

Recovery of Uranium from Seawater. XII. Preparation and Characterization of Lightly Crosslinked Highly Porous Chelating Resins Containing Amidoxime Groups

HIROAKI EGAWA,* NALAN KABAY, TAKETOMI SHUTO, and AKINORI JYO

Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860, Japan

SYNOPSIS

A number of lightly cross-linked poly(acrylonitrile-co-divinylbenzene) beads (RN-5) have been synthesized by suspension polymerization. The use of solvating diluents such as chloroform, dichloroethane, and tetrachloroethane resulted in copolymer beads having highly porous structures. The chelating resins containing amidoxime as a functional group (RNH-5) have been prepared by the reaction of copolymer beads with 3% hydroxylamine in methanol. A detailed analysis is made of the pore structure of lightly cross-linked copolymers of acrylonitrile-divinylbenzene and their amidoxime derivatives in the anhydrous state including pore-size distribution, specific surface area, and pore structure in the aqueous media by means of gel permeation chromatography (GPC). A set of experiments have been performed to ascertain the potential of the resins for the adsorption of uranium from seawater. Because of their modified pore structures, the chelating resins exhibited a marked adsorption rate for uranium in seawater as high as $23 \mu\text{g}$ of U/cm^3 of resin/day without alkaline treatment.

INTRODUCTION

Uranium is an element of considerable technological importance because of its role in the nuclear fuel cycle. During the last two decades, further research has been directed to recovering uranium from non-conventional resources. Despite the low concentration of uranium in seawater, at a level of 3 parts in 10^9 , special emphasis has been placed on the recovery of uranium from seawater.¹⁻³

The chelating resins containing amidoxime groups have found wide application in the recovery of uranium from seawater. We prepared a number of chelating resins containing amidoxime as a functional group and investigated their adsorption capacities for uranium in seawater.⁴⁻¹¹ Elsewhere,¹² we described the use of macroreticular chelating resins containing phosphino and/or phosphano groups for uranium uptake from seawater. Additionally, the same resins were explored for the secondary con-

centration process of uranium from acidic eluates.^{13,14}

Hollow-fiber adsorbents containing amidoxime groups were also employed for the recovery of uranium from seawater. Their adsorption capacities were significantly enhanced by the alkaline treatment.¹⁵

More recently, we have described lightly cross-linked porous chelating resins containing amidoxime groups prepared from poly(acrylonitrile-co-divinylbenzene) beads synthesized with a divinylbenzene content of 5 mol % and in the presence of toluene as a porogen. After a 1.0 mol dm^{-3} NaOH solution was brought into contact with chelating resins, the ability to take up uranium became highly important.¹⁶

The modification of polymer networks by a porogenic agent has long been known to produce significant changes in their properties.¹⁷⁻²¹ The relationship between the physical structure and the performance of chelating resins led us to tackle the question of producing chelating resins having a highly porous structure. This paper embodies the effect of various porogenic agents such as tetrachlo-

* To whom correspondence should be addressed.

roethane, dichloroethane, and chloroform on the properties of lightly cross-linked copolymers of acrylonitrile-divinylbenzene and their amidoxime derivatives. Beyond that, the recovery of uranium from seawater has been systematically studied using these high-performance adsorbents.

EXPERIMENTAL

Preparation of Lightly Cross-Linked Highly Porous Chelating Resins (RNH-5)

Acrylonitrile and divinylbenzene (55%) were purified as previously described.⁸ Tetrachloroethane, dichloroethane, chloroform, *o*-dichlorobenzene, toluene, and methyl isobutyl ketone were G.P.R. grades, used without further purification. As a polymerization initiator, azobisisobutyronitrile (AIBN) purchased commercially was purified by recrystallization from ethanol prior to use. The copolymer beads of acrylonitrile and divinylbenzene (RN-5) were synthesized by suspension polymerization according to a previously reported procedure.⁸ All the resins prepared in the presence of tetrachloroethane, dichloroethane, chloroform, *o*-dichlorobenzene, toluene, and methyl isobutyl ketone were 5 mol % cross-linked.

For the preparation of polyacrylamidoxime resins (RNH-5), beads in the diameter range of 32–60 mesh were selected. The insertion of amidoxime groups into the polymeric matrix was carried out by the reaction of poly(acrylonitrile-*co*-divinylbenzene) beads with 3% hydroxylamine in methanol at 80°C for 2 h. Details of the materials and the procedures have been described elsewhere.⁸ The alkaline treatment was performed using a 1.0 mol dm⁻³ NaOH solution at 30°C for 72 h. The ion-exchange capacities of the resins were determined by the usual methods.⁸

The designations used in this paper are interpreted as follows:

Example 1: RN-5 indicates an acrylonitrile-divinylbenzene copolymer with a nominal cross-link ratio of 5 mol %. Example 2: RNH-5 indicates an amidoxime derivative of RN-5.

Characterization of Pore Structure

The pore volume and the pore radius were obtained using a Carlo-Erba mercury porosimeter (Model 1520). The specific surface area was measured on a Yuasa surface area apparatus, following the BET method.

The pore structure in the swollen state was characterized by gel permeation chromatography (GPC) using a Jasco 880-PU Intelligent HPLC pump and a Shodex refractive index detector (Model SE-61). The calibration curves were obtained by plotting the average molecular weights (\overline{M}_n) against the peak elution volumes in water of standard samples of dextrans (T10, T40, T70, T500, and T2000; Pharmacia Co.), maltopentaose, maltotriose (Sigma Co.), ribose (Kohjin Co.), and D₂O (Nakarai Co.).

Analysis and Spectroscopy

Elemental analyses (C, H, N) were performed on a Yanaco CHN Corder (Model MT-3) instrument. IR spectra were recorded in KBr pellets on a Jasco J-0055 spectrophotometer (400–4000 cm⁻¹). Solid-state ¹³C-cross-polarization and magic-angle spinning nuclear magnetic resonance (CP-MAS ¹³C-NMR) spectra were recorded on a Varian XL-400 spectrometer at 8 kHz of magic-angle spinning.

Swelling Measurements

About 0.5 g of resin was weighed, W (g); after immersion in deionized water at room temperature for 24 h, the volume of wet resin V (cm³) was measured. The swelling volume V (H₂O) was calculated according to the following equation:

$$\text{Swelling volume} = V/W \text{ (wet-cm}^3\text{/dry-g)}$$

The swelling volume of the alkali-treated resin V (NaOH) was also measured.

Batchwise Adsorption of UO₂²⁺

An amount of 50 mg of resin was immersed in a solution (20 cm³) containing UO₂²⁺ (0.01 mol dm⁻³) as its nitrate at 30°C for 24 h. The amount of UO₂²⁺ adsorbed (i.e., mmol UO₂²⁺/g resin) was calculated from the colorimetric determination of the UO₂²⁺ content of the supernatant using salicylic acid.

Columnar Adsorption of Uranium from Seawater

A glass column (inner diameter 1.0 cm) was packed with wet-settled resin (0.5 g) previously immersed in 3% NaCl solution for 24 h. The seawater (20 dm³) was delivered upflow to the column at a flow rate of 900 cm³ h⁻¹. All the adsorption trials were carried out at 30°C. After the seawater (20 dm³) had passed through the column, the resin was rinsed with deionized water in the column, and then the ad-

sorbed uranium was eluted with 10 bed volumes of 0.5 mol dm⁻³ H₂SO₄ solution at a flow rate of 4.5 cm³ h⁻¹ (downflow). Also, bicarbonate eluants such as NH₄HCO₃ (2.0 mol dm⁻³) and NaHCO₃ (1.0 mol dm⁻³) were used besides H₂SO₄ during the columnar recycling tests. The uranium in the eluate was determined colorimetrically with Arsenazo III and the amount of uranium uptake (i.e., μg U/g R and/or μg U/cm³ R (R: resin)) was calculated.

A larger-scale column operation was performed in a plastic column (inner diameter 6.0 cm) packed with 50 cm³ wet-settled volume of resin immersed in 3% NaCl solution at room temperature for 24 h prior to use.

RESULTS AND DISCUSSION

Syntheses and Characterizations

The suspension polymerization of acrylonitrile and divinylbenzene was carried out in the presence of various organic solvents as porogenic agents, yielding a resin nominally 5% (mol %) cross-linked (RN-5). The use of dichloroethane, tetrachloroethane, chloroform, and *o*-dichlorobenzene as a porogen produced lightly cross-linked copolymer beads having highly porous structures that are different from those obtained using toluene or methyl isobutyl ketone.

The thermodynamic solvent-polymer interaction is well known to affect the physical pore structure and the swelling behavior of polymer networks.¹⁷⁻²² A striking indication of the influence of the solvent upon the polymer network may be seen by inter-

preting the solubility parameter difference of the polymer and the solvent.²³ As can be seen in Table I, a comparatively small difference between the solubility parameter of the selected solvent and that of polyacrylonitrile corresponded to a higher degree of macroporosity, represented by a large specific surface area. Thus, the use of dichloroethane, tetrachloroethane, chloroform, and *o*-dichlorobenzene produced a highly porous network architecture.

A methanolic solution of 3% hydroxylamine was used to functionalize the copolymer beads. The IR spectrum of the resulting resin shows ligand peaks at 3000–3500 cm⁻¹ (broad, N—H and/or O—H stretching vibrations), 1650 cm⁻¹ (C=N stretch vibration), 920 cm⁻¹ (N—O stretch vibration), and 2225 cm⁻¹ (remaining nitrile group) [Fig. 1(A)].

When dichloroethane, tetrachloroethane, chloroform, and *o*-dichlorobenzene were employed as a porogenic agent during the suspension polymerization, the resulting chelating resins bearing amidoxime groups (RNH-5) were highly porous. A comparison of the pore-size distribution curves as a function of porogen is shown in Figure 2.

As summarized in Table I, these highly porous chelating resins were characterized by having a large specific surface area (up to about 31 m² g⁻¹) and a small average pore radius. However, the use of toluene and methyl isobutyl ketone as a porogen resulted in chelating resins that differ significantly in pore structures that are characterized by a relatively small specific surface area and a large average pore radius.

From Table I it can be noticed that the highly porous chelating resins exhibited a higher adsorption

Table I The Characteristics of RNH-5^a

Porogen ^b	S.P. ^c (cal/cm ³) ^{1/2}	SSA ^d (m ² /g)		Pore Volume (cm ³ /g)	Average Pore Radius (Å)	C _a ^e (meq/g)	C _c ^f (meq/g)	UO ₂ ⁺ Adsorbed (mmol/g)
		RN-5	RNH-5					
Toluene	8.9	42.6	22.5	0.800	689	3.15	1.00	0.77
Dichloroethane	9.8	51.8	28.2	0.363	220	3.23	1.02	0.91
Tetrachloroethane	9.8	60.8	31.3	0.289	222	3.45	1.16	0.96
Chloroform	9.4	61.4	28.8	0.366	221	3.45	1.13	0.94
Methyl isobutyl ketone	8.4	36.6	22.4	0.789	593	3.37	1.16	0.81
<i>o</i> -Dichlorobenzene	10.0	42.0	26.9	0.531	338	3.31	1.02	0.94

^a Functionalization: NH₂OH/CN = 0.6 (mol ratio), 80°C, 2 h.

^b 100% (vol %).

^c Solubility parameter (Refs. 24 and 25); S. P. (polyacrylonitrile): 12.75.

^d Specific surface area.

^e Anion-exchange capacity.

^f Cation-exchange capacity.

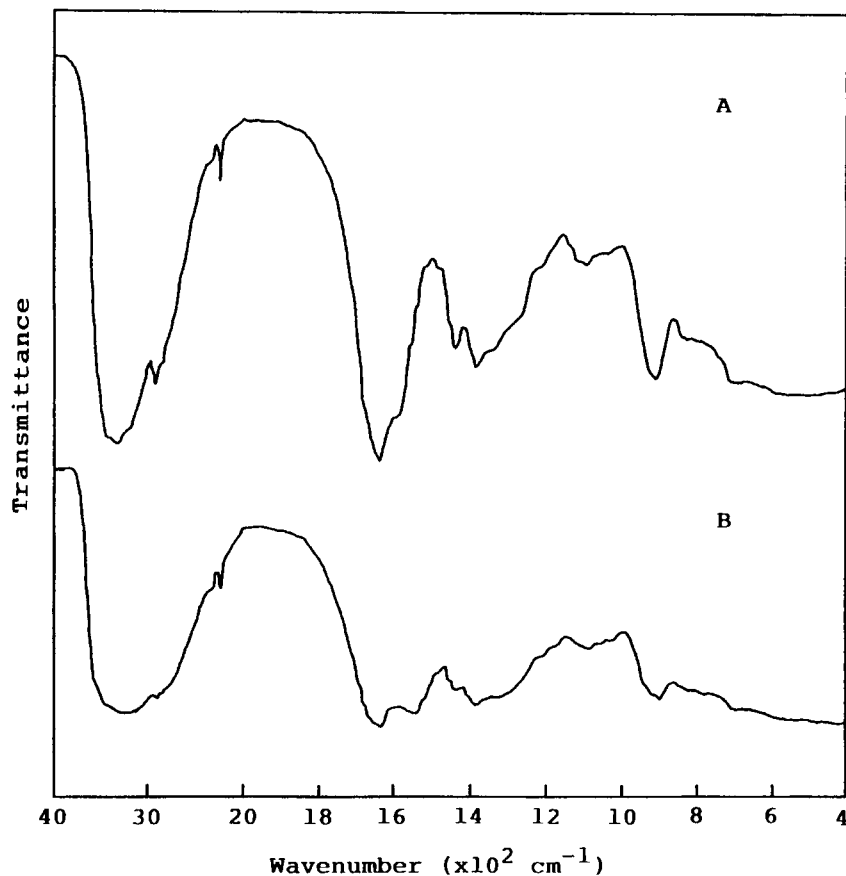


Figure 1 IR spectrum of RNH-5: (A) nontreated resin; (B) alkali-treated resin.

capacity for UO_2^{2+} , although no significant change was observed in both anion- and cation-exchange capacities as a function of porogenic agent.

Resin Performances for Uranium from Seawater

Kunin²⁶ pointed out that a resin of higher swelling can be formed by lowering the degree of cross-linking. According to Kun and Kunin,^{26,27} this modification in resin pore structure results in a higher rate of exchange and higher capacity for ions of high molecular weight.

With this perspective in mind, we explored the potential of our lightly cross-linked highly porous chelating resins for the uptake of uranium from seawater, where it predominantly occurs as a tricarbonate complex ion that is as large as 9.7 Å in diameter.²⁸

These highly porous chelating resins synthesized in the presence of dichloroethane, tetrachloroethane, and chloroform exhibited a much higher adsorption rate than did their less porous analog formed using toluene as a porogen.

Also, the effect of alkaline treatment on the adsorption rate of uranium from seawater was investigated. The resins all gave a higher uranium uptake due to the enhanced diffusion rate caused by the alkaline treatment. The results are summarized in Table II.

From the viewpoint of pore structure in the swollen state, the alkaline treatment greatly enhanced the formation of micropores due to the increased hydrophilicity based on the high swelling. As elucidated in our previous paper,¹⁶ gel permeation chromatography provides further evidence for the presence of micropores in the swollen state. Thus, uranium could easily attain to fixed donating atoms through diffusion in the micropores due to the high swelling.

On the other hand, little definitive work providing insight into the nature of the resulting chemical structure after the alkaline treatment was reported in the literature. Unfortunately, neither elemental analysis nor IR spectra gave distinct information. For comparison, the IR spectrum recorded after the alkaline treatment is shown in Figure 1(B). The

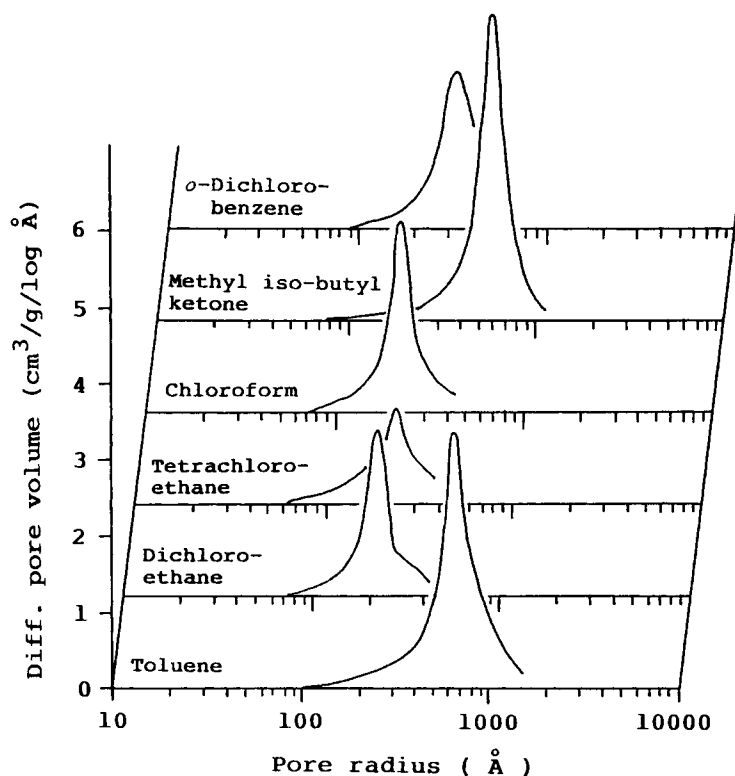


Figure 2 Pore-size distribution curves of RNH-5 as a function of porogenic agent.

alkali-treated RNH-5 displayed an infrared absorption band at 1560 cm^{-1} usually ascribed to the carboxylate group. This was possibly because of the partial hydrolysis of the amidoxime and the remaining nitrile groups by the alkaline treatment. In fact, the characteristic peak corresponding to the nitrile group at 2225 cm^{-1} of the alkali-treated RNH-5 is somewhat smaller than that of the nontreated one, indicating the possible hydrolysis of the re-

maining nitrile group. The amidoxime peak at 920 cm^{-1} (N—O stretch vibration) has become very broad after the alkaline treatment, suggesting the possible conversion of the amidoxime group. However, no further information was found about the resulting chemical structure.

To the best of our knowledge, the effect of alkaline treatment on the chemical structure of fiber adsorbents, first reported in 1990 by Kobuke et al.²⁹ was

Table II Effect of Porogen on the Recovery of Uranium from Seawater

Porogen	Nontreatment				Alkaline Treatment ^e				
	$V(\text{H}_2\text{O})^a$ (cm^3/g)	$V(\text{NaCl})^b$ (cm^3/g)	U Uptake ^c		$V(\text{NaOH})^d$ (cm^3/g)	$V(\text{H}_2\text{O})^a$ (cm^3/g)	$V(\text{NaCl})^b$ (cm^3/g)	U Uptake ^c	
			($\mu\text{g}/\text{g R}$)	($\mu\text{g}/\text{cm}^3\text{ R}$)				($\mu\text{g}/\text{g R}$)	($\mu\text{g}/\text{cm}^3\text{ R}$)
Toluene	3.2	3.2	20.1	6.3	5.4	5.1	4.8	69.2	14.4
Dichloroethane	2.5	2.5	55.4	22.3	4.8	4.7	4.4	75.0	17.0
Tetrachloroethane	2.8	2.7	56.2	20.8	4.9	4.6	4.3	76.8	17.9
Chloroform	2.6	2.6	57.4	22.1	4.9	4.6	4.4	76.7	17.4

^a Volume in H_2O .

^b Volume in 3% NaCl.

^c Resin 0.5 g; seawater 20 dm^3 , flow rate $900\text{ cm}^3/\text{h}$, 30°C .

^d Volume in 1 mol dm^{-3} NaOH.

^e 1 mol dm^{-3} NaOH, 30°C , 72 h.

obtained by ^{13}C -NMR spectroscopy. Recently, we reported that solid-state (CP-MAS) ^{13}C -NMR spectra gave some information on the startling change in the chemical structure of the hollow-fiber adsorbents by the alkaline treatment.¹⁵ At that time, we showed that the amidoxime group seemed to be partially converted to cyclic imidedioxime and carboxylic acid.

In this work, we carried out additional measurements using solid-state (CP-MAS) ^{13}C -NMR spectroscopy to confirm the possible conversion of the amidoxime group on RNH-5 by the alkaline treatment. Figure 3 shows the results obtained.

The highly porous poly (acrylonitrile-*co*-divinylbenzene) beads (RN-5) were reacted with a methanolic NH_2OH solution. The resulting resin (RNH-5) gave three signals in the range 120–190 ppm. The peak at 158 ppm is assigned to amidoxime, whereas the peaks at 123 and 179 ppm, to the remaining nitrile and carboxyl groups, respectively, by referring to Kobuke et al.²⁹ [Fig. 3(A)].

The (CP-MAS) ^{13}C -NMR spectrum of the alkali-treated RNH-5 is shown in Figure 3(B). The spectrum shows a certain decrease at 158 and 123 ppm,

corresponding to the peaks of amidoxime and the remaining nitrile groups, respectively. A noticeable increase was found at 179 ppm originating from the carboxyl groups. The small peak at 149 ppm may be assigned to cyclic imidedioxime. However, no further evidence was found for the formation of cyclic imidedioxime after the alkaline treatment.

Although there are some variations and obscure peaks due to the discrepancies in the polymer matrices, these spectra agree substantially with our previous solid-state (CP-MAS) ^{13}C -NMR spectral data of the hollow-fiber adsorbents.¹⁵

As we¹⁵ and others³⁰ have previously reported, the uranium adsorption of fiber adsorbents was virtually zero without alkaline treatment since the uranyl tricarbonate complex ion in seawater is hardly diffused into the fiber adsorbent, which prevents the free movement of such a bulky ion. In this work, however, the results of the columnar adsorption work indicated that a considerable potential existed with these highly porous chelating resins for the uranium adsorption without alkaline treatment. Here, in summary, two major factors appear to be as follows:

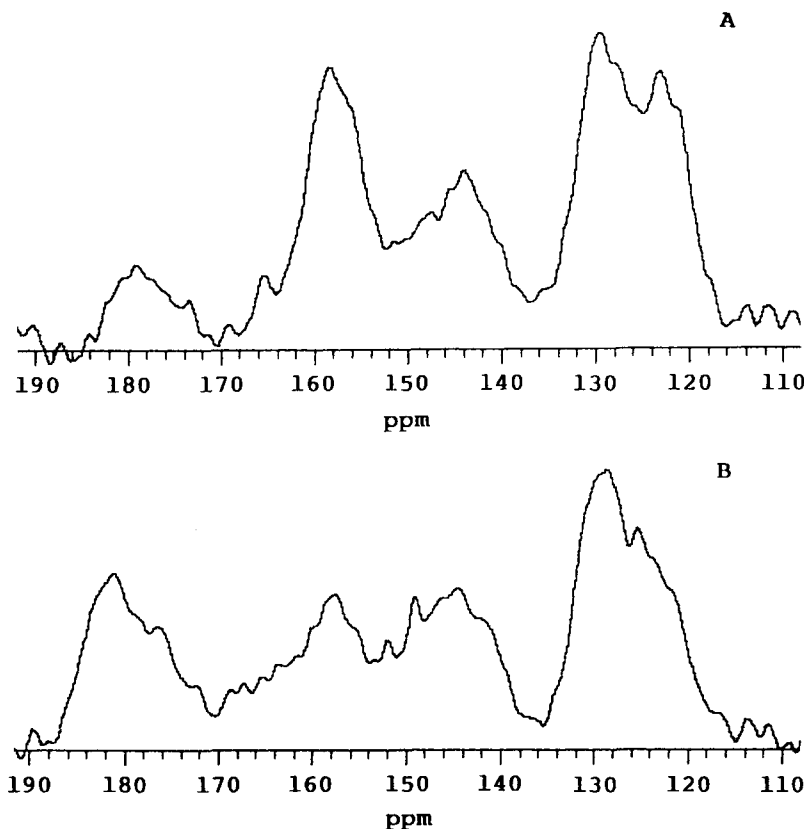


Figure 3 (CP-MAS) ^{13}C -NMR spectrum of RNH-5: (A) nontreated resin; (B) alkali-treated resin.

1. The diffusion of uranium within the resin structure is sufficiently fast due to a highly porous structure. This is shown more clearly by gel permeation chromatography, which is discussed in the next part.
2. The results obtained by solid-state (CP-MAS) ^{13}C -NMR spectroscopy confirmed that the amidoxime group was involved in the chelation as the main component. When, however, the resin is brought into contact with the alkali, the amidoxime group seems to be partially converted into cyclic imidodioxime and carboxylic acid. Unfortunately, little quantitative information was obtained about the degree of this conversion.

Undoubtedly, the highly porous chelating resins provide a more favorable pore structure for the rapid rate of diffusion of the uranyl tricarbonate complex ion than did those previously developed. Also, the alkaline treatment enhanced the potential for much faster adsorption characteristics. With the above in mind, it was speculated that both pore structure in the swollen state and chemical structure contribute to the overall performance achieved.

Pore Structure Analysis of Swollen Resins

Recently, we have reported that the pore structure analysis of macroreticular chelating resins in the

swollen state, which is obtained by gel permeation chromatography, is essential to understand the relationship between the pore structure and the adsorption of large molecules such as the uranyl tricarbonate complex ions.³¹ The method employed was that described by Kuga.³²

The calibration graphs of RNH-5 prepared in the presence of dichloroethane and chloroform during the suspension polymerization showed similarities with respect to their highly porous structures [Fig. 4(A)]. The formation of pores that permit the entrance of species of higher molecular weight [as is exactly our case with dextran (T110), (T70), (T40), and (T10)] is noticeable from the calibration graphs. Therefore, these resins showed marked discrepancies from those prepared in the presence of toluene as a porogen at the same divinylbenzene content in their adsorption abilities of uranium from seawater.

By contrast, the alkaline treatment caused remarkable changes in the pore structure [Fig. 4(B)]. As the resins swell in the alkaline medium, the size of the resin particle increases. This extreme expansion resulted in a certain decrease in the amount of pores that dextran (T110), (T70), and (T40) can permeate. However, a noticeable increase was observed in those of which dextran (T10) can permeate. As we reported before,³¹ the existence of pores that dextran (T10) can permeate leads to the increase in the adsorption rate of uranium.

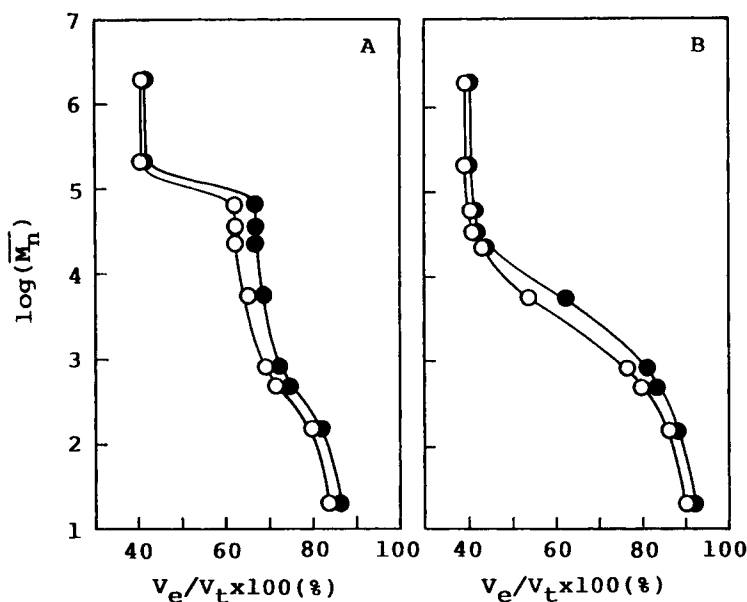


Figure 4 Calibration curves of GPC for RNH-5. Eluate: Deionized water. Flow rate: 0.5 cm^3/min . Water-soluble standard sample: dextran, sugar, D_2O . Stationary phase: RNH-5 (60–100 mesh); 50×300 mm. (A) Nontreated resin: (O) RNH-5(DCE-100); (●) RNH-5(CH-120). (B) alkali-treated resin: (O) RNH-5(DCE-100); (●) RNH-5(CH-120).

Variations in Porogen Content

Varying the proportion of tetrachloroethane, dichloroethane, and chloroform as a porogenic agent from 60 to 120 vol % at constant divinylbenzene content (5 mol %) during the suspension polymerization has evidently influenced the specific surface area, the pore volume, and the average pore radius of the corresponding polymer matrices and their amidoxime derivatives. An increase in porogen content resulted in highly porous structures characterized by enhanced specific surface area, small average pore radius, and, hence, large pore volume. The use of dichloroethane, tetrachloroethane, and chloroform, respectively, as a porogen exhibited a similar pattern. As can be seen in Figure 5, the relationship between the porogen content and the pore-size distribution curve appeared to be similar for each porogen. Despite having different overall physical characteristics, the elemental analysis showed that there is almost no difference in the content of nitrogen with an increase in porogen content (Table III). From the nitrogen content, the amount of acrylonitrile converted into the copolymer was calculated to be the same as the initial value of the monomeric mixture for each RNH-5. As expected, however, no information was found about the amount of amidoxime groups formed during the functionalization from the elemental analysis of RNH-5. This is possibly consistent with the existence of other functional groups such as nitrile and carboxyl groups besides amidoxime.

The effect of increasing the amount of porogenic agent on the properties of resins is given in Table IV. The specific surface area, the pore volume, and the average pore radius for RNH-5 (TCE) prepared at 100 vol % of tetrachloroethane, which corresponded to the resin of maximum specific surface area, are $24.8 \text{ m}^2 \text{ g}^{-1}$, $0.302 \text{ cm}^3 \text{ g}^{-1}$, and 208 \AA , respectively. The respective values for RNH-5 (DCE) prepared at 100 vol % of dichloroethane are $30.8 \text{ m}^2 \text{ g}^{-1}$, $0.435 \text{ cm}^3 \text{ g}^{-1}$, and 256 \AA . Those for RNH-5 (CH) prepared at 120 vol % of chloroform are $29.7 \text{ m}^2 \text{ g}^{-1}$, $0.304 \text{ cm}^3 \text{ g}^{-1}$, and 168 \AA , respectively.

Bearing in mind that there is a relationship between the porosity and the performance of a resin for the diffusion of ions of high molecular weight,²⁷ the effect of changing the proportion of porogenic agent on the uptake of uranium from seawater was examined in columnar adsorption tests. Figure 6 shows that increasing the percent of dichloroethane, chloroform, and tetrachloroethane, respectively, from 60 to 100% resulted in a marked increase in the uranium uptake. A significant uranium uptake as high as $23 \mu\text{g}$ of U/cm^3 resin/day was achieved

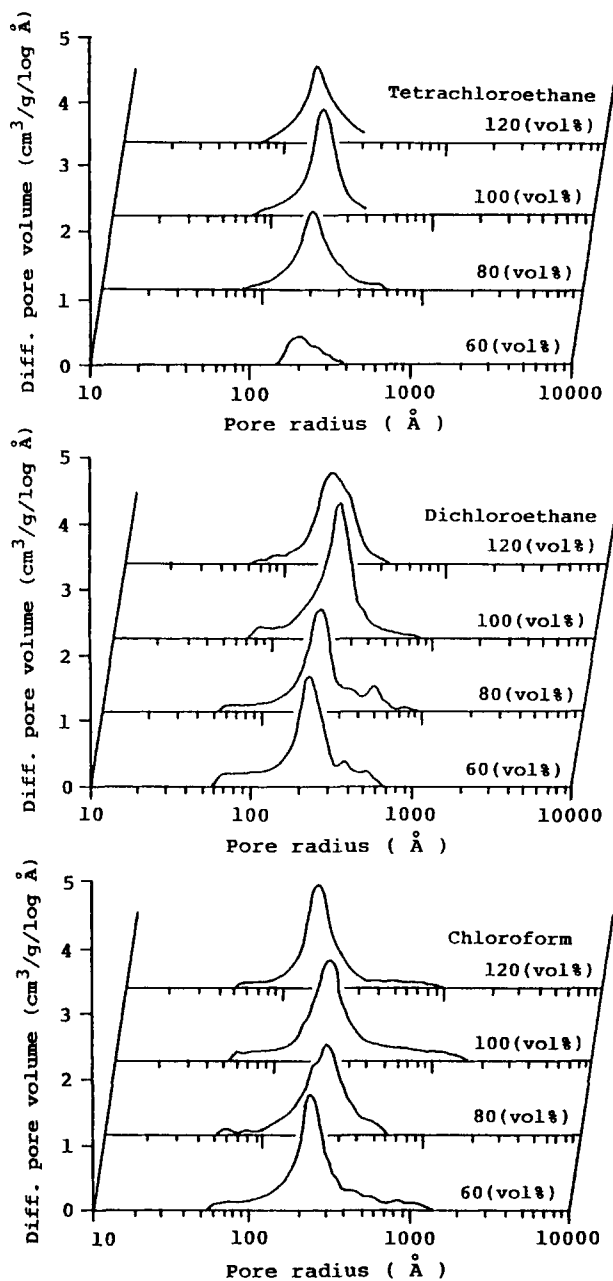


Figure 5 Pore-size distribution curves of RNH-5 at various porogen contents.

without conditioning with 1.0 mol dm^{-3} NaOH. As explained above, the increased adsorption abilities of the resulting resins by the alkaline treatment can be attributed to the changes in the physical and the chemical structures of resins in the alkaline medium.

Functionalization with Hydroxylamine

In the literature, several attempts have been made for the preparation of polyacrylamidoxime.^{33,34} It was

Table III Elemental Microanalysis

Porogen ^a		Microanalysis (%)					
		RN-5			RNH-5		
Abbreviation	Vol %	C	H	N	C	H	N
DCE	60	71.54	6.01	21.47	52.16	6.81	22.88
DCE	80	71.53	5.97	20.97	51.17	6.75	22.77
DCE	100	71.36	6.16	21.10	51.25	6.76	23.06
DCE	120	71.25	6.18	20.96	50.23	6.77	22.70
CH	60	71.72	6.24	21.45	51.32	6.67	22.87
CH	80	71.37	6.23	21.15	51.40	6.81	23.33
CH	100	71.47	6.22	21.30	50.00	6.72	23.07
CH	120	70.92	6.04	20.89	50.06	6.84	23.11

^a DCE: dichloroethane; CH: chloroform.

mentioned that the reaction product differs markedly depending upon the reaction conditions, e.g., temperature, pH, and reaction solvent.

For comparison, the highly porous poly(acrylonitrile-*co*-divinylbenzene) beads synthesized in this study were functionalized with hydroxylamine under the conditions that follow the pattern we and others have previously experienced. The results are summarized in Table V.

The experimental procedure recommended by Omichi et al.³⁰ consists in preparing hydroxylamine from its aqueous hydrochloride solution (3%), adding KOH until pH 7 and then MeOH such that

MeOH/H₂O (vol/vol) is 1/1. The polyacrylamidoxime resins have been prepared from poly(acrylonitrile-*co*-divinylbenzene) beads (0.5 g), adding an excess amount of NH₂OH (150 cm³) prepared according to this method and keeping the reaction mixture at 80°C for 2 h (Method A).

Kobuke et al.²⁹ treated polyacrylonitrile (0.76 g) with NH₂OH · HCl (1.9 g) in the presence of a half-molar equivalent of Na₂CO₃ (1.4 g) in an aqueous EtOH solution (10 cm³) under reflux. They identified the cyclic imidedioxime in the product. The poly(acrylonitrile-*co*-divinylbenzene) beads (0.5 g) have been functionalized with NH₂OH (150 cm³)

Table IV Effect of Porosity on the Properties of RNH-5^a

Porogen ^b		SSA (m ² /g)		Pore Volume (cm ³ /g)	Average Pore Radius (Å)	C _a (meq/g)	C _c (meq/g)	V (NaCl)	
Abbreviation	Vol %	RN-5	RNH-5					(cm ³ /g) NT ^c	(cm ³ /g) AT ^c
TCE	60	36.9	16.3	0.094	201	3.7	1.3	2.2	3.2
TCE	80	46.1	20.0	0.264	208	3.8	1.5	2.4	3.6
TCE	100	60.8	24.8	0.302	208	3.8	1.6	2.6	4.1
TCE	120	64.1	24.8	0.230	154	3.8	1.6	2.8	4.5
DCE	60	40.9	21.5	0.335	225	3.7	1.2	2.0	3.2
DCE	80	49.4	25.7	0.345	229	3.8	1.5	2.2	3.6
DCE	100	71.6	30.8	0.435	256	3.8	1.6	2.6	4.1
DCE	120	67.3	31.4	0.393	202	3.8	1.6	2.6	4.7
CH	60	42.6	22.5	0.369	238	3.7	1.2	2.2	3.2
CH	80	44.6	24.2	0.362	240	3.7	1.5	2.4	3.6
CH	100	61.4	27.6	0.333	220	3.7	1.6	2.6	4.1
CH	120	72.7	29.7	0.304	168	3.8	1.6	2.7	4.6

^a NH₂OH/CN (mol ratio): 1.5.

^b TCE: tetrachloroethane; DCE: dichloroethane; CH: chloroform.

^c NT: nontreated resin; AT: alkali-treated resin.

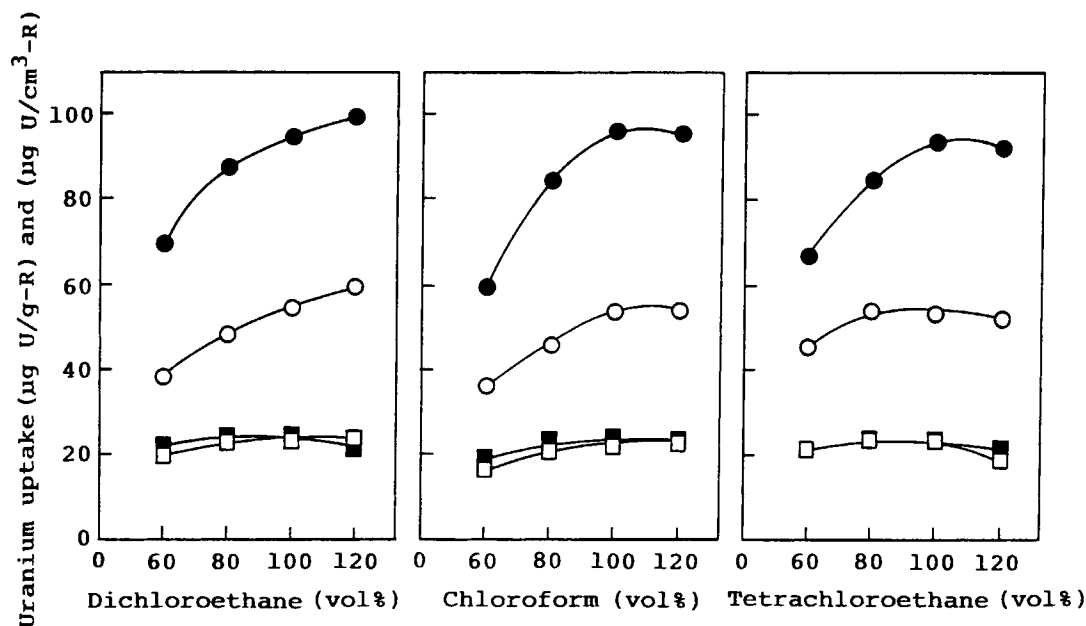


Figure 6 Effect of porosity on the uranium uptake from seawater. Uranium uptake— $\mu\text{g/g R}$: (○) nontreatment; (●) alkaline treatment. $\mu\text{g/cm}^3 \text{R}$: (□) nontreatment; (■) alkaline treatment.

prepared using this procedure at 90°C for 2 h (Method B).

Method C is a variant of Method A. Instead of using the $\text{MeOH} - \text{H}_2\text{O}$ mixture (1 : 1) at pH 7, the reaction was performed employing an $\text{EtOH} - \text{H}_2\text{O}$ mixture (1 : 1) as a reaction solvent at pH 4. Methods A, B, and C comprised the subsequent washing stages with deionized water at room temperature and then with 50% aqueous MeOH at 70°C for 1 h, when the functionalization was complete.

To date, the most used process that we described for the preparation of polyacrylamidoxime consists in using a solution of 3% free NH_2OH in MeOH

(127 cm^3) and keeping the reaction mixture (resin 5 g) at 80°C for 2 h (Method D). After the reaction, the chelating resin is washed well with deionized water. In the case of Method E, a variant of Method D has been followed. A comparative excess of NH_2OH (100 cm^3) was used for the functionalization of the copolymer beads (2 g), keeping the other conditions analogous to those described in Method D. The other difference was the postwashing process, which is similar to that described for Methods A, B, and C, respectively.

The specific surface areas of the resulting resins prepared by Methods A, B, D, and E are very similar.

Table V Functionalizations with Hydroxylamine at Various Conditions

Method ^a	SSA (m^2/g)	Pore Volume (cm^3/g)	Average Pore Radius (\AA)	C_o (meq/g)	C_c (meq/g)	$V(\text{NaCl})$ (cm^3/g)	Nontreatment		Alkaline Treatment ^b		
							U Uptake		U Uptake		
							($\mu\text{g/g R}$)	($\mu\text{g/cm}^3 \text{R}$)	(cm^3/g)	($\mu\text{g/g R}$)	($\mu\text{g/cm}^3 \text{R}$)
A	29.1	0.645	392	3.3	2.0	2.7	26.5	9.8	4.6	85.0	18.5
B	28.8	0.627	436	2.9	2.3	2.8	29.6	10.6	4.6	74.6	16.2
C	65.6	0.460	405	0.1	0.2	2.8	14.4	5.1	4.4	38.0	8.6
D	29.7	0.304	168	3.8	1.6	2.7	61.0	22.6	4.6	96.0	20.9
E	28.0	0.615	373	3.9	2.1	3.0	66.0	22.0	4.6	94.0	20.4

^a Resin: RN-5 (CH-120).

^b Methods A, B, C, and E by 2.5% KOH at 80°C , 1 h; Method D by 1.0 mol dm^{-3} NaOH at 30°C , 72 h.

The IR spectrum showed that Method C resulted in very poor functionalization since the neutralization of $\text{NH}_2\text{OH} \cdot \text{HCl}$ was not complete at pH 4 for the preparation of NH_2OH . Therefore, the specific surface area analogous to that of polymer matrix and very low ion-exchange capacities were obtained. Methods A, B, C, and E gave the products of a larger average pore radius than that of obtained by Method D. The postwashing process in 50% aqueous MeOH appeared to lead to a significant change in the pore structure. Methods D and E gave apparently higher uranium uptakes that correspond to higher anion-exchange capacities.

Flow-rate Tests

The effect of space velocity, SV (h^{-1}), on the uranium uptake from seawater was investigated, increasing the amount of the resin from 12.5 to 500 mg during the columnar adsorption tests. The seawater (20 dm^3) was passed upflow to the column at a flow rate of $900 \text{ cm}^3 \text{ h}^{-1}$ at 30°C . The dependence of uranium uptake on the SV for both nontreated and alkali-treated resins is shown in Figure 7. The results of varying the SV showed that as SV increased from 600 to 3000 h^{-1} , the increase in uranium uptake was sufficiently fast. However, it can no longer increase with a further increase in SV .

Columnar Elution and Recycling of Resins

The preliminary investigation concerning the performance of various eluting agents has been already reported.¹⁶ Sulfuric acid (0.5 mol dm^{-3}) proved to be the most generally useful stripping reagent for

removing uranium from the chelating resins with an efficiency of ca. 100%.

Here it is important to bear in mind that the resin with a low degree of cross-linking has much less chemical stability than that with a high degree of cross-linking in an acid solution.¹⁰ As we reported before, the reduction in resin capacity by the acid treatment may be partially due to the degradation of amidoxime groups and may be attributed to the gradual deterioration in micropores as well.⁹ With this in mind, the carbonate eluants such as Na_2CO_3 , NaHCO_3 , $(\text{NH}_4)_2\text{CO}_3$, and NH_4HCO_3 in various concentrations were tested previously.¹⁶ They did yield a quantitative stripping for uranium and long-term performance as well.

In the present study, the highly porous chelating resins were subjected to the cyclic adsorption and elution with H_2SO_4 (0.5 mol dm^{-3}), NH_4HCO_3 (2.0 mol dm^{-3}), and NaHCO_3 (1.0 mol dm^{-3}) as eluting agents. The results are shown in Figure 8. Not surprisingly, the alkali-treated resins gave markedly higher uranium adsorption, compared with the nontreated resins. Here it will be recalled that the alkaline treatment affects the micropore formation and the chemical structure as well.

Despite its advantage of higher elution efficiency, sulfuric acid seems to cause a significant reduction in the resin capacity after three cycles. In the case of the alkali-treated resins, the resin capacity was $71 \pm 4\%$ of the initial capacity in cycles 4–10. When, however, NH_4HCO_3 (2.0 mol dm^{-3}) and NaHCO_3 (1.0 mol dm^{-3}) were used for removing uranium from the chelating resins, the resin capacities seemed to remain stable after a consecutive 10 cycles. The elution efficiencies of the bicarbonate eluants were

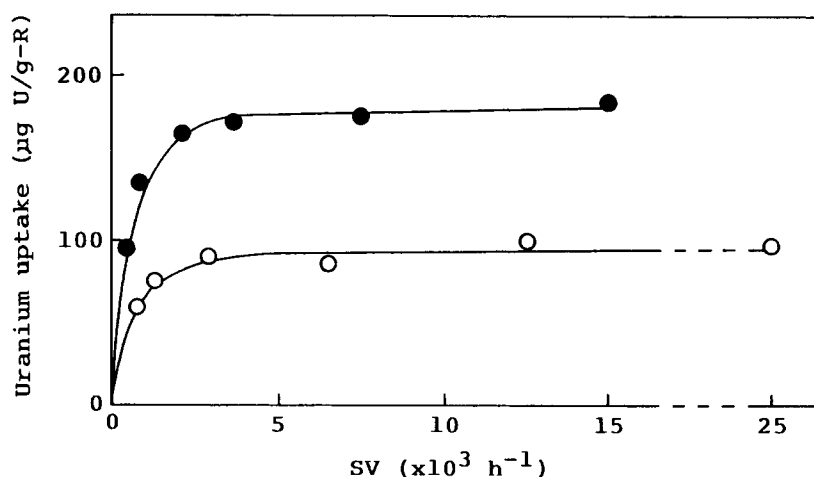


Figure 7 Recovery of uranium from seawater as a function of SV : (○) nontreated resin; (●) alkali-treated resin.

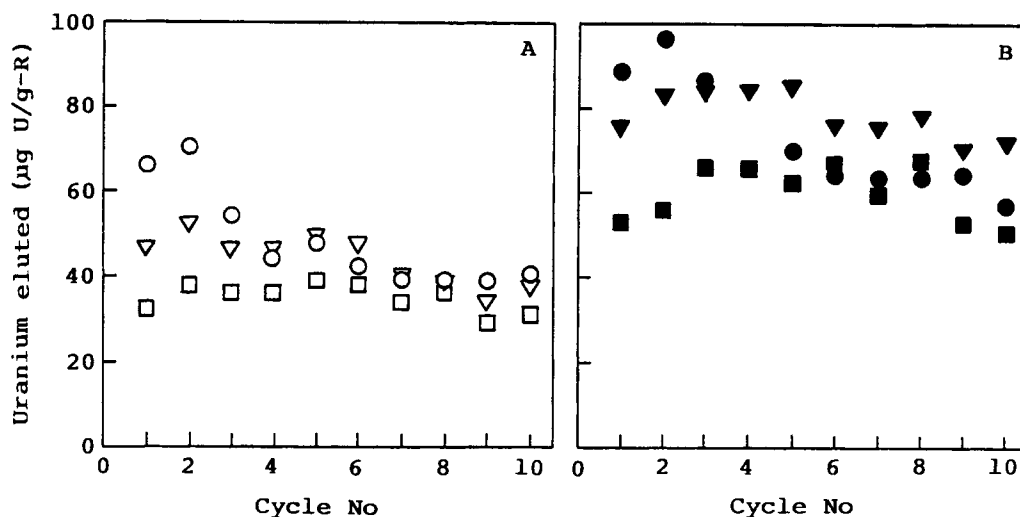


Figure 8 Adsorption-elution cycles using various eluting agents: (A) nontreated resin; (B) alkali-treated resin. Adsorption: columnar (upflow), flow rate $900 \text{ cm}^3 \text{ h}^{-1}$, 30°C , resin RNH-5(CH-120) 0.5 g , seawater 20 dm^3 . Elution: flow rate $4.5 \text{ cm}^3 \text{ h}^{-1}$. (○, ●) $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$; (▽, ▼) $2.0 \text{ mol dm}^{-3} \text{ NH}_4\text{HCO}_3$; (□, ■) $1.0 \text{ mol dm}^{-3} \text{ NaHCO}_3$.

apparently less than that obtained by H_2SO_4 (0.5 mol dm^{-3}). The uranium adsorbed by the alkali-treated resins was removed with $87 \pm 6\%$ and $66 \pm 7\%$ of elution efficiencies by means of NH_4HCO_3 (2.0 mol dm^{-3}) and NaHCO_3 (1.0 mol dm^{-3}), respectively. The results were encouraging for moving to large-scale columnar adsorption trials.

Large-scale Adsorption Tests

An attempt was made to determine the adsorption rates of the highly porous chelating resins for ura-

nium in seawater. A plastic column (inner diameter 6.0 cm) was packed with wet-settled resin (50 cm^3) that previously contacted with sodium chloride solution (3%) to keep the ionic strength the same as that in seawater. At a flow rate of $SV \ 640 \text{ h}^{-1}$, seawater was delivered upflow to the column. It was concluded that these resins exhibited a better overall performance than hitherto. From Figure 9, it can be seen that the adsorption of uranium increased against the contact time during 30 days of experimental periods. The adsorption rates obtained were higher than those of less porous chelating resins.

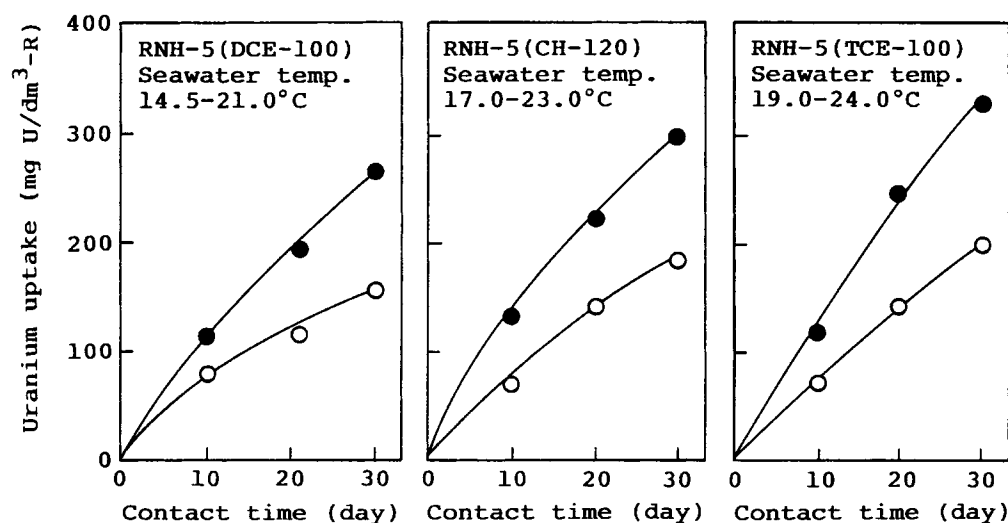


Figure 9 The plots of adsorption rates during the large-scale performance tests: (○) nontreated resin; (●) alkali-treated resin. Adsorption: columnar (upflow), column $60 \text{ mm} \times 1 \text{ m}$, resin 50 cm^3 , $SV \ 640 \text{ h}^{-1}$. Elution: resin 1.0 cm^3 , H_2SO_4 (0.5 mol dm^{-3}) 10 cm^3 , $SV \ 3 \text{ h}^{-1}$.

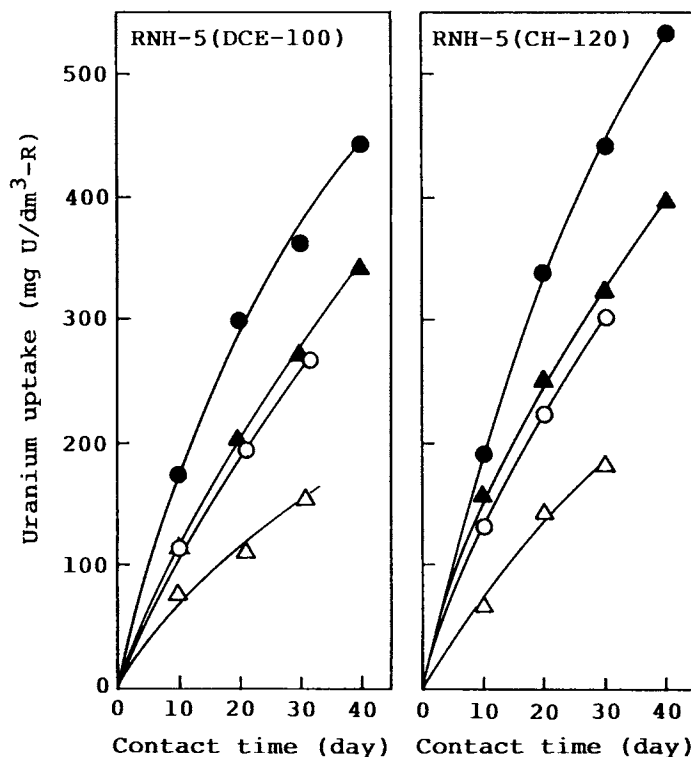


Figure 10 The effect of seawater temperature on the adsorption rates. RNH-5(DCE-100): (Δ) NT; (\circ) AT (April-May). Seawater temp: 14.5–21.0°C: (\blacktriangle) NT; (\bullet) AT (Aug-Sept). Seawater temp: 27.5–32.0°C. RNH-5(CH-120): (Δ) NT; (\circ) AT (May-June). Seawater temp: 17.0–23.0°C: (\blacktriangle) NT; (\bullet) AT (Aug-Sept). Seawater temp: 27.5–32.0°C. (NT: nontreated resin; AT: alkali-treated resin.)

Preliminary investigation concerning the effect of seawater temperature on the adsorption of uranium was reported before.¹⁶ For comparison, the resins prepared in this study were subjected to the adsorption tests from April to September. The time plots of the uranium adsorption as a function of seawater temperature are shown in Figure 10. The resins exhibited remarkably enhanced adsorption rates during August–September, compared to those obtained in April–June, since the adsorption capacity increased markedly with increasing temperature. A superior adsorption rate as high as 157 mg of U/dm³ resin/10 days (408 mg of U/kg resin/10 days) was achieved without alkaline treatment in August (seawater temperature: 27.5–32.0°C). When the same resin was treated with 1.0 mol dm⁻³ NaOH at 30°C for 72 h, an adsorption rate as high as 191 mg of U/dm³ resin/10 days (684 mg of U/kg resin/10 days) was obtained (seawater temperature: 27.5–32.0°C).

Summarizing the experimental results, we have seen that the lightly cross-linked highly porous chelating resins containing amidoxime groups show a high adsorption rate for uranium in seawater, based

on the multiple interaction of the pore structure in the swollen state and the chemical structure. Future studies will investigate the recycle use of these adsorbents. We are pursuing the examination of the ability of the highly porous chelating resins to maintain their adsorbing power for uranium over a long period in service.

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