# Recovery of Uranium from Sea Water. IV. Influence of Crosslinking Reagent on the Uranium Adsorption of Macroreticular Chelating Resin Containing Amidoxime Groups

HIROAKI EGAWA, MORIO NAKAYAMA, TAKAMASA NONAKA, and EIICHI SUGIHARA, *Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860, Japan*

## Synopsis

Macroreticular chelating resins (RNH) containing amidoxime groups with various degrees of crosslinking were synthesized by using various amounts of ethyleneglycol dimethacrylate (1G), dimethyleneglycol dimethacrylate (2G), triethyleneglycol dimethacrylate (3G), tetraethyleneglycol dimethacrylate (4G), and nanoethyleneglycol dimethacrylate (9G) as crosslinking reagent. The effect of crosslinking reagents on the pore structure, ion exchange capacity, swelling ratio, and adsorption ability for uranium of RNH was investigated. RNH (RNH–1G) prepared by using 1G were showed to have macroreticular structures by the measure of specific surface area. RNH–1G had the high adsorption ability and physical stability. Though RNH (RNH–4G) obtained by using 4G have little macroreticular structure (macropore), these resins showed the high adsorption ability for uranium by the treatment with 0.1 mol dm$^{-3}$ NaOH at 30°C for 15 h (alkali treatment). These results suggest that the formation of not only the favorable macropore but also the micropore is important for the effective recovery of uranium in sea water, whereas RNH–4G was defined to be low physical and chemical stability. For the preparation of RNH which have effective pore structure for the recovery of uranium, chemical, and physical stability, the simultaneous use of divinylbenzene (DVB) and 1G or 4G as crosslinking reagent was examined (abbreviated as RNH–DVB–1G and RNH–DVB–4G). The specific surface area of RNH–DVB–1G increased with an increase of 1G used. These RNH–DVB–1G have been shown the high adsorption ability for uranium. On the other hand, the specific surface area and adsorption ability for uranium of RNH–DVB–4G decreased with an increase of 4G used. Repeated use did not cause the deterioration of both RNH–DVB–1G and RNH–DVB–4G. This result suggests that the simultaneous use of DVB and 1G or 4G contributed the improvement of chemical and physical stability. In particular, RNH–DVB–1G has the effective macropore and micropore for the recovery of uranium.

## INTRODUCTION

Uranium in sea water is present at the trace concentration of (2.8–3.3 mg. dm$^{-3}$) with many other elements. The amount of uranium dissolved in the oceans of the world is estimated to be ca. 4 billion tons. Accordingly, the development of selective adsorbents for uranium is essential for effective recovery of uranium in sea water. In earlier research, we synthesized the macroreticular chelating resins (RNH) containing amidoxime groups and reported that the RNH prepared from the macroreticular acrylonitrile–divinylbenzene copolymer beads were highly effective for recovery of uranium from sea water and pore structure of RNH affected greatly the selective

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adsorption ability for uranium.[1-4] It was confirmed by other several workers the chelating resin containing a amidoxime groups were the most promising sorbents for the recovery of uranium from sea water.[5-9] However, these resins are not still satisfactory for the use in industry, and so the chelating resin containing amidoxime groups which have further physical and chemical stability and high adsorption rate for uranium in sea water is required. In this study, the RNH with various pore structure was prepared with several crosslinking reagents and the influence of pore structure of the RNH on the adsorption of uranium in sea water was discussed. The chemical and physical stability of RNH were also investigated.

## EXPERIMENTAL

### Preparation of Macroreticular Chelating Resin Containing Amidoxime Groups

A macroreticular acrylonitrile–polyethyleneglycol dimethacrylate or divinylbenzene (DVB) copolymer beads (RN) were synthesized by suspension polymerization in the presence of toluene as diluent. A solution of purified acrylonitrile, crosslinking reagents, toluene (80 vol %/monomer), and benzoyl peroxide (2 mmol/50 cm$^3$ monomer) was combined in an auto crave with a solution of $Na_2SO_4$ (30 g), gelatin (0.3 g), $CaCO_3$ (5 g) in 500 cm$^3$ of water. Polyethyleneglycol used as crosslinking reagent were ethyleneglycol dimethacrylate (1G), diethyleneglycol dimethacrylate (2G), triethyleneglycol dimethacrylate (3G), tetraethyleneglycol dimethacrylate (4G), and nanoethyleneglycol dimethacrylate (9G). Divinylbenzene (DVB) was used as technical grade (containing 55% DVB). The mixture was stirred, until monomers were dispersed as fine droplets. The suspension was heated to 60°C. Polymerization was carried out at 60–70°C for 4 h. Then the suspension was heated to 90°C and kept at this temperature for 1 h. The product was filtered off and washed with 1 mol dm$^{-3}$ HCl, hot water, and methanol. After drying, copolymer beads with desired diameter were selected (32–60 mesh).

A solution of sodium hydroxide in methanol was added dropwise to the solution of hydroxylamine hydrochloride in methanol. After the mixture was stirred sufficiently, sodium chloride precipitated was filtered. A concentration of free hydroxylamine in it was determined by titration with 0.5 mol dm$^{-3}$ hydrochloric acid after 1 cm$^3$ of the filtrate was diluted with 49 cm$^3$ of water. Amidoxime groups were introduced to the RN by means of the reaction of RN (8 g) in pressure bottles with a solution (80 cm$^3$) of 3% hydroxylamine in methanol for 2 h at 80°C.

The product (RNH) was filtered off, washed with pure water until hydroxylamine was not released to the wash water, air-dried, and dried *in vacuo* at 40°C for 2 h.

### Treatment of the RNH with Sodium Hydroxide Solution (Alkali Treatment)

The RNH (1 g) was treated with 100 cm$^3$ of 0.1 mol dm$^{-3}$ sodium hydroxide solution at 30°C for 15 h. The resulting resin was washed with deionized water until the wash water became neutral, air-dried, and dried *in vacuo* at 40°C for 2 h.

## Treatment of the RNH with Hydrochloric Acid Solution (Acid Treatment)

RNH (1 g) was treated with 100 cm$^3$ of 1 mol dm$^{-3}$ hydrochloric acid solution at 60°C for 5 h. The resulting resin was washed with deionized water until the wash water became neutral, air-dried, and dried *in vacuo* at 40°C for 2 h.

## Measurement of Macroreticular Structure (Macropore)

Macropore was characterized by the specific surface area, pore volume, and average pore radius. Specific surface areas of RNH were measured on a Yuasa surface area apparatus (BET method). Pore volumes and average pore radius of RNH were determined on a Carlo-Erba mercury porosimeter (Model 1520).

## Measurement of Apparent Anion Exchange Capacity

RNH (0.5 g) and 100 cm$^3$ of 0.1 mol dm$^{-3}$ hydrochloric solution were shaken in a glass-stoppered Erlenmeyer flask at 30°C for 15 h. The anion exchange capacity was determined by titrating the concentration of Cl$^-$ in the supernatant with an AgNO$_3$ solution.

## Measurement of Apparent Cation Exchange Capacity

RNH used for the measurement of anion exchange capacity was washed with deionized water until the wash water became neutral, air-dried, and dried *in vacuo* at 40°C for 2 h. The RNH (0.25 g) and 50 cm$_3$ of 0.1 mol dm$^{-3}$ sodium hydroxide solution were shaken in a glass-stoppered Erlenmeyer flask at 30°C for 15 h. After shaking, a 5 cm$^3$ of supernatant was titrated with 0.1 mol dm$^{-3}$ hydrochloric acid solution, and Cl$^-$ released to the 5 cm$^3$ of supernatant was separately titrated with 0.05 mol dm$^{-3}$ AgNO$_3$ solution. The cation exchange capacity was determined by the substrate of Cl$^-$ released from the amount of sodium hydroxide exhausted. In the case of RNH after acid treatment, after cation exchange capacity was measured, anion exchange capacity was measured.

## Adsorption of Uranium from Spiked Sea Water

RNH (0.1 g) and 25 cm$^3$ of natural sea water spiked with UO$_2$(NO$_2$) · 2H$_2$O · (10 mg dm$^{-3}$ concentration of U) were shaken at 30°C for 1 h. The resin was then filtrated and the filtrate was taken for the spectrophotometric determination of uranium with arsenazo-III.

## Recovery of Uranium from Sea Water by Column Method

RNH was treated with a 3% sodium chloride solution for 24 h at room temperature, and then 1.5 cm$^3$ of this RNH was packed in the glass column (a diameter of 1 cm). Natural sea water (20 dm$^3$) was passed through this column at a space velocity (SV) of 300 h$^{-1}$ at 25–30°C. The uranium adsorbed on the RNH was eluted by passing 10 bed volume of a 0.5 mol dm$^{-3}$ sulfuric acid solution through the column at SV 3 h$^{-1}$. Uranium in eluate was determined spectrophotometically with arsenazo III. After this, RNH was washed with water until the wash water became neutral; the sorption–elution procedure was repeated.

## RESULTS AND DISCUSSION

### Effect of Crosslinking Reagents on Pore Structures of RNH

RN with various degrees of crosslinking were synthesized by using various amounts of 1G, 2G, 3G, 4G, and 9G in the presence of a constant volume (80 vol% per monomer) of toluene as diluent. Chelating resins containing amidoxime groups were prepared by the reaction of the above RN with hydroxylamine in methanol (abbreviated as RNH–1G, –2G, –3G, –4G, and –9G):
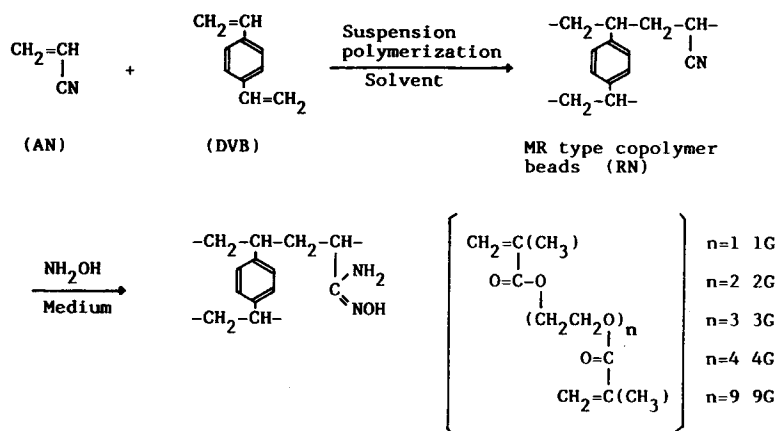


Scheme 1.    Preparation of chelating resins containing amidoxime groups.

Pore characteristics (specific surface area, average pore radius, and pore volume) of these resins are shown in Table I. These results indicate that pore structure of RNH obtained is influenced by the crosslinking reagent. Macroreticular structures of resins, in general, are characterized by having large specific surface areas. The specific surface area of RNH–1G increased with an increase in the degree of crosslinking. Compared with RNH–1G, both RNH–2G and –3G had small specific surface areas. In each series of these RNH, as the degree of crosslinking increased, average pore radius decreased. On the other hand, since the specific surface area of RNH–4G with the high degree of crosslinking and RNH–9G was not measured, it was shown that these resins did not have macroreticular structure.

### Effect of Crosslinking Reagents on the Ion Exchange Capacity

The effect of crosslinking reagents on the anion exchange capacity of RNH–1G and –9G was investigated. The content of amidoxime group introduced to each resin was evaluated from the anion exchange capacity. As shown in Figure 1, it was found that the content of amidoxime group decreased with an increase in the degree of crosslinking, and was not almost affected by the varieties of crosslinking reagent. Since amidoxime groups

TABLE I
Pore Structure of RNH–1G, –2G, –3G, –4G, and –9G

| Crosslinking reagent (mol %) | | Specific surface area (m²/g) | Average pore radius (Å) | Pore volume (cm³/g) |
|---|---|---|---|---|
| 1G[a] | 10 | 1.4 | 2977 | 0.85 |
| | 20 | 17.3 | 473 | 0.46 |
| | 30 | 54.8 | 211 | 0.56 |
| | 40 | 102.0 | 129 | 0.40 |
| | 50 | 140.0 | 143 | 0.44 |
| 2G[b] | 10 | 1.8 | 2927 | 0.82 |
| | 20 | 9.1 | 1023 | 0.50 |
| | 30 | 12.6 | 584 | 0.48 |
| | 40 | 16.9 | 368 | 0.43 |
| | 50 | 13.7 | 260 | 0.24 |
| 3G[c] | 10 | 12.6 | 756 | 0.58 |
| | 20 | 12.2 | 583 | 0.33 |
| | 30 | 11.7 | 511 | 0.22 |
| | 40 | 9.9 | 217 | 0.12 |
| | 50 | 12.1 | 186 | 0.09 |
| 4G[d] | 10 | 7.6 | 461 | 0.17 |
| | 20 | 0.8 | 307 | 0.04 |
| | 30 | 0.4 | 318 | 0.04 |
| | 40 | 0.0 | — | — |
| | 50 | 0.0 | — | — |
| 9G[e] | 10 | 0.0 | — | — |
| | 20 | 0.0 | — | — |

[a] Ethyleneglycol dimethacrylate.
[b] Diethyleneglycol dimethacrylate.
[c] Triethyleneglycol dimethacrylate.
[d] Tetraethyleneglycol dimethacrylate.
[e] Nanoethyleneglycol dimethacrylate.

behave as the amphoteric groups, the cation exchange capacity was also measured. As shown in Figure 1, the cation exchange capacity also decreased with an increase in the degree of crosslinking, but the cation exchange capacity of RNH with a high degree of crosslinking was higher than the anion exchange capacity of the resin. These results indicate that the acidic groups such as hydroxamic acid and carboxylic groups beyond amidoxime groups have been formed in the course of the reaction of RN with hydroxylamine solution. The changes of ion exchange capacity of RNH after alkali treatment are also shown in Figure 1. The anion exchange capacity of RNH only decreased by alkali treatment, whereas the change of cation exchange capacity by alkali treatment increased in order of RNH–1G, –2G, –3G, –4G, and –9G. From these increases of cation exchange capacity it may be concluded that the carboxylic groups were formed by the hydrolysis of nitrile groups and ester groups in crosslinking reagents. In fact, the formation of carboxylic groups could be recognized from the infrared spectrum, which exhibited the characteristic adsorption of carboxylate groups at 1560 cm$^{-1}$. However, it was
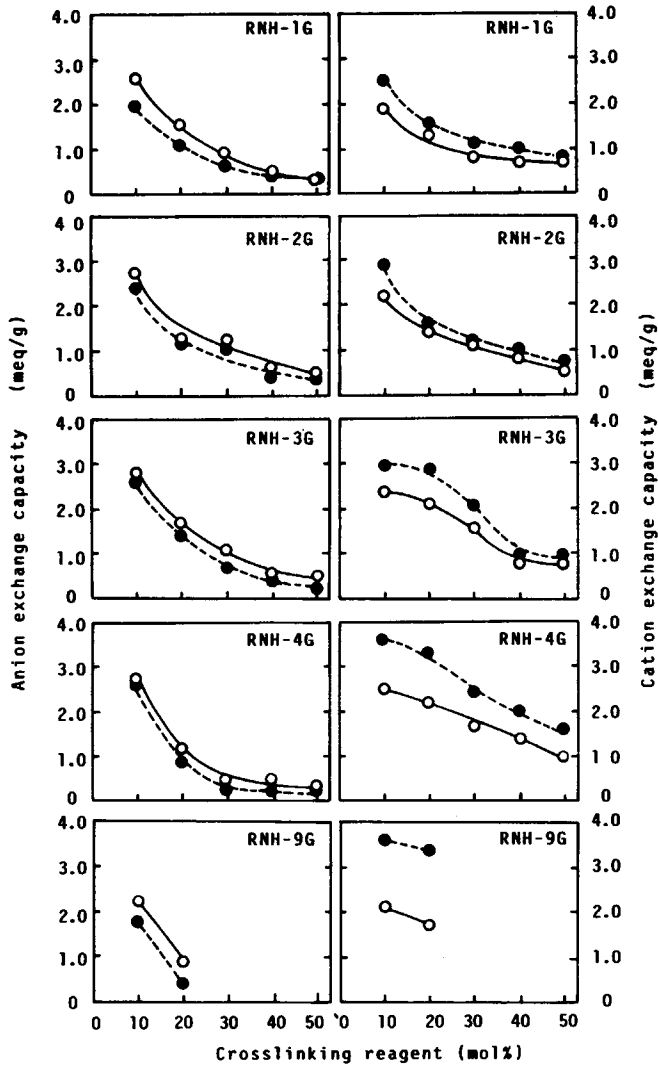
Fig. 1.  Effect of crosslinking reagent on the ion exchange capacity: (—○—) nontreated resin; (---●---) alkali-treated resin.

difficult to discuss the content of acidic groups on the resins on the basis of cation exchange capacity.

## Swelling Ratio of RNH

Swelling ratio of RNH are shown in Table II. RNH–4G and –9G, which have shown the large increase of cation exchange capacity by alkali treatment, were found to give the large swelling ratio $(V_3/V_1)$ by alkali treatment. These large swelling attributed to the increase of hydrophilicity based on formation of carboxylic groups by the hydrolytic cleavage of crosslinking. On the other hand, the series of RNH–1G exhibited the smallest swelling ratio $(V_3/V_1)$, and

TABLE II
Specific Surface Area after Alkali Treatment and
Swelling Ratio of RNH–1G, –2G, –3G, –4G, and –9G

| Crosslinking reagent (mol %) | | $V_1$[a] | $V_2$[a] | $V_3$[a] | Swelling ratio | | Specific surface area[b] |
|---|---|---|---|---|---|---|---|
| | | | ($cm^3/g$) | | $V_2/V_1$ | $V_3/V_1$ | ($m^2/g$) |
| 1G | 10 | 2.0 | 2.8 | 3.6 | 1.4 | 1.8 | 3.9 |
| | 20 | 1.9 | 2.5 | 2.6 | 1.3 | 1.3 | 22.9 |
| | 30 | 1.9 | 2.3 | 2.1 | 1.2 | 1.1 | 54.8 |
| | 40 | 2.0 | 2.5 | 2.4 | 1.3 | 1.2 | 96.7 |
| | 50 | 1.9 | 2.3 | 2.1 | 1.2 | 1.1 | 120.0 |
| 2G | 10 | 2.2 | 3.6 | 6.6 | 1.6 | 3.0 | 3.0 |
| | 20 | 1.8 | 2.6 | 3.3 | 1.4 | 1.8 | 16.2 |
| | 30 | 1.8 | 2.3 | 2.4 | 1.3 | 1.3 | 18.0 |
| | 40 | 1.7 | 2.3 | 2.4 | 1.4 | 1.4 | 24.8 |
| | 50 | 1.5 | 2.1 | 2.0 | 1.4 | 1.3 | 18.5 |
| 3G | 10 | 2.0 | 2.5 | 9.1 | 1.2 | 4.6 | 1.2 |
| | 20 | 1.6 | 2.2 | 4.6 | 1.3 | 2.9 | 0.0 |
| | 30 | 1.6 | 2.0 | 3.0 | 1.2 | 1.9 | 0.0 |
| | 40 | 1.5 | 2.0 | 2.1 | 1.3 | 1.4 | 0.0 |
| | 50 | 1.4 | 1.9 | 2.1 | 1.3 | 1.5 | 0.0 |
| 4G | 10 | 1.4 | 2.3 | 17.4 | 1.6 | 12.4 | 0.7 |
| | 20 | 1.3 | 2.1 | 8.0 | 1.6 | 6.2 | 0.0 |
| | 30 | 1.1 | 1.8 | 4.0 | 1.6 | 3.6 | 0.0 |
| | 40 | 1.4 | 2.7 | 4.7 | 1.9 | 3.4 | 0.0 |
| | 50 | 1.1 | 2.0 | 2.7 | 1.8 | 2.5 | 0.0 |
| 9G | 10 | 1.3 | 2.9 | 38.1 | 2.3 | 29.3 | 0.0 |
| | 20 | 1.1 | 2.6 | 15.5 | 2.4 | 14.1 | 0.0 |

[a] $V_1$ = dry volume of RNH ($cm^3/g$); $V_2$ = wet volume of RNH ($cm^3/g$); $V_3$ = wet volume of RNH after alkali treatment.
[b] RNH after alkali treatment, washing with water, and drying.

the specific surface area of RNH–1G was found not to decrease by alkali treatment. It follows that RNH–1G have the physical stability.

## Adsorption Ability of RNH for Uranium

We had already reported that pore structure of RNH prepared from macroreticular acrylonitrile–divinylbenzene copolymer greatly affects the adsorption ability for uranium.[2,3] Accordingly, RNH synthesized in this study was expected to show the various adsorption ability for uranium. First, the adsorption ability of each RNH for uranium was tested by use of sea water spiked with uranyl nitrate (U concentration of 10 mg $dm^{-3}$). Each dry resin was shaken with the above sea water. The adsorption of uranium on the RNH within 60 min are shown in Figure 2. RNH prepared with 30 mol % of 1G was found to adsorb about 83% of uranium added and gave the highest adsorption of RNH without alkali treatment. In the case of the other RNH, RNH prepared with 30 mol % of 2G or 40 mol % of 3G showed also comparatively high adsorption of uranium, but it was found that there was a tendency for the adsorption of uranium to decrease in order of RNH–1G, –2G, –3G, and –4G. Thus the rapid adsorption of uranium onto RNH–1G is based on the formation of effective macropore. Though RNH–4G had no macroreticular
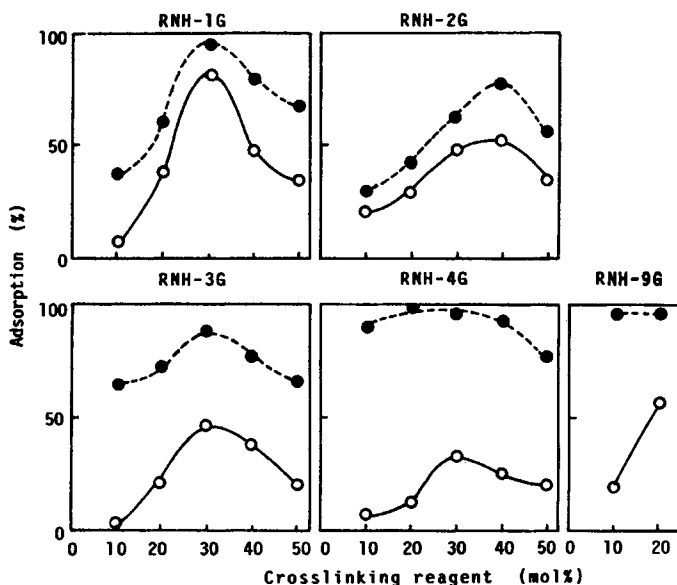
Fig. 2. Effect of crosslinking reagent on the adsorption of uranium: resin 0.1 g; sea water 25 cm$^3$ (250 $\mu$g of uranium was added in it); shaking 30°C, 1 h; (—o—) nontreated resin; (---•---) alkali-treated resin.

structure, the adsorption of uranium on RNH-4G increased remarkably by alkali treatment. This large increase can be attributed to the formation of favorable pore structure (micropore) based on the large swelling of RNH caused by alkali treatment. RNH-9G also gave the high adsorption of uranium by alkali treatment, but the physical destruction of RNH-9G was caused by the large swelling. Uranium in natural sea water is known to be present as not uranyl ion but stable tricarbonate uranyl complex anion $(UO_2(CO_3)_3^{4-})$. So, the next investigation of adsorption ability for uranium was carried out with natural sea water. In order to recover a trace amount of uranium in sea water, it is too important that large volumes of sea water contact with adsorbents which have a high adsorption rate. In this experiment, natural sea water (20 dm$^3$) was passed through a column packed with
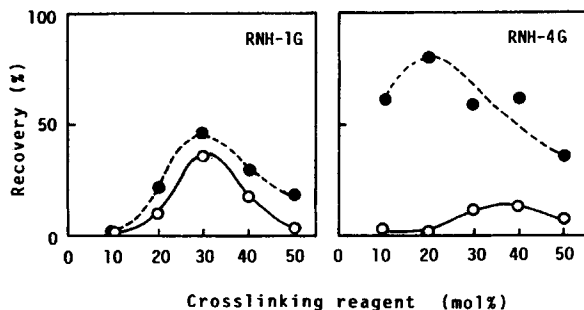


Fig. 3. Effect of crosslinking reagent on the recovery of uranium from sea water by column method: resin 1.5 cm$^3$; sea water 20 dm$^3$ (down flow, SV 300 h$^{-1}$, temp 25–30°C); elution 0.5 mol dm$^{-3}$ H$_2$SO$_4$ 10 dm$^3$/dm$^3$ R (SV 3 h$^{-1}$); (—o—) non-treated resin; (---•---) alkali-treated resin.
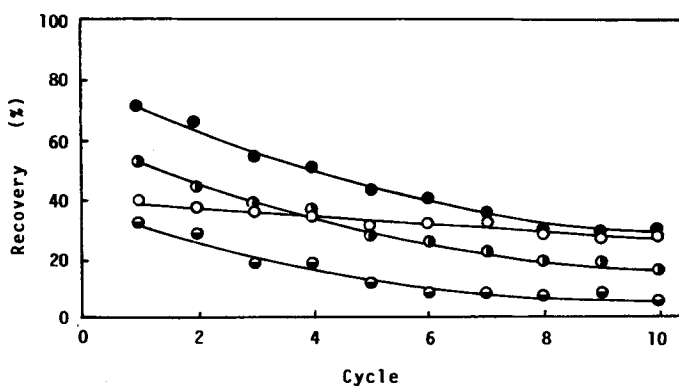
Fig. 4.   Recycle for recovery of uranium from sea water by column method: loading, sea water 20 dm$^3$, SV 300 h$^{-1}$; temp 25°C; elution 0.5 mol dm$^{-3}$ H$_2$SO$_4$ 10 dm$^3$/dm$^3$ R, SV 3 h$^{-1}$; resin 1.5 cm$^3$ (RNH–4G treated with 0.5 mol dm$^{-3}$ H$_2$SO$_4$ after alkali treatment); (○) RNH–4G (10 mol %); (●) RNH–4G (20 mol %); (◑) RNH–4G (30 mol %); (◒) RNH–4G (40 mol %).

1.5 cm$^3$ of RNH–1G and –4G at the high flow rate (SV 300 h$^{-1}$) for the better evaluation of adsorption ability. The recovery are shown in Figure 3. RNH–1G and –4G after alkali treatment, which exhibited the effective adsorption behavior in spiked sea water, showed the high adsorption ability for uranium in natural sea water. In particular, RNH–4G after alkali treatment was found to have a higher adsorption rate. These results suggest that the formation of not only the favorable macropore but the micropore is important in order to carry out the effective recovery of uranium in natural sea water.

### Durability of RNH–1G and –4G

For the industrial recovery of uranium from sea water, the adsorbent which possessed the high chemical and physical stability is desirable because of long-term recycling procedures. First, in order to test a durability of RNH–4G, the adsorption–elution procedure was repeated 10 times. (In this case, RNH–4G after alkali treatment were pretreated with 0.5 mol dm$^{-3}$ sulfuric acid solution, which was used as eluting reagent at the elution of uranium before recycles.) As shown in Figure 4, RNH prepared with 20 mol % of 4G gave 75% of recovery at the first cycle, but shows a gradual decrease of the recovery during recycles. RNH prepared with 30, 40, and 50 mol % of 4G also exhibited a decrease of the recovery. These decreases of recovery reflect an instability of amidoxime groups against the acidic solution used at the elution of uranium. On the other hand, RNH prepared with 10 mol % of 4G (RNH–4G10) showed little decrease of recovery during recycles, although this resin gave only 40% of recovery at the first cycle because of the depression of swelling by the pretreatment with 0.5 mol dm$^{-3}$ H$_2$SO$_4$. This result indicates that amidoxime group contents of RNH–4G10 was very much higher than that of other RNH–4G; consequently, the decrease of amidoxime groups during recycles groups had little effect on the recovery of uranium in 20 dm$^3$ of sea water loaded.

The chemical stability of RNH–1G and –4G against the acidic solution was assessed from the change of anion exchange capacity after it was immersed in
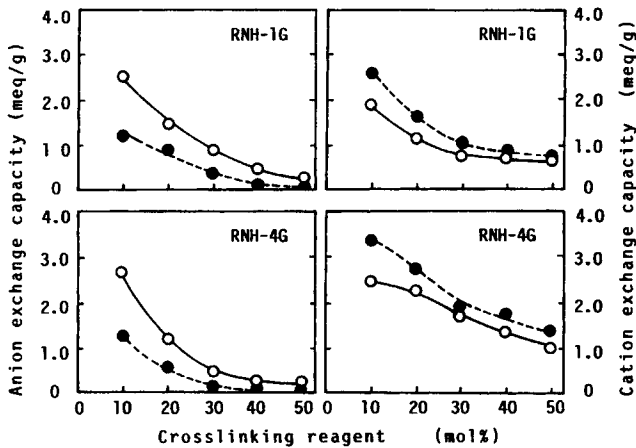
Fig. 5. Effect of crosslinking reagent on the ion exchange capacity after acid treatment:
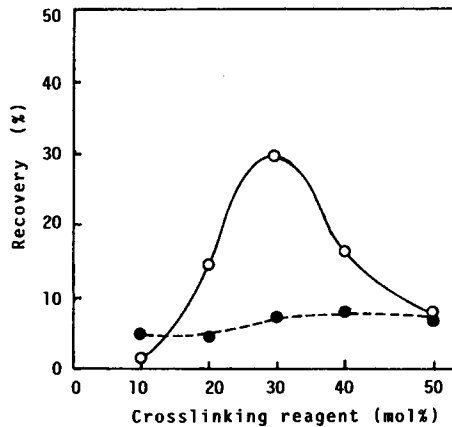(—○—) nontreated resin; (---●---) acid-treated resin.



Fig. 6. Recovery of uranium from sea water with RNH–1G and –4G after acid treatment:
loading, sea water 20 dm³, SV 300 h⁻¹; temp 25–30°C; elution 0.5 mol dm⁻³ H₂SO₄ 10 dm³/dm³
R, SV 3 h⁻¹. Resin (1.5 cm³): (—○—) RNH–1G; (---●---) RNH–4G.

hydrochloric acid solution at 60°C for 5 h (abbreviated as acid treatment).
The results are shown in Figure 5. The anion exchange capacity of these RNH
decreased by acid treatment; consequently, the low stability of amidoxime
groups against the acid solution was confirmed.

Next, these RNH after acid treatment were applied to recovery of uranium
from sea water. As shown in Figure 6, RNH prepared with 30 mol % of 1 G
(RNH–1G30) gave about 40% of recovery for uranium in sea water in spite of
a decrease of anion exchange capacity by acid treatment. On the other hand,
RNH–4G was almost not be able to recover uranium. These results indicate
that the adsorption rate of uranium was affected by the pore structure of
resins rather than the amount of amidoxime groups when the amount of
loading sea water was small. It was confirmed by the measurement of specific
surface area that the macroreticular structure of RNH–G was not changed by
acid treatment, and it was considered that RNH–4G had the favorable size of

micropore for the adsorption of uranium by the dissociation of weak acidic groups in the case of alkali treatment, but the same micropore was not formed in the case of acid treatment.

It is concluded that the formation of the macroreticular structure and micropore is necessary for the recovery of uranium with RNH. RNH–4G, which has no macroreticular structure, had the high adsorption rate of uranium, because of the formation of micropore by the large swelling after alkali treatment, whereas RNH–4G was defined to be low physical and chemical stability.

## Modification of RNH by the Simultaneous Use of Hydrophobic and Hydrophilic Crosslinking Reagent

RNH prepared with DVB as crosslinking reagent (abbreviated as RNH–DVB) have an effective macroreticular structure and high physical stability, and, in addition, chemical stability of RNH–DVB was confirmed to increase with an increase in the degree of crosslinking.[10] RNH–DVB is effective in the view of large scale recovery of uranium from sea water. However, RNH–DVB prepared with the above 15 mol % of DVB indicated a low adsorption rate because of the decrease of hydrophilicity. For the preparation of RNH which have effective macropore and micropore for the recovery of uranium, simultaneous use of hydrophobic crosslinking reagent (DVB) and hydrophilic crosslinking reagent (1G or 4G) was examined (abbreviated as RNH–DVB–1G and RNH–DVB–4G, respectively). The amount of DVB used was 10 mol % and the total amount of crosslinking reagent was 10–25 mol %. The specific surface area and anion exchange capacity of these resins are listed in Table III. The adsorption of uranium from spiked sea water is shown in Figure 7. The specific surface area of RNH–DVB–1G increased with an increase in the amount of 1G used with 10 mol % of DVB. The simultaneous use of DVB and 1G contributed to the formation of macroreticular structure. In addition, from the results that RNH–DVB–1G after alkali treatment showed high adsorption rate for uranium, it was recognized that 1G contributed to the formation of micropore. On the other hand, the specific

TABLE III
Specific Surface Area of RNH–DVB–1G or –4G

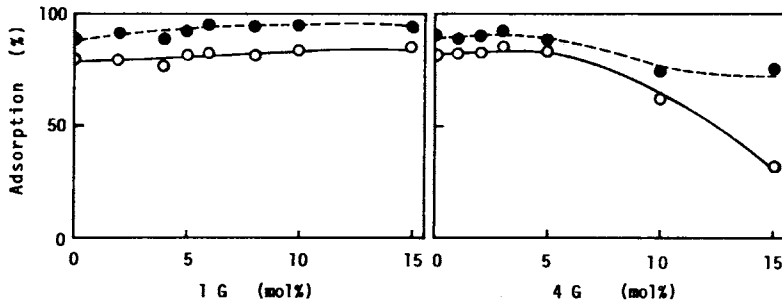| DVB | 1G or 4G | Specific surface area (m²/g) | |
|---|---|---|---|
| (mol %) | | RNH–DVB–1G | RNH–DVB–4G |
| 10 | 0 | 39.0 | 43.1 |
| 10 | 1 | — | 48.9 |
| 10 | 2 | 39.4 | 47.8 |
| 10 | 3 | — | 46.5 |
| 10 | 4 | 40.7 | — |
| 10 | 5 | 47.2 | 53.2 |
| 10 | 6 | 60.7 | — |
| 10 | 8 | 69.3 | — |
| 10 | 10 | 81.3 | 9.8 |
| 10 | 15 | 114.0 | 0.0 |

Fig. 7. Effect of crosslinking on the adsorption of uranium: sea water 25 cm³ (250 μg of uranium was added in it); shaking 30°C, 1 h; Resin (RNH–DVB–1G and –4G), 0.1 g (DVB: 10 mol %, 1G or 4G: 0–15 mol %); (—○—) nontreated resin; (---●---) alkali-treated resin.
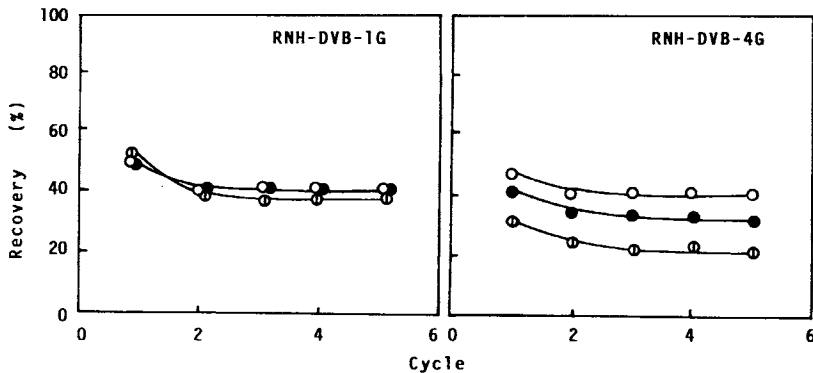


Fig. 8. Recycle for recovery of uranium from sea water by column method: loading, sea water 20 dm³, SV 300 h⁻¹; temp 25–30°C; elution 0.5 mol dm⁻³ H₂SO₄ 10 dm³/dm³ R, SV 3 h⁻¹; resin 1.5 cm³, RNH–DVB–1G and –4G (DVB, 10 mol %), 1G or 4G: (○) 5 mol %; (●) 10 mol %; (Φ) 15 mol %.

surface area of RNH–DVB–4G prepared with the range from 2 to 5 mol % of 4G had 40–50 m²/g, but that of RNH–DVB–4G prepared with more than 5 mol % of 4G decreased remarkably. The decrease of the specific surface area resulted in a decrease of the adsorption of uranium. Though the adsorption of uranium increased by alkali treatment of RNH–DVB–4G, the degree of increase was smaller than that observed in the case of RNH–4G because a large degree of swelling became difficult by DVB used simultaneously with 4G as the crosslinking reagent. The recovery of uranium from sea water showed the tendency as same as the adsorption of uranium from spiked sea water, as shown in Figure 8. Each RNH–DVB–1G have been shown the high adsorption ability for uranium, whereas the adsorption ability of RNH–DVB–4G decreased with an increase in the amount of 4G used. In the case of both RNH–DVB–1G and RNH–DVB–4G, repeated use did not cause deterioration. These results suggest that the simultaneous use of DVB and 1G or 4G contributed to the increase of chemical and physical stability. In particular, RNH–DVB–1G has the macropore and micropore for the recovery of uranium, and the characterization of RNH–DVB–1G for practical application as an adsorbent for uranium from sea water is under investigation.

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