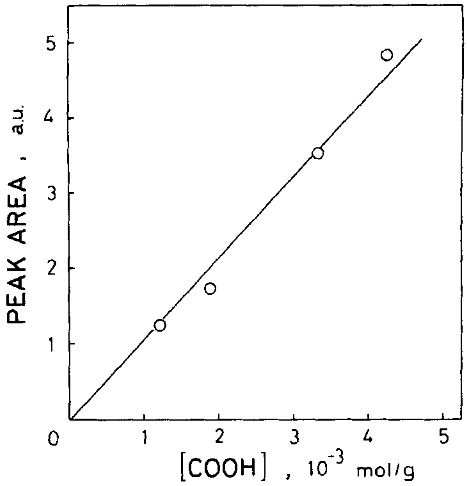


FIG. 8. Relationship between the amount of carboxyl groups in AOF-AAc and the peak area observed in the distribution curves of carboxyl groups as shown in Fig. 7.

presence of two peaks indicates that carboxyl groups in the amounts indicated in Fig. 7 exist only in the surface region of AOF. The peak area under the distribution curve has a linear relationship with the amount of carboxyl groups as shown in Fig. 8. It is interesting that the peak position is not on the surface but about 10–20 μm under the surface. This is due to the fact that the highest grafting yield is obtained in this region where the movement of growing chains of grafting is more restricted than the movement on the surface, and the resultant termination rate of graft polymerization is small (*20*).

In accordance with the distribution pattern of carboxyl groups inside

TABLE 1
Change in Diameter of AOF and AOF-AAc under Various Conditions

Conditions	AOF	AOF-AAc
Original	1	1
After contact with alkali[a]	1.04	1.06
After contact with seawater[b]	1.04	1.09

[a] 80°C, 10 min.
[b] 30°C, 24 h.

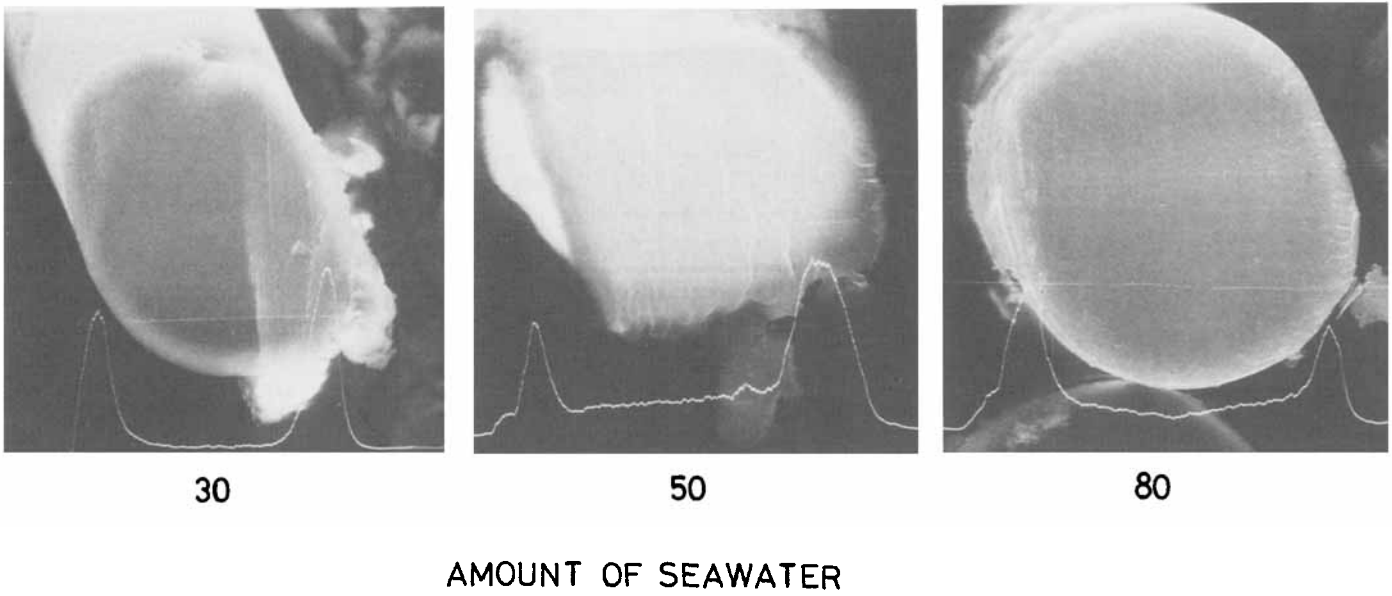
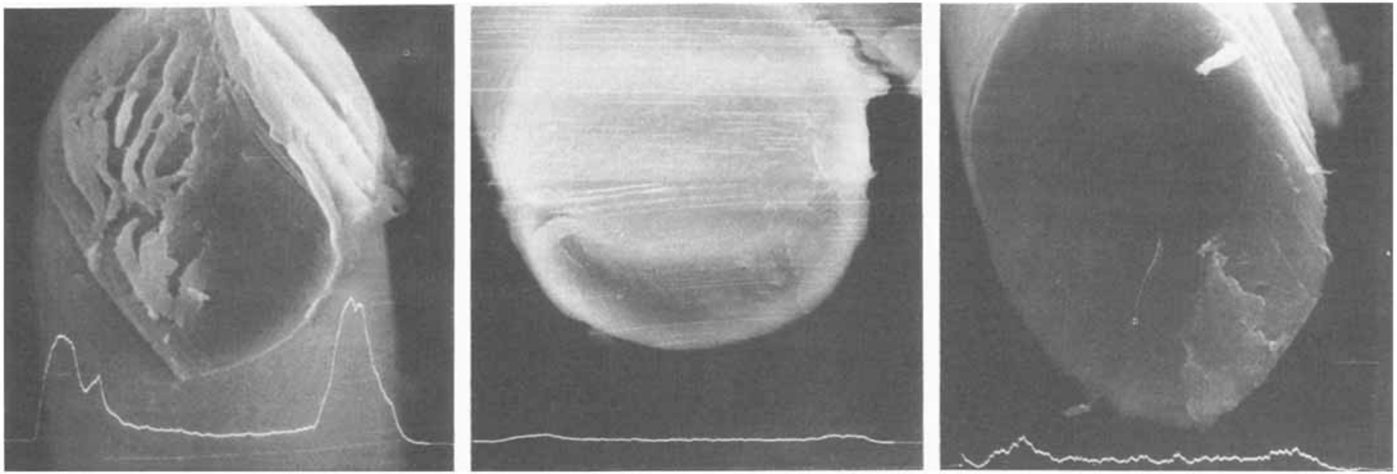


FIG. 9. Distribution curves of Ca^{2+} in AOF-AAc for the semibatch process under the same conditions as shown in Fig. 3.

(a)



0 min , 500cps

5 min , 500 cps

15 min , 100 cps

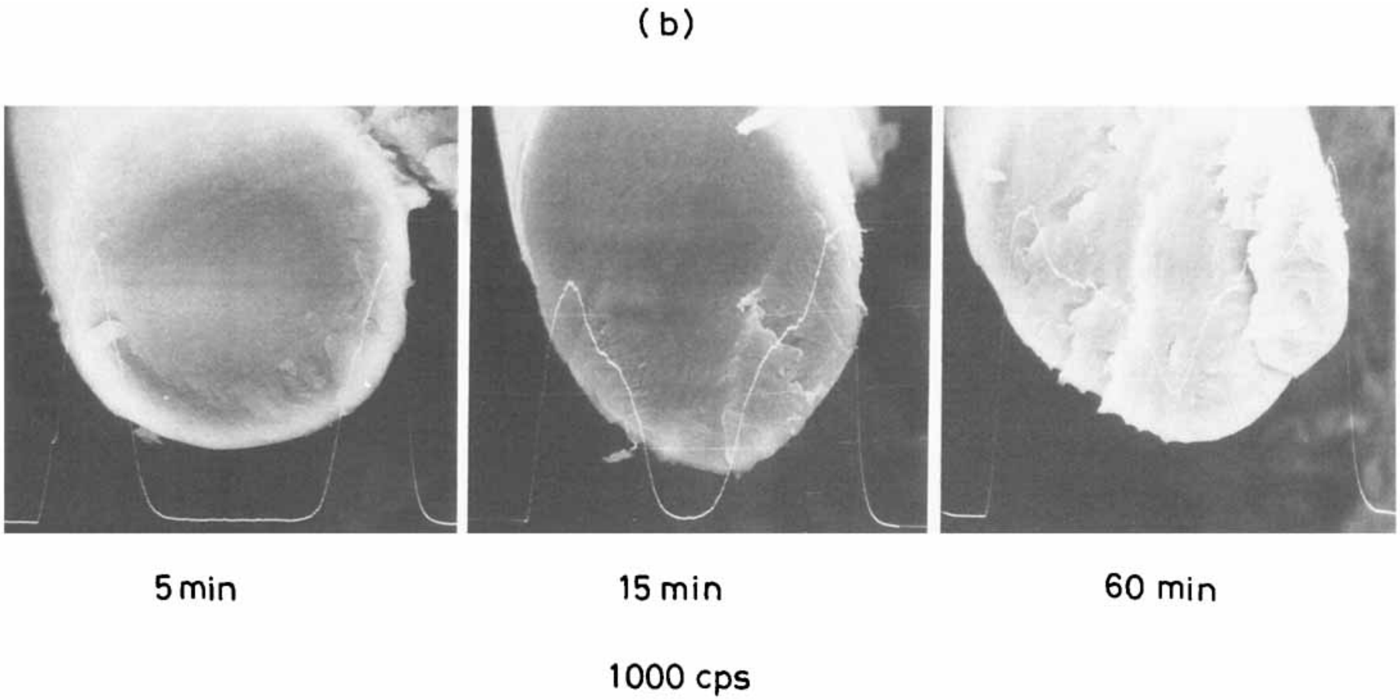


FIG. 10. Changes in distribution curves of (a) Ca^{2+} and (b) Cu^{2+} by contact with AOF-AAc containing Ca^{2+} with the solution of Cu^{2+} (15 mM).

AOF, the distribution of alkaline earths occurs mainly in the surface region as shown in Fig. 9. The increase in the amount of seawater supplied changes neither the peak height nor the distribution pattern for alkaline earths. Therefore, by comparing Figs. 7 and 9 it can be seen that the distribution patterns for carboxyl groups and for alkaline earths are virtually the same. The adsorption of alkaline earths is therefore entirely due to carboxyl groups of the graft chains in AOF.

The interaction between alkaline earths and carboxyl groups is, however, not strong. As shown in Fig. 10, the alkaline earths adsorbed are easily removed by the introduction of heavy metal ions such as Cu^{2+}, which is adsorbed and distributed inside the fiber in the place of alkaline earths. This result suggests that the recovery of heavy metals such as uranyl ions from seawater are little affected by the adsorption of alkaline earths and alkalies. Actually, the concentration factor for uranium proved to be at least 10^3 that for alkaline earths (*18*).

The stability of AOF and AOF-AAc to various treatments was investigated as shown in Table 1. The diameter of AOF-AAc increased by 6% from the original by contact with alkali solution and an additional 3% by subsequent contact with seawater. The change in diameter of AOF-AAc is evidently larger than that of AOF. This is due to the increase of hydrophilicity of poly(AAc) graft chains in AOF-AAc. However, these values are still sufficiently small when compared with the values observed in other types of AOF made from acrylic synthetic fibers (*16*).

REFERENCES

1. Y. Ozawa, T. Murata, H. Yamashita, and F. Nakajima, *J. Nucl. Sci. Technol., 17*, 634 (1980).

2. H. Yamashita, Y. Ozawa, F. Nakajima, and T. Murata, *Bull. Chem. Soc. Jpn., 53*, 1, 1331, 3050 (1980).

3. H. Yamashita, Y. Ozawa, F. Nakajima, and T. Murata, *Sep. Sci. Technol., 16*, 676 (1981).

4. Yu. P. Novikov and V. M. Komarevsky, *Radiochem. Radioanal. Lett., 48*, 45 (1981).

5. N. Jaffrezic and M. H. Andrade, *J. Radioanal. Chem., 55*, 307 (1980).

6. N. Jaffrezic, M. H. Andrade, and D. H. Trang, *J. Chromatogr., 201*, 187 (1980).

7. I. Tabushi, Y. Kobuke, and T. Nishiya, *Nature, 280*, 665 (1979).

8. I. Tabushi, Y. Kobuke, K. Ando, M. Kishimoto, and E. Ohara, *J. Am. Chem. Soc., 102*, 5947 (1980).

9. K. Sugasaka, S. Katoh, H. Takai, H. Takahashi, and Y. Umezawa, *Sep. Sci. Technol., 16*, 971 (1981).

10. M. B. Collela, S. Siggia, and R. M. Barnes, *Anal. Chem., 52*, 967 (1980).

11. S. Fried, A. M. Friedeman, and J. C. Sullivan, *Environ. Sci. Technol., 15*, 834 (1981).

12. J. Borzekowski, M. J. Driscoll, and F. R. Best, *Trans. Am. Nucl. Soc.*, p. 44 (1983).

13. H. J. Schenk, L. Astheimer, E. G. Witte, and K. Schwochau, *Sep. Sci. Technol., 17*, 1293 (1982).

14. L. Astheimer, H. J. Schenk, E. G. Witte, and K. Schwochau, *Ibid., 18*, 307 (1983).
15. D. Heitkamp and K. Wagener, *Ind. Eng. Chem., Process Des. Dev., 21*, 781 (1982).
16. S. Katoh, K. Sugasaka, K. Sakane, N. Takai, H. Takahashi, Y. Umezawa, and T. Itagaki, *J. Chem. Soc. Jpn.*, pp. 1449, 1455 (1982).
17. J. Okamoto, T. Sugo, A. Katakai, and H. Omichi, *J. Appl. Polym. Sci., 30*, 2967 (1985).
18. H. Omichi, A. Katakai, T. Sugo, and J. Okamoto, *Sep. Sci. Technol., 20*, 163 (1985).
19. T. Sugo, A. Katakai, H. Omichi, and J. Okamoto, Unpublished Data.
20. H. Omichi and K. Araki, *J. Polym. Sci., Polym. Chem. Ed., 14*, 2773 (1976).

Received by editor May 13, 1985