

Recovery of Uranium from Seawater V. Preparation and Properties of the Macroreticular Chelating Resins Containing Amidoxime and Other Functional Groups

HIROAKI EGAWA, MORIO NAKAYAMA, TAKAMASA
NONAKA, HIDEKI YAMAMOTO, and KEIJI UEMURA,
*Department of Applied Chemistry, Faculty of Engineering, Kumamoto
University, Kurokami 2-39-1, Kumamoto, Japan*

Synopsis

We have synthesized macroreticular chelating resins containing amidoxime groups from acrylonitrile (AN)-divinylbenzene (DVB)-alkyl acrylate, alkyl methacrylate, or vinylpyridine (VPy) copolymer beads. It was found that the chelating resin (RNMH)-containing amidoxime groups prepared from AN-DVB-methyl acrylate (MA) indicated the highest adsorption ability for uranium in seawater. Hydroxamic acid and carboxylic groups in addition to amidoxime groups were formed during the reaction of the copolymer beads with a methanol solution of hydroxylamine. The adsorption ability for uranium was greatly influenced by the physical pore structure (macropore) and the pore structure formed by the swelling (micropore). RNMH (RNMH10-10) prepared with 10 mol% of DVB and 10 mol% of MA had the highest adsorption ability and physical stability for uranium. On the other hand, improved adsorption ability for uranium was not observed in the case of the macroporous resins (RNPyH) prepared by the copolymerization of VPy as the basic component. After seawater was passed through the column packed with RNMH10-10 at a space velocity (SV) of 180 h^{-1} (up-flow) for 10 days, the amount of uranium adsorbed on the resin was about $100 \text{ mg/dm}^3\text{-R}$ and 260 mg/kg-R .

INTRODUCTION

Since atomic power is expected to play an important role in energy resources, the industrial system of uranium recovery from natural seawater, which contains approximately 4 billion tons of uranium, must be established in the near future. We have already synthesized the macroreticular chelating resins containing amidoxime¹⁻⁶ and dihydroxyphosphino and/or phosphono groups,⁷ which are highly effective for the recovery of uranium from seawater.⁸⁻¹¹ In this research, it has become apparent that the physical and chemical structure of adsorbents greatly influence the adsorption ability for uranium from seawater. In recent years there have been reports on the synthesis of some adsorbents and the application of uranium recovery from seawater (e.g., chelating resins containing dithiocarbamate groups,¹² amidoxime groups,^{13,14} 1,2-dihydroxyanthraquinone groups,¹⁵ and aminomethylphosphonic acid groups.^{16,17}) In these reports, the physical and chemical structure of uranium adsorbents seems not to be well defined. In our recent study,⁶ the macroreticular chelating resins containing amidoxime groups with various pore structures have been prepared by using several crosslinking reagents, and the influence of the pore structure on the adsorption ability for uranium was

investigated.

In this article, we have synthesized the macroreticular chelating resins containing amidoxime groups from acrylonitrile(AN)-divinylbenzene(DVB)-alkyl acrylate, alkyl methacrylate, or vinylpyridine (VPy), and investigated the influence of the pore structure and neighboring groups on the uranium adsorption ability of these resins.

EXPERIMENTAL

Preparation of Macroreticular Chelating Resins Containing Amidoxime Groups

Macroreticular AN-DVB-alkyl acrylate, alkyl methacrylate, or VPy copolymer beads were synthesized by the same method described previously.⁶ A commercial reagent of AN was purified by distillation under nitrogen. DVB was used as technical grade (contain 55% DVB), and was washed free of polymerization inhibitor with $1 \text{ mol} \cdot \text{dm}^{-3}$ sodium hydroxide followed by several water washes. Methyl, ethyl, butyl, and octyl acrylate (MA, EA, BA, and OA) and methyl, ethyl, and butyl methacrylate (MMA, EMA, and BMA) were selected as alkyl acrylates and methacrylates. These monomers were purified by vacuum distillation. The copolymer beads obtained with MA, EA, BA, OA, MMA, EMA, and BMA are abbreviated as RNM, RNE, RNB, RNO, RNMM, RNEM, and RNBEM respectively. VPy(4-vinylpyridine) was used as received. The copolymer beads obtained with VPy are abbreviated as RNPy. These copolymer beads were treated with a 3% hydroxylamine methanol solution at 80°C for 2 h. These products (abbreviated as RNMH, RNEH, RNBH, RNOH, RNMMH, RNEMH, RNBEMH, and RNPyH, respectively) were washed with pure water until hydroxylamine was not released in the wash water, then were air-dried, and dried in vacuo at 40°C for 6 h. Each resin (1 g) was treated with 100 cm^3 of $0.1 \text{ mol} \cdot \text{dm}^{-3}$ sodium hydroxide solution at 30°C for 15 h (alkali treatment) or with a 100 cm^3 of $1 \text{ mol} \cdot \text{dm}^{-3}$ hydrochloric acid solution at 60°C for 5 h (acid treatment). The resulting resins were washed with deionized water until the wash water became neutral and then were air-dried and dried in vacuo at 40°C for 2 h. An apparent anion and cation exchange capacity of the above resins were measured by the method previously reported.⁶

Apparatus

Specific surface area of resins was measured on a Yuasa surface area apparatus (BET method). Pore volume, average radius, and peak radius of resins were determined on a Carlo-Erba mercury porosimeter (Model 1520). Infrared (IR) spectra were recorded in KBr pellet on a JASCO A-702 spectrophotometer. Metal ions were determined by in-coupled plasma emission spectrometry with Jyarel-ash ICPA mark II.

Measurement of Swelling Ratio

A volume (V_1) of dry resin was measured with a graduated glass filter. After the dry resin (1 g) was added to the distilled water (100 cm^3), the mixture was

allowed to stand at room temperature for 24 h with occasional shaking. The volume (V2) of wet resin was measured with the graduated glass filter. The volume (V3) of wet resin after alkali or acid treatment was measured. Swelling ratio was calculated by the following equation.

$$\text{Swelling ratio} = \frac{\text{volume of wet resin}}{\text{volume of dry resin}}$$

Measurement of Adsorption Capacity for Silver(I) and Copper(II) Ions

In a glass-stoppered Erlenmeyer flask were placed 0.125 g of the resin and 50 cm³ of buffered metal ion solution (0.01 mol · dm⁻³ Ag⁺ and Cu²⁺), and the mixture was shaken at 30°C for 24 h. The amounts of Ag⁺ and Cu²⁺ adsorbed on the resins were calculated from the determination of Ag⁺ and Cu²⁺ in the supernatant.

Adsorption of Uranium from Spiked Seawater

The resin (0.1 g) and 25 cm³ of natural seawater spiked with UO₂(NO₃)₂ · 6H₂O (10 mg · dm⁻³ concentration of U) were shaken at 30°C for 1 h. The resin was filtered off and then the filtrate was taken for the spectrophotometric determination of uranium with arsenazo-III.

Recovery of Uranium from Seawater by Column Method

The recovery of uranium from seawater was carried out by means of column operation. The wet resin (1.5 cm³) was treated with 3% NaCl solution for 24 h at room temperature and packed in glass column (1.0 cm in diameter). Natural seawater (20 dm³) was passed through the column at a space velocity (SV) of 300 h⁻¹ (down-flow) or at a SV of 60, 180, and 300 h⁻¹ (up-flow) at 28–30°C. The uranium adsorbed on the resins was eluted by passing 10 bed volume of a 0.5 mol · dm⁻³ sulfuric acid solution through the column at a SV of 3 h⁻¹. The uranium in eluate was determined spectrophotometrically with arsenazo III.

On a large scale, 200 cm³ of wet resin treated with 3% NaCl solution for 24 h after alkali treatment, was packed in plastic column (65 mm in diameter). The resin was contacted with natural seawater for 98 days. At several days interval, 3 cm³ of resin was collected from the column and the uranium adsorbed on the resins was calculated from the amount of uranium eluted with 1 mol · dm⁻³ sulfuric acid solution.

RESULTS AND DISCUSSION

Preparation and Properties of RNMH, RNEH, RNBH, RNOH, RNMMH, RNMEH, RNMBH

We have reported in our previous paper¹⁷ that the chelating resins containing amidoxime groups with various pore structures were prepared from

TABLE I
Synthesis of Macroreticular AN-DVB-Alkyl Acrylate or Methacrylate Copolymer Beads^a

Copolymer abbreviation	Copolymerized alkylacrylate or alkylmethacrylate	Elementary analysis			Acrylonitrile in copolymer (mmol/g)
		H(%)	C(%)	N(%)	
RN	NON	6.53	75.07	16.70	11.9
RNM	MA	6.69	73.48	14.52	10.4
RNE	EA	6.84	72.82	13.87	9.1
RNB	BA	7.04	74.47	13.12	9.4
RNO	OA	6.92	74.10	12.26	8.8
RNMM	MMA	7.00	74.93	9.99	7.1
RNEM	EMA	7.29	76.12	9.17	6.6
RNBMM	BMA	7.77	75.64	8.48	6.1

^aThese copolymers were synthesized in the presence of 10 mol% of DVB and 10 mol% of alkyl acrylate or methacrylate.

polyacrylonitrile crosslinked with several crosslinking reagents, and the resins prepared with the hydrophilic crosslinking reagent such as tetraethyleneglycol dimethacrylate exhibited the high adsorption ability for uranium because of the increase of hydrophilicity by the formation of acidic groups, whereas these resins were defined by low chemical and physical stability. Accordingly, the copolymerization of AN, DVB, and alkyl acrylate or alkyl methacrylate is expected to produce the very rigid macroporous resins and form such acidic groups as hydroxamic acid and carboxylic groups in addition to amidoxime groups during the reaction of the copolymer beads with hydroxylamine. The copolymer beads of AN and either alkyl acrylate or alkyl methacrylate were prepared with 10 mol% of DVB as crosslinking reagent and toluene (80 vol% per monomer) as diluent. MA, EA, BA, OA, MMA, EMA, and BMA (10 mol%) were used as alkyl acrylate and methacrylate. The results of elemental analysis of these copolymer beads are shown in Table I. The content of the

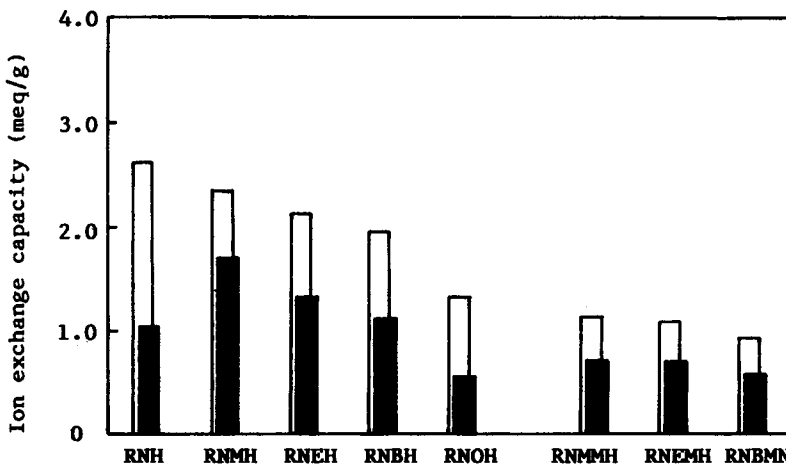


Fig. 1. Effect of alkyl acrylate or methacrylate copolymerized on the ion exchange capacity: (□) anion exchange capacity; (■) cation exchange capacity.

nitrile group in the copolymer beads was calculated from the N content. The anion exchange capacity of resins prepared by the reaction of the copolymer beads with hydroxylamine is shown in Figure 1. The content of amidoxime group introduced to each resin was evaluated from the anion exchange capacity. RNMH, RNEH, RNBH, and RNOH prepared from AN-DVB-alkyl acrylate copolymer beads gave a higher anion exchange capacity than RNMMH, RNEMH, and RNBMH prepared from AN-DVB-alkyl methacrylate copolymer beads. In the case of resins prepared with alkyl acrylate, the amidoxime groups content decreased in order of RNMH, RNEH, RNBH, and RNOH. This tendency corresponded to that of N content of copolymer beads except RNOH. RNMH and RNEH gave a higher cation exchange capacity than that of the resin (RNH) prepared from AN-DVB copolymer beads because of the acidic groups such as hydroxamic acid and carboxylic groups formed by the reaction of acrylate groups with hydroxylamine. These ion exchange capacities did not change with the alkali treatment.

In order to examine the adsorption ability of these resins for uranium in natural seawater, 20 dm³ of seawater was passed through a column packed with 1.5 cm³ of the resins at the high flow rate of SV of 300 h⁻¹ (down-flow) for better evaluation. In the case of the resins prepared from AN-DVB-alkyl acrylates, the recovery of uranium decreased in order of RNMH, RNEH, RNBH, and RNOH. On the other hand, RNMMH, RNEMH, and RNBMH gave low recovery of uranium (Fig. 2). This tendency depended on the hydrophilicity and pore structure of the resins rather than the content of amidoxime groups. Since the recovery of uranium of all resins increased by the alkali treatment, it was found that the use of alkyl acrylate or alkyl methacrylate contributed to increasing the adsorption ability for uranium.

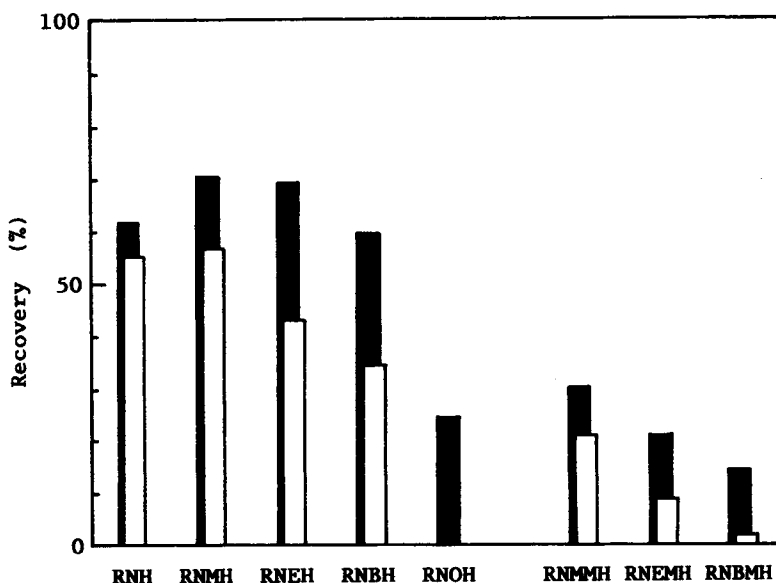


Fig. 2. Recovery of uranium from seawater by column method (down-flow): loading, seawater 20 dm³, SV 300 h⁻¹; temp. 25°C; elution: 0.5 mol · dm⁻³ H₂SO₄ 10 dm³/dm³-R, SV 3 h⁻¹; resin 1.5 cm³ (wet volume); (□) nontreated resin; (■) alkali-treated resin.

TABLE II
Synthesis of RNM

RNM		Elementary analysis			Acrylonitrile in RNM (mmol/g)
DVB (mol%)	MA	H(%)	C(%)	N(%)	
6	0	6.21	72.36	19.75	14.1
6	5	6.32	71.66	18.51	13.2
6	10	6.50	71.77	17.32	12.4
6	20	6.54	69.18	14.69	10.5
6	30	6.76	68.21	11.76	8.4
6	40	6.86	67.39	9.10	6.5
6	50	6.93	66.73	6.69	4.8
10	0	6.39	75.10	16.42	11.7
10	5	6.56	74.30	15.45	11.0
10	10	6.64	73.46	14.24	10.2
10	20	6.63	72.63	11.65	8.3
10	30	6.90	73.15	10.43	7.5
10	40	6.89	70.27	7.20	5.1
10	50	7.00	69.71	5.17	3.7
13	0	6.83	77.03	14.00	10.0
13	5	6.89	76.20	13.01	9.3
13	10	7.00	75.43	11.98	8.6
13	20	6.93	74.36	9.70	6.9
13	30	7.11	73.50	7.66	5.5
13	40	7.15	72.58	5.84	4.2
13	50	7.29	71.62	4.20	3.0

This increase is attributed to the favorable pore structure (micropore) formed by the swelling based on the dissociation of acidic groups such as hydroxamic acid and carboxylic groups. From the results of this screening test, it was suggested that the adsorption ability for uranium of the resins prepared from AN-DVB-alkyl acrylate or alkyl methacrylate was improved by means of alkali treatment, and RNMH especially indicated higher adsorption ability for uranium than RNH. In order to investigate the influence of copolymerized MA in more detail, the preparation of RNMH from the copolymer beads with the various compositions of MA, DVB, and AN was planned.

The Properties of RNMH. First, the effect of crosslinking and acidic groups on the properties of RNMH was investigated by varying the amount of DVB and MA copolymerized. AN-MA-DVB copolymer beads (RNM) were prepared with 6, 10, and 13 mol% of DVB (abbreviated as RNM6, RNM10, and RNM13). N content of RNM was decreased with an increase in the amount of MA or DVB as shown in Table II. The anion and cation exchange capacity of various RNMH prepared by the reaction of the RNM with hydroxylamine are shown in Figure 3. In the series of RNMH with the same degree of crosslinking, the anion exchange capacity decreased with an increase in the amount of MA, whereas the cation exchange capacity showed a tendency to increase with an increase in the amount of copolymerized MA. These changes can be easily explained by the decrease of AN content in

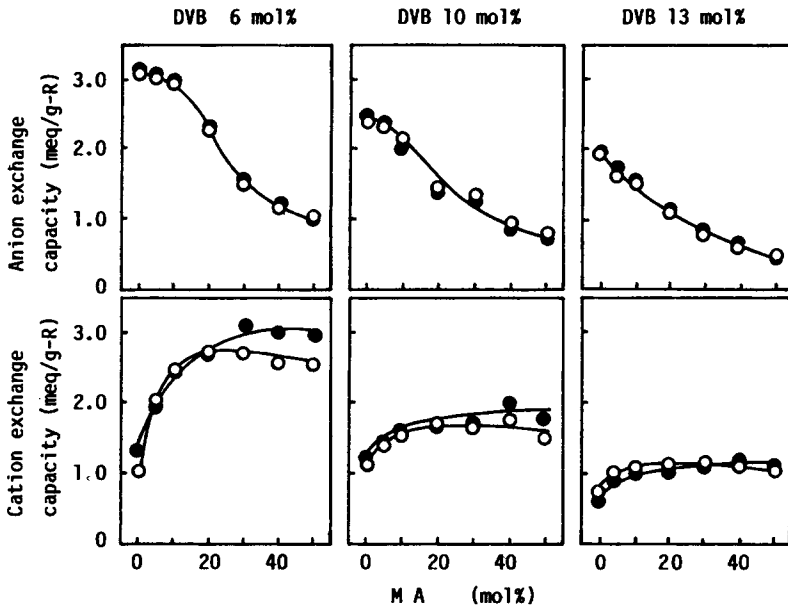


Fig. 3. Effect of DVB and MA on the ion exchange capacity: (○) nontreated resin; (●) alkali-treated resin.

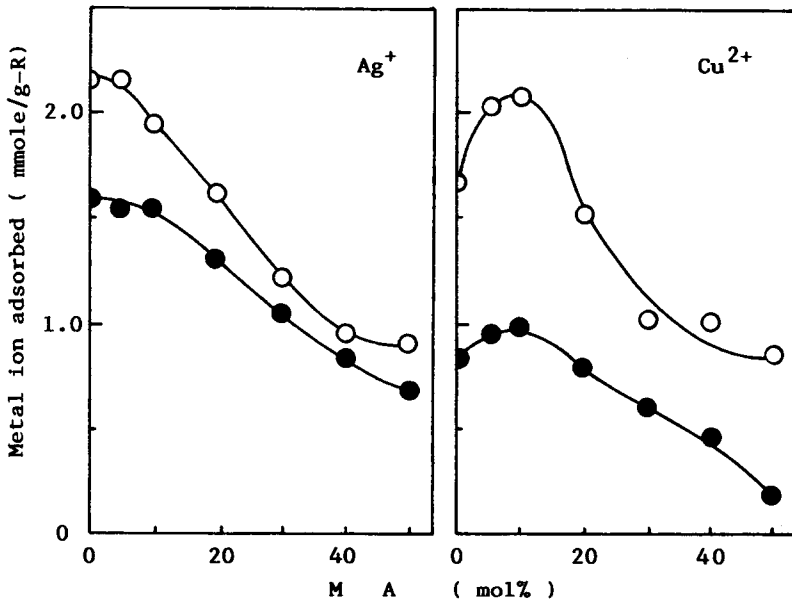


Fig. 4. Effect of MA copolymerized on the metal ions adsorbed: resin 0.125 g (RNMH6); metal ion solution 50 cm³ (0.01M); shaking 30°C, 24 h; initial pH; (●) 3, (○) 5 (the difference between initial and final pH was within 0.5).

copolymer beads and the formation of the acidic groups such as hydroxamic acid and carboxylic groups based on the increase of copolymerized MA. Changes of anion and cation exchange capacity after alkali treatment are also shown in Figure 3. Since the anion exchange capacity was not changed by alkali treatment, the amidoxime groups were found to be hardly hydrolyzed by a weak alkaline solution. On the other hand, increase of cation exchange capacity by means of alkali treatment was observed in the RNMH6 and RNMH10 prepared from the copolymer beads with the high content of MA. This increase was considered to be based on the alkaline hydrolysis of esters. The introduction of the functional groups, in general, decreases with an increase in the degree of crosslinking, but the chemical and physical stability increase. In this case, the increase of cation exchange capacity by alkali treatment decreased with an increase of the crosslinking degree.

The adsorption capacity for Ag^+ and Cu^{2+} was measured with RNMH6 which has the highest anion and cation exchange capacity. As shown in Figure 4, it was found that the effect of copolymerized MA on the adsorption of Ag^+ and Cu^{2+} was different, and the adsorption of these metal ions was also affected by pH of metal ion solution. The difference of the functional groups introduced into the resin reflected the amount of Ag^+ and Cu^{2+} adsorbed on

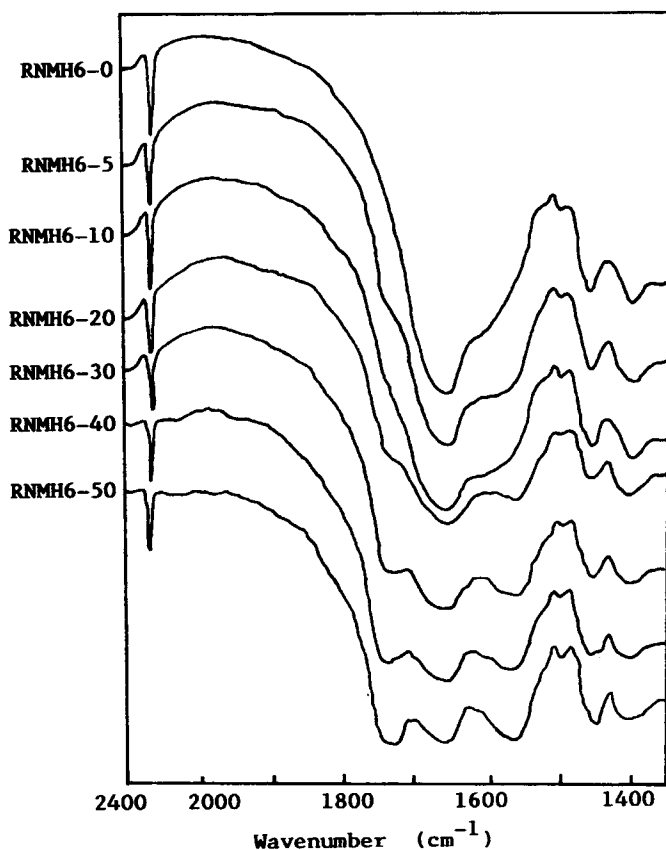


Fig. 5. IR spectra of RNMH6.

TABLE III
Effect of MA and DVB on specific surface area

MA (mol%)	Specific surface area (m ² /g)					
	RNMH6		RNMH10		RNMH13	
	non ^a	alkali ^b	non ^a	alkali ^b	non ^a	alkali ^b
0	29.7	36.1	50.9	54.3	57.6	72.6
5	26.5	35.2	41.7	51.3	57.9	73.2
10	21.6	32.5	41.4	46.8	58.0	71.6
20	12.4	0.0	42.1	11.7	63.8	58.1
30	14.7	0.0	65.5	20.2	70.2	35.3
40	24.3	0.1	70.2	0.5	77.7	36.9
50	57.7	0.0	86.2	0.0	75.6	27.9

^a Nontreated resin.

^b Alkali-treated resin.

RNMH6. The amount of Ag⁺ adsorbed from a solution adjusted at pH 3 tended to decrease with an increase in copolymerized MA. This tendency agreed very closely with that of anion exchange capacity. These results suggested that only amidoxime groups of RNMH participate in the adsorption of Ag⁺ at pH 3. On the other hand, the adsorption of Cu²⁺ from a solution at pH 3 or 5 did not correspond to the amidoxime content. This fact indicated that the adsorption of Cu²⁺ was based on the chelation of Cu²⁺ with the amidoxime groups and hydroxamic groups at pH 3, and with the carboxylic groups in addition to above functional groups at pH 5. The formation of the carboxylic groups by the increase of copolymerized MA could be recognized from the infrared spectrum which exhibited the characteristic adsorption of carboxylate groups at 1560 cm⁻¹ as shown in Figure 5. However, it was difficult to distinguish clearly between amidoxime group and hydroxamic acid group from the infrared spectrum.

The specific surface areas of RNMH are shown in Table III. The effect of MA and DVB copolymerized on the physical pore structure (macropore) was evaluated from the results. Macroporous structures of resins are characterized by having large specific surface areas. From this viewpoint, it is found that the RNMH (RNMH13) prepared with 13 mol% of DVB has the macropore. On the other hand, the specific surface area of the RNMH (RNMH6) prepared with 6 mol% of DVB decreased remarkably with alkali treatment with an increase in the amount of copolymerized MA. In particular, surface area of RNMH6, which was prepared from copolymer beads with MA in the range of 20 to 50 mol%, could not be measured. The change of specific surface area by alkali treatment decreased with an increase in the degree of crosslinking. These results indicate that RNMH13 has the higher physical stability than RNMH6. However, it is necessary to form not only macropore but also micropore in order to effectively recover uranium in seawater. Although it is difficult to evaluate the formation of micropore, the measurement of swelling ratio could help to estimate the formation in the case of the RNH prepared with the hydrophilic crosslinking reagents.⁶ Therefore, dry and wet volume of

TABLE IV
Effect of MA and DVB on the Degree of Swelling

MA (mol%)	RNMH6					RNMH10					RNMH13				
	V1	V2	V3	V2/V1	V3/V1	V1	V2	V3	V2/V1	V3/V1	V1	V2	V3	V2/V1	V3/V1
0	2.0	2.7	2.9	1.3	1.4	1.9	2.6	2.6	1.4	1.4	2.2	2.6	2.6	1.2	1.2
5	2.0	2.6	2.9	1.3	1.5	1.9	2.5	2.6	1.3	1.4	2.0	2.5	2.6	1.2	1.3
10	1.9	2.5	3.1	1.3	1.6	1.9	2.5	2.6	1.3	1.4	2.2	2.5	2.6	1.1	1.2
20	1.7	2.1	3.9	1.3	2.3	1.8	2.4	2.7	1.3	1.5	2.0	2.4	2.8	1.2	1.4
30	1.7	2.1	3.8	1.3	2.2	1.9	2.7	2.8	1.4	1.5	2.0	2.3	2.6	1.2	1.3
40	1.9	2.3	3.8	1.2	2.0	2.1	2.4	2.9	1.2	1.4	2.0	2.3	2.6	1.2	1.3
50	2.4	3.0	3.8	1.2	1.6	2.0	2.4	2.9	1.2	1.4	1.9	2.0	2.4	1.1	1.3

V1: Dry volume of nontreated resin (cm^3/g).

V2: Wet volume of nontreated resin (cm^3/g).

V3: Wet volume of alkali-treated resin (cm^3/g).

V2/V1, V3/V1: Swelling ratio.

RNMH and swelling ratio are listed in Table IV. It was found that RNMH6 after alkali treatment gave higher wet volume (V3) than RNMH10 or RNMH13. In particular, V3 of RNMH6 prepared with 20–50 mol% of MA was in the range 3.7–3.8 cm^3/g . V3 of the RNMH10 or RNMH13 was less than 3.0 cm^3/g . High V3 of RNMH6 with high MA content was based on the low degree of crosslinking and the increase of hydrophilicity by the formation of acidic groups. Furthermore, effects of these pore characteristics on the adsorption ability was investigated.

First, the adsorption ability of above resins was examined by batch method. The dry resin (0.1 g) was shaken with spiked seawater (U concentration of 10 $\text{mg} \cdot \text{dm}^{-3}$) at 30°C for 1 h. The adsorption of uranium calculated from the amount of uranium remaining in the supernatant is shown in Figure 6. Next, the investigation of adsorption ability for uranium in natural seawater was carried out by column method the same as a screening test. The results obtained are shown in Figures 6 and 7. There was hardly any difference in the tendency for the adsorption of uranium from spiked seawater by batch method and the recovery of uranium from seawater by column method. It was found that the recovery of uranium was not directly proportional to the content of amidoxime groups, and depended on the amount of DVB and MA

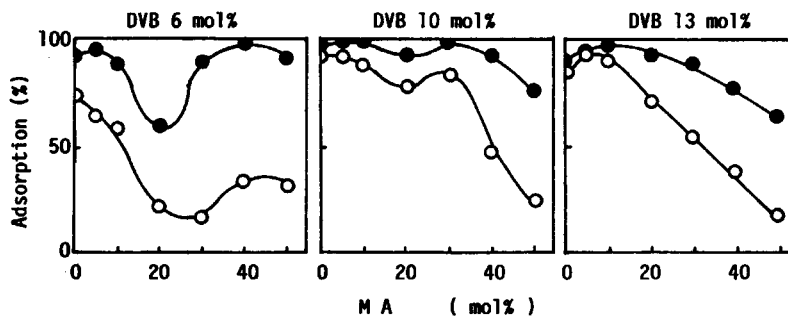


Fig. 6. Effect of DVB and MA on the adsorption of uranium: seawater 25 cm^3 (250 μg of uranium was added); shaking 30°C, 1 h; resin 0.1 g; (○) nontreated resin; (●) alkali-treated resin.

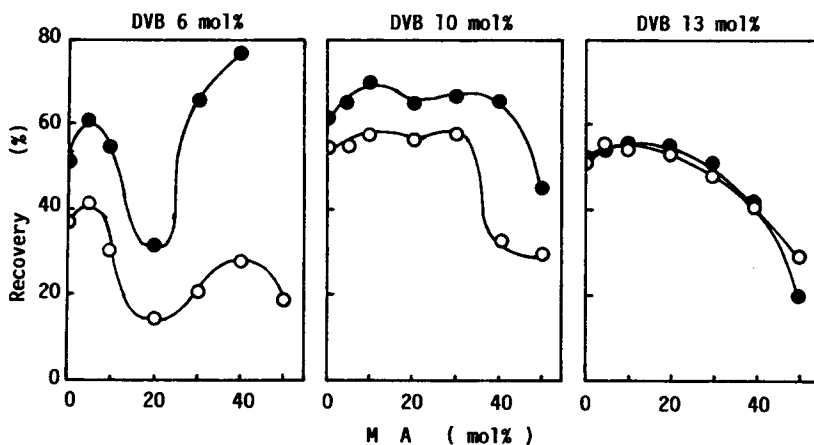


Fig. 7. Recovery of uranium from seawater by column method (down-flow): loading, seawater 20 dm^3 , SV 300 h^{-1} , temp. 25°C ; elution $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$ $10 \text{ dm}^3/\text{dm}^3\text{-R}$ (SV 3 h^{-1}); resin 1.5 cm^3 ; (○) nontreated resin; (●) alkali-treated resin.

copolymerized, namely the crosslinking and the acidic groups formed. In the case of RNMH6 (RNMH6-20) prepared with 20 mol% of MA, remarkable decrease of adsorption ability was observed which was reproducible. Although all RNMH after alkali treatment showed higher adsorption ability than RNMH before alkali treatment, the adsorption ability of RNMH6-20 was lower than other resins. The unique dependence of uranium adsorption ability on the amount of copolymerized MA may be explained by a little formation of both macropore and micropore. In fact, when the RNMH6-20 was treated with a stronger alkaline solution, the adsorption ability for uranium increased. These results suggest that the formation of micropore greatly influences the increase of uranium adsorption ability for the resins with low degrees of crosslinking. As the degree of crosslinking was higher, the variation of uranium adsorption ability by alkali treatment decreased, due to the formation of micropore inhibition by crosslinking. But physical stability increased with an increase in the degree of crosslinking. It is concluded that RNMH10 exhibited the highest adsorption ability of the series of RNMH by the formation of effective macropore and micropore for the uranium recovery. Therefore,

TABLE V
The Pore Structure of RNMH

Resin	Pore volume (cm^3/g)	Pore radius (\AA)	
		Peak	Average
RNMH10-0	0.512	156	190
RNMH10-5	0.493	178	203
RNMH10-10	0.453	161	179
RNMH10-20	0.469	139	172
RNMH10-30	0.587	104	145
RNMH10-40	0.436	125	136
RNMH10-50	0.381	99	124

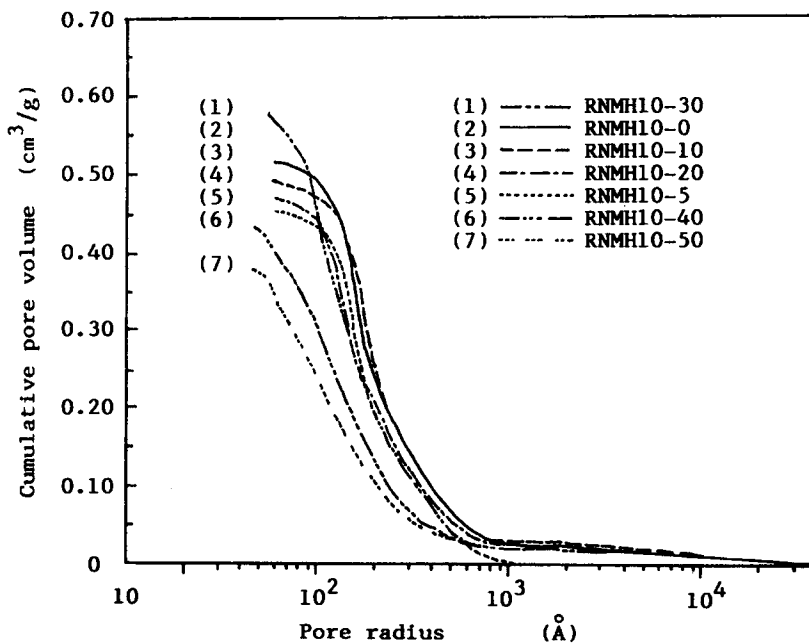


Fig. 8. Pore size distribution curves of RNMH10.

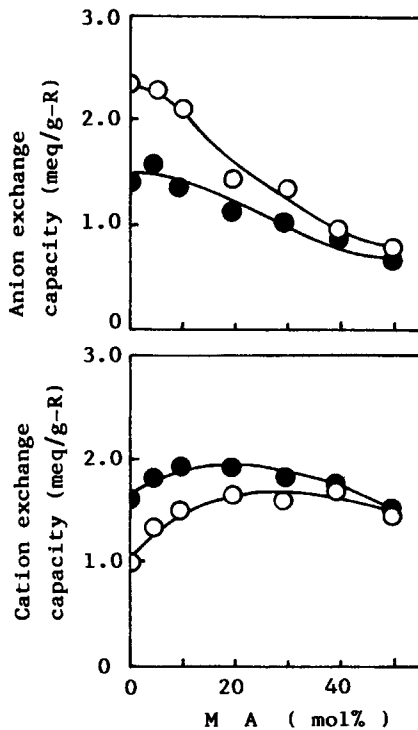


Fig. 9. Effect of MA copolymerized on the ion exchange capacity after acid treatment; (○) nontreated resin; (●) acid-treated resin.

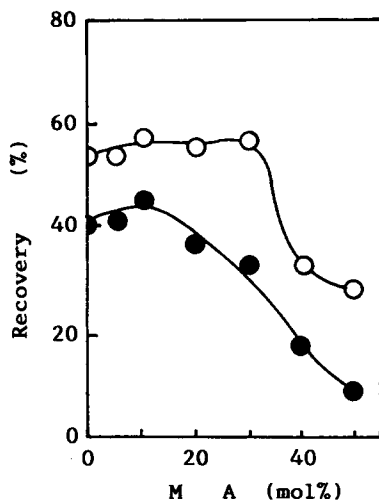


Fig. 10. Recovery of uranium from seawater with RNMH10 after acid treatment: (○) nontreated resin; (●) acid-treated resin.

macropore of RNMH10, in detail, was characterized by the measurement of pore volume, peak pore radius, average pore radius, and pore size distribution. As shown in Table V and Figure 8, it was ascertained that all RNMH10 (RNMH10-0-50) prepared with 0-50 mol% of MA have the macroporous structure. In particular, the macropore of RNMH10-0, 5, 10, and 20 hardly exhibited the change made by the amount of copolymerized MA. However, the pore volume and peak pore radius of RNMH10-30, 40 and 50 showed the tendency to decrease in that order. This tendency corresponded to that of the uranium adsorption ability of the RNMH without alkali treatment.

The Durability of RNMH. From a practical viewpoint, it is desirable that the adsorbent for uranium in seawater possess high chemical and physical stability because of long-term recycling procedures. In order to examine the chemical stability of RNMH against the acidic solution, the series of RNMH10 were treated with $1 \text{ mol} \cdot \text{dm}^{-3}$ hydrochloric acid solution at 60°C for 5 h (abbreviated as acid treatment). Chemical changes during acid treatment were evaluated by measurement of the ion exchange capacity. The results are showed in Figure 9. The anion exchange capacity was decreased and cation exchange capacity was increased by acid treatment. These changes of anion exchange capacity indicate that the amidoxime group was hydrolyzed to change the acidic groups such as hydroxamic acid and carboxylic groups. This hydrolysis of amidoxime groups decreased with an increase of copolymerized MA. These RNMH10, after acid treatment, were applied to recovery of uranium from seawater. As shown in Figure 10, the RNMH (RNMH10-5 and 10) prepared with 5 and 10 mol% of MA gave recovery of above 40%. As MA content increased further, recovery of uranium decreased. This decrease is perhaps due to the changes of pore structure rather than the decrease of amidoxime groups by acid treatment because the decrease of the uranium recovery did not correspond to that of amidoxime content. From the fact that RNMH with the many acidic groups showed the lower recovery of uranium, it

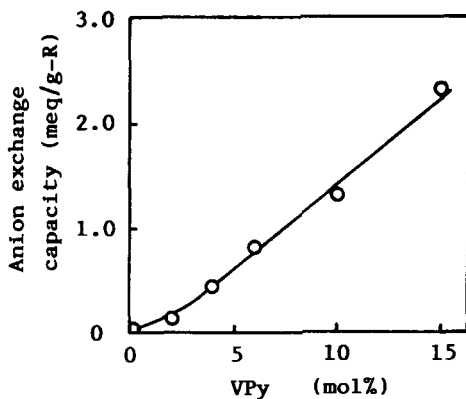


Fig. 11. Effect of VPy copolymerized on the anion exchange capacity of RNPy.

was speculated that the formation of effective micropore for uranium recovery was depressed by acid treatment.

The Properties of RNPyH. As described above, the introduction of acidic groups enhanced the hydrophilicity of the resin and resulted in increased adsorption ability for uranium. Next, the influence of the introduction of basic groups on the adsorption ability for uranium was investigated. Vinylpyridine (VPy) was chosen as the basic component to be copolymerized. Although AN-DVB copolymer beads (RN) or AN-DVB-MA copolymer beads (RNM) do not contain the ion exchange groups, AN-DVB-VPy copolymer beads (RNPy), which have the pyridine residues as a weak basic groups, gave the anion exchange capacity (Fig. 11). The anion exchange capacity increased with an

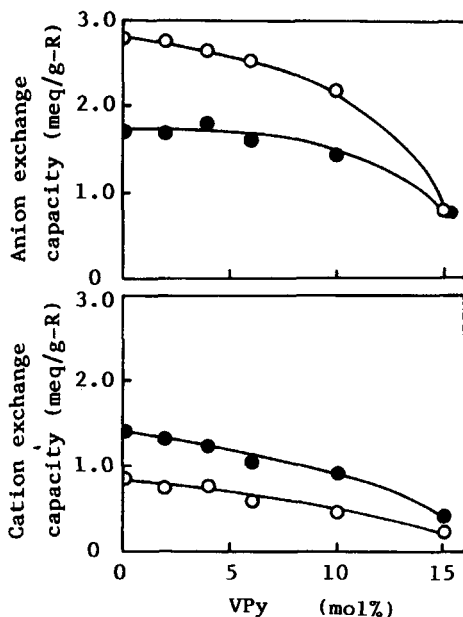


Fig. 12. Effect of VPy copolymerized on the ion exchange capacity: (○) nontreated resin; (●) acid-treated resin.

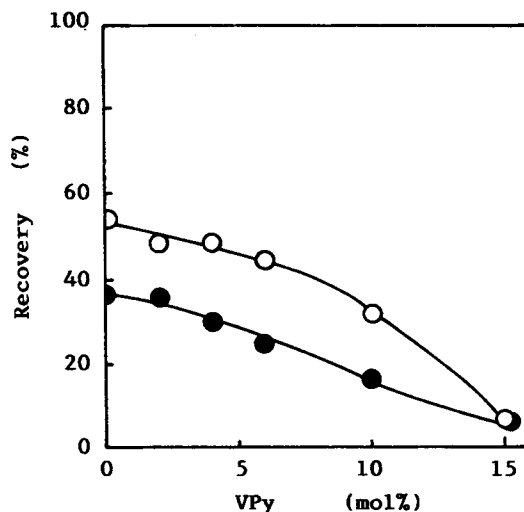


Fig. 13. Effect of VPy copolymerized on the recovery of uranium by column method (down-flow): loading, seawater 20 dm^3 , SV 300 h^{-1} , temp. 28°C ; elution $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$ $10 \text{ dm}^3/\text{dm}^3\text{-R}$ (SV 3 h^{-1}); resin 1.5 cm^3 ; (○) nontreated resin; (●) acid treated resin.

increase in the amount of copolymerized VPy. The anion exchange capacity (Fig. 12), was determined by subtracting the anion exchange capacity of RNP_y from that of RNP_yH, and the results correspond to the content of amidoxime groups formed on the RNP_yH. Next, RNP_yH was treated with 1 M hydrochloric acid at 60°C for 5 h, and the anion exchange capacity determined with the same method are also shown in Figure 12. The ion exchange capacity had a tendency to decrease with an increase in the amount of copolymerized VPy, the same as that of RNMH10, whereas it was found that the recovery of uranium from seawater decreased linearly with increased copolymerized VPy (Fig. 13). In spite of the fact that the RNP_yH10-15 had about 1 mmol/g resin of anion exchange capacity, it was difficult to recover the uranium from seawater. Swelling ratio, specific surface area, pore char-

TABLE VI
Specific Surface Area and Swelling Ratio of RNP_yH

DVB	VPy (mol%)	Specific surface area (m^2/g)		V1	V2	V3	Swelling ratio	
		RNP _y H	RNP _y H*				V2/V1	V3/V1
10	0	41.9	49.2	1.8	2.5	2.6	1.4	1.4
10	2	42.5	49.4	1.8	2.5	2.6	1.4	1.4
10	4	38.6	47.1	1.9	2.6	2.6	1.4	1.4
10	6	43.7	49.6	1.8	2.6	2.7	1.4	1.5
10	10	40.8	44.3	2.0	2.6	2.7	1.3	1.4
10	15	44.6	48.1	2.3	2.9	2.9	1.3	1.3

RNP_yH*: acid-treated resin.

V1: dry volume.

V2: wet volume.

V3: acid wet volume.

TABLE VII
 Pore Structure of RNPyH

DVB	RNPyH VPy (mol%)	Pore volume (cm ³ /g)	Pore radius (Å)	
			Peak	Average
10	0	0.388	121	159
10	2	0.405	113	194
10	4	0.391	125	188
10	6	0.420	125	184
10	10	0.439	134	205
10	15	0.528	150	229

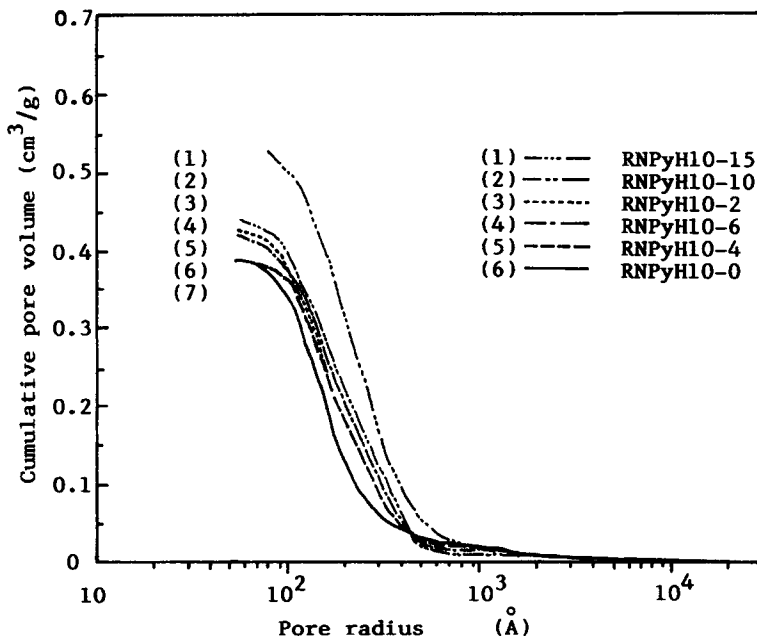


Fig. 14. Pore size distribution of RNPyH.

acteristics, and pore size distribution of RNPyH are listed in Tables VI and VII and Figure 14. Specific surface area did not decrease with the increase of pyridine residue nor by the acid treatment. Pore volume, peak radius, and average pore radius had a tendency to increase with an increase in copolymerized VPy. These results indicate that all RNPyH have the rigid macroporous structure although the remarkable decrease of uranium recovery could not be explained by means of the change of the macropore. On the other hand, although it is not easy to describe quantitatively the micropore formed, the swelling ratio was measured in order to obtain some of this information. These results are also shown in Table VI. Although V_2/V_1 slightly decreased with increased copolymerized VPy, it was impossible to define adequately the alterations of micropore from the measurement of swelling degree. It might be concluded that the decrease of adsorption ability for uranium of RNPyH with high VPy content is based not only on the change of pore structure but also

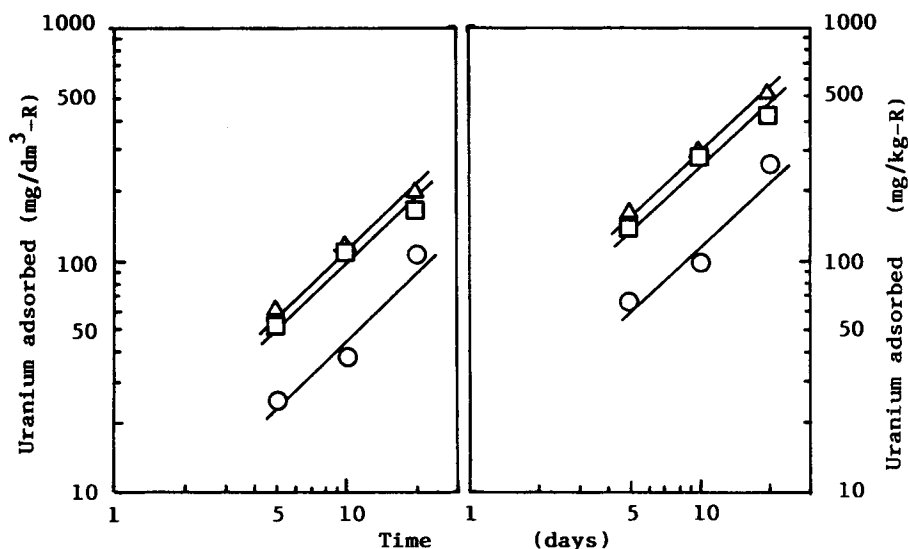


Fig. 15. The recovery of uranium from seawater by column method (up-flow): flow rate; (Δ) SV 300 h^{-1} , (\square) SV 180 h^{-1} , (\circ) SV 60 h^{-1} ; temp. $28\text{--}30^\circ\text{C}$.

the properties of this basic component (pyridine residue). To clarify the influence of the basic group on the adsorption ability, it is necessary to synthesize the resin-containing amidoxime groups and the other basic group, and to characterize those resins in detail.

Applicability of RNMH to the Industrial Uranium Recovery from Seawater

In order to examine the industrial applicability of RNMH10-10, which showed the highest adsorption ability for uranium in this study, the natural seawater was passed through a column packed with the RNMH10-10 by up-flow. In order to investigate the adsorption rate, 1.5 cm^3 of wet resin was packed in a small column (10 mm in diameter), and was contacted with natural seawater during 5, 10, and 20 days at a flow rate of SV 60, 180, and 300 h^{-1} . The uranium adsorbed on the resins was shown in Figure 15. From the data, the adsorption rate of uranium on the RNMH10-10 was evaluated in the initial stage. When the flow rate increased from SV 60 to 180 h^{-1} , the uranium adsorbed on the RNMH10-10 greatly increased. After seawater was passed through the column at SV 180 h^{-1} for 10 days, the amount of uranium adsorbed on the resin was about $100 \text{ mg/dm}^3\text{-R}$ and 260 mg/kg-R . This value means that 80% of uranium in seawater was recovered. When seawater was passed through the column at SV 300 h^{-1} , the uranium adsorbed exhibited a small increase. This high adsorption rate of uranium on RNMH10-10 indicates that this resin has sufficient applicability to the industrial recovery of uranium from seawater.

On a large scale, seawater (uranium concentration: $2.8\text{--}3.1 \mu\text{g} \cdot \text{dm}^{-3}$) was passed through the column (65 mm in a diameter) packed with a 200 cm^3 of wet resin at a flow rate of SV 120 h^{-1} . This experiment was carried out during

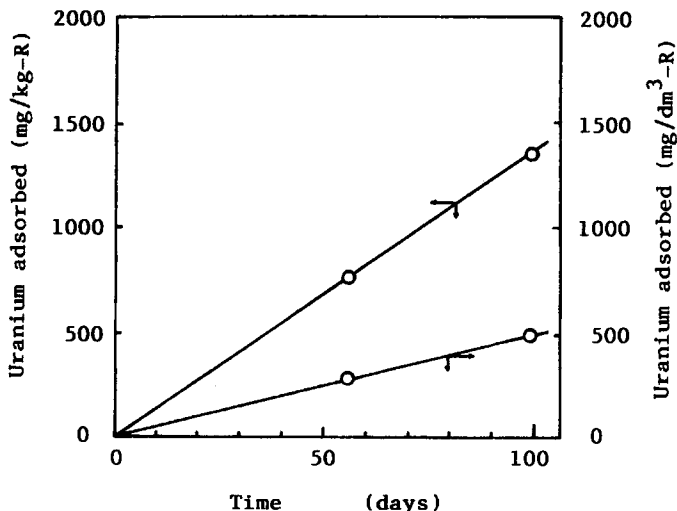


Fig. 16. Recovery of uranium from seawater during long period: flow rate SV 120 h^{-1} (April–July).

from April to July. The time course of uranium adsorption is shown in Figure 16. After a loading period of 98 days the uranium adsorbed on RNMH10-10 reached 1270 mg/kg-R and $495 \text{ mg/dm}^3\text{-R}$. If seawater is passed through the column at high flow rate, the amount of uranium adsorbed would be much increased.

CONCLUSION

The macroporous chelating resins containing amidoxime groups were prepared from AN-DVB-alkyl acrylate, alkyl methacrylate, or vinyl pyridine copolymer beads. The copolymerization of alkyl acrylate, alkyl methacrylate, or vinyl pyridine brought about the acidic or basic groups in the resins and influenced the formation of pore structure. It was concluded that the formation of macropore and micropore was important in order to improve the adsorption ability for uranium. Introduction of acidic groups was efficient to form the micropore. The RNMH prepared from AN-DVB(10 mol%)-MA(10 mol%) possessed the high physical stability and high adsorption rate based on the macropore and micropore.

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