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Development of Sorbers for the Recovery of Uranium from Seawater. Part 2. The Accumulation of Uranium from Seawater by Resins Containing Amidoxime and Imidoxime Functional Groups

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Abstract

Hydroxylamine derivatives of cross-linked poly(acrylonitriles), so-called poly(acrylamidoxime) resins, are suitable for the accumulation of uranium from natural seawater of pH = 8.1–8.3. Depending on the method of manufacture, these sorbers yield excellent uranium loadings up to some thousand ppm which roughly equals the average uranium content of actually explored uranium ores. The rate of uranium uptake, which is 5–30 ppm/d at room temperature, increases with increasing temperature of seawater. Uranium can be eluted by 1 *M* HCl with an elution efficiency of more than 90%. Owing to a certain instability of the uranium binding groups in acid eluants, the uranium uptake decreases with increasing number of sorption-elution cycles. Hydroxylamine derivatives of poly(acrylonitrile) are shown to contain simultaneously at least two kinds of functional groups: open-chain amidoxime groups which are stable and cyclic imidoxime groups which are unstable in 1 *M* HCl. Experimental evidence is presented that the uptake of uranium from natural seawater is closely related to the presence of cyclic imidoxime configurations in the polyacrylic lattice. Polystyrene and poly(glycidylmethacrylate)-based amidoxime and imide dioxime resins are less effective in extracting uranium from natural seawater.

INTRODUCTION

Previous studies on the possibility of extracting uranium from seawater clearly identified the sorptive concentration by means of a suitable solid sorber as the only feasible process for large-scale recovery (*1*) and

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recognized the crucial importance of adequate sorber characteristics for the elaboration of an acceptable engineering design (*2*). Since the properties of hitherto known inorganic sorbers such as hydrous titanium oxide still fall short of those required for a practical recovery system (*2, 3*), our research work within the uranium from seawater project of the Nuclear Research Centre of Jülich was early focused on the development of more suitable sorber materials on the basis of ion-exchange resins. These meet the stringent requirements of high physical and chemical stability in seawater, fast and more selective uptake of uranium, and a sufficient loading capacity. Systematic screening tests comprising about 200 organic polymer lattices functionalized with strongly and weakly acidic and basic as well as with chelating groups revealed hydroxylamine derivatives of poly(acrylonitriles), so-called poly(acrylamidoximes), to be the most promising candidate sorbers (*2, 3*).

Monomeric amidoximes and imide dioximes are known to form colored complexes with many transition metal cations and have been used as analytical reagents for the determination of several metals (*4, 5, 9*). Uranyl ions are reported to form strong complexes with benzamidoxime (*6*), salicylamidoxime (*7*), nicotinamidoxime (*8*), and succinimide dioxime (*9*). U.S. patents claim the use of long-chain amidoximes such as capramidoxime and phenylacetamidoxime (*10*) and of amidoxime esters with enhanced solubility in hydrocarbon solvents (*11*) for the solvent extraction of uranyl and other metal ions from aqueous solutions.

Belgian papers demonstrate the feasibility of producing polymeric amidoximes from poly(acrylonitriles) for application in the photographic (*12, 13*) and textile dyeing industry (*14*). A German patent from 1960 reports the recovery of heavy metals from solutions by granular poly(acrylamidoximes) (*15*). American inventions from 1963 pertain to the extraction of metals from dilute solutions by poly(amidoximes) derived from fibrous homopolymers and copolymers of acrylonitrile and from fibrous polymers to which acrylonitrile has been added as a side chain such as cyanoethylated cellulose or cyanoethylated insolubilized poly(vinyl alcohol) (*16, 17*). In particular, the amidoxime of a cyanoethylated cotton flannel fabric is reported to recover 67% of uranium from a seawater-like solution containing 1.5 ppb of uranium in the form of uranyl acetate (*16*).

Divinylbenzene cross-linked poly(acrylamidoxime) resins were successfully applied to the determination of trace metals in natural waters (*18–20*). A condensation polymer containing oxamidoxime functional groups was claimed to separate uranium from artificial seawater (*21*).

By 1977 a resin became commercially available for which the complexing ability was attributed to amidoxime groups [Duolite ES 346 (*22, 23*)].

Preliminary seawater trials within our screening program rapidly demonstrated the ability of the functional groups of this resin to compete with carbonate in complexing uranyl ions at $\mathrm{pH} \geq 8$ (*2, 3, 24*); furthermore, it turned out to be superior to other sorbers with respect to the selectivity of uranium uptake from natural seawater and loading capacity (*2, 3, 25–28*). These encouraging results initiated our research program in polymer chemistry which was mainly devoted to the further development and optimization of amidoxime- and amidoxime-related resins with the objective to provide a substantially improved sorber material for application in a uranium from seawater recovery plant.

The present paper is intended to summarize these KFA activities, to document the actual status of sorber development, and to identify the areas of needed future research work such as the problem of the long-term recyclability of amidoxime sorbers in relation to the arrangement of uranium binding sites. The very decisive importance of this point seems not to be well realized in recent Japanese papers dealing with the recovery of uranium from seawater by poly(acrylamidoxime) granules (*29–35*) and fibers (*33–35*).

EXTRACTION OF URANIUM FROM SEAWATER BY THE DUOLITE ES 346 POLY(ACRYLAMIDOXIME) RESIN

Experimental

The water content of the wet resin was calculated from the weight loss found after 24 h of exposure of finely ground samples to 50°C and reduced pressure (10 mmHg). The carbon, nitrogen, and hydrogen contents were determined by a Perkin-Elmer Model 240 D elemental analyzer. Apparent densities were measured pycnometrically; bulk densities were calculated from the weight of samples of 5 mL of wet resin. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer using the KBr pellet technique. Specific surface areas were obtained from BET measurements (Micrometrics, Type 2100 D). Pore volumes and pore size distributions were measured by mercury porosimetry (Carlo Erba, Model Series 200).

Long-term matrix stability tests of the Duolite ES 346 resin in seawater were run in a test plant located in the Gulf Stream near Miami (Light House Fowey Rocks). Differential pulse polarographic measurements (PAR

Models 174 A and 303) yielded valuable information on the chemical stability of the amidoxime and related functional groups in seawater-like and elution solutions such as aqueous ammonium carbonate and hydrochloric acid. Hydroxylamine resulting from hydrolytic cleavage of oxime bonds was reduced at $pH = 5.3$ and $E_p = -1.60$ V (vs SCE) according to (*36*)

$$NH_2OH + 2e^- + H_2O \rightarrow NH_3 + 2OH^-$$

The uranium uptake of the resin was pursued by means of batch and column experiments. On a laboratory scale a quantity corresponding to 1 g of dry resin was either shaken several times with 1 L of unspiked natural seawater for 2 h or packed in small columns, 8 mm in diameter, and contacted with seawater at an upward flow rate of 0.5 L/h.

Larger scale experiments comprising 250 mL of resin fractions fluidized in 1.25 L conical columns ($\tan \alpha = 0.035$; lower diameter, 4.00 cm; upper diameter, 7.35 cm; height, 48.00 cm) were performed in collaboration with GKSS (Forschungszentrum Geesthacht) and UEB (Uranerzbergbau GmbH, Bonn) in the German North Sea (Biologische Anstalt Helgoland).

The uranium content of the loaded resin was determined fluorimetrically after ashing the samples. The accurate determination of uranium in natural and depleted seawater necessitated a preconcentration step using silica gel columns; in the range of 0.1–10 μg/L, the error turned out to be less than 10% (*37, 38*).

In order to study the mechanism of uranium retention, a solution of 227.7 mg of $Na_4[UO_2(CO_3)_3]$ (*39*) in 100 mL of distilled water was shaken with 2 g of the wet resin. After 7 d of equilibration the uranium concentrations of both the resin and the solution were determined fluorimetrically, the carbonate concentration of the solution was measured by use of a Beckman TOC-Analyzer.

Uranium concentration versus particle diameter profiles were recorded by electron probe microanalysis* of cut beads of a resin sample which had accumulated about 300 ppm of uranium from natural seawater.

Elution experiments were carried out in cylindrical columns (diameter, 2.50 cm; height, 80 cm) at elution rates ranging from 1 to 6 bed volumes per hour. All reagents were of highest purity available.

*The authors are indebted to Mr H. Gruebmeier from IRW of KFA for performing these measurements.

Results and Discussion

Resin Specification

Duolite ES 346 is a cross-linked macroporous resin for which the complexing ability is attributed to amidoxime groups (*22*). It is supplied in the form of cream-colored beads of diameters ranging from 0.2 to 1.2 mm. The sieve analysis of the material yields the fractions <0.3 mm (0.2%), 0.3–0.4 mm (2.4%), 0.4–0.6 mm (53.4%), 0.6–0.8 mm (34.5%), 0.8–1.0 mm (7.5%), and >1.0 mm (2.0%). Table 1 compares some properties of the supplied resin to those of a further purified sample. Fabrication residues are removed by the successive treatment of the resin with hydrochloric acid and sodium hydroxide solutions, resulting in a distinct increase in both pore volume and water regain. For practical uranium uptake experiments the resin was—unless otherwise quoted—employed in the delivered form without purification steps. From the nitrogen content of 19.62%, a theoretical capacity as high as 7 mmol of amidoxime groups per gram of dry resin can be calculated, assuming no other nitrogen-containing functionalities. The practical UO_2^{2+} capacity is quoted to be 0.2 mmol/g at pH = 2.0 (*23*) which would imply a maximum uranium loading of nearly 50,000 ppm. The resin has proved to be mechanically resistant against seawater; within 6 months of service in a fluidized bed, no deterioration of the resin beads surface was detectable. Its functional groups appear to be rather stable at the pH of natural seawater; the quantity of hydroxylamine released by hydrolytic cleavage of oxime bonds is negligible and amounts to 0.09 mmol NH_2OH per gram of dry resin in 42 d.

TABLE 1
Properties of the Duolite ES 346 Complexing Resin

	Supplied resin	Purified sample
Carbon content (%)	52.70	52.42
Nitrogen content (%)	19.62	21.19
Hydrogen content (%)	7.38	7.43
Water regain (g H_2O/g of dry resin)	1.00	1.44
Apparent densities (g/mL of wet resin)	1.10	1.05
(g/mL of dry resin)	0.55	0.43
Bulk density (g of dry resin/mL)	0.35	0.30
BET surface area (m^2/g)	49	57
Pore volume (cm^3/g)	0.43	0.70
Mean pore radius (Å)	300	300

Uranium Uptake from Seawater, Loading Capacity and Selectivity

Owing to the relatively high carbonate concentration in normal seawater of pH $\approx$ 8.2, uranium predominantly occurs as the thermodynamically very stable $[UO_2(CO_3)_3]^{4-}$ complex anion which, however, easily releases free UO_2^{2+} cations if the seawater becomes acidified (*1, 2*). Ordinary cation exchangers like Amberlite IRC 75 with —COOH functional groups (Fig. 1) are able to accumulate uranium from seawater at sorber adjusted pH values lower than 7, but they display a decrease in sorption efficiency with increasing pH during successive contacting of 1 g of the resin with 1 L of seawater; after 9 batch experiments the uranium content of the resin even decreases, indicating some elution of the loaded sorber by seawater at pH > 7.0. Obviously, such a material is not suitable for a recovery of uranium from seawater.

A successful sorber must be capable of operating at the normal pH of seawater since any direct or indirect acidification of the enormous volumes of seawater to be processed must be rejected for ecologic and economic reasons (*2, 3*). Figure 1 illustrates that the Duolite ES 346 resin meets this stringent requirement. Neglecting a minor acidification at the beginning, the pH of

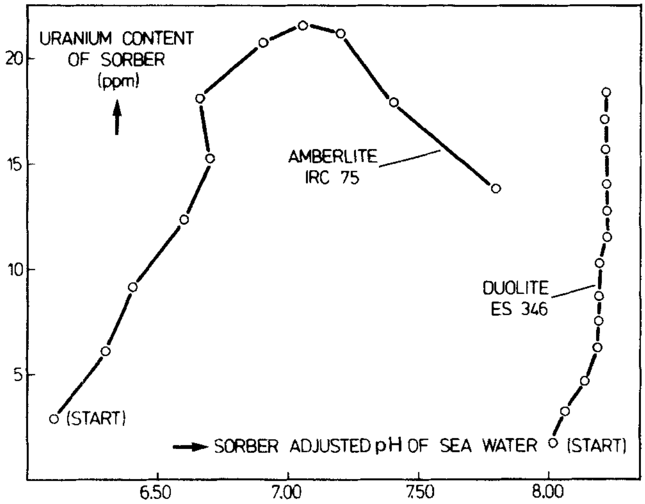


FIG. 1. Uranium content of sorbers versus pH of seawater during successive batch contacting of 1 g of sorber with 1 L of seawater. The uranium content of the sorbers was calculated from the uranium concentrations of the depleted seawater.

seawater remains remarkably constant at its normal value of pH = 8.2 whereas the uranium content of the resin increases continuously.

Although amidoxime resins are claimed to have some anion exchange capacity (*22, 34*), uranium is probably retained as the UO_2^{2+} cation. This is inferred from experiments with pure $Na_4[UO_2(CO_3)_3]$ solutions at uranium concentrations much higher than that of seawater. After 7 d of equilibration of 1 g of Duolite ES 346 with 100 mL of an aqueous solution of $Na_4[UO_2(CO_3)_3]$ containing 1000 ppm of uranium, the resin had sorbed about 72% of the uranium whereas the carbonate content of the solution remained unchanged. These results are compatible with a sorptive mechanism involving essentially direct ligand exchange reactions at the binding sites of the resin without previous decomposition of the $[UO_2(CO_3)_3]^{4-}$ complex by hydrogen ions.

The rate of diffusion of the voluminous uranyl tricarbonate anion through the resin pores to the active sites and the rate of ligand exchange reactions at these sites are both expected to increase with increasing temperature. Consequently the rate of uranium uptake from natural seawater is found to increase by some 50% in going from 15 to 30°C (Fig. 2). Therefore, any practical uranium from seawater recovery plant using the Duolite ES 346 resin should preferentially be located in warm ocean currents such as the Gulf Stream, and it is for this reason that our long-term loading experiments on the island of Heligoland (Figs. 3 and 4; Table 2) were performed with prewarmed seawater of 28°C.

Rapid loading kinetics are highly desirable in order to minimize the sorber inventory. The rate a of uranium uptake has been shown to be dependent on the sorption efficiency η, on the time τ of contact between the sorber and the seawater, and on the concentration γ_B of the sorber in the fluidized recovery bed (*2*) and may be approximated by

$$a \approx \eta \tau^{-1} \gamma_B^{-1}$$

The parameters η, τ, and γ_B are expected to decrease with increasing flow rate $\dot{V}_{sw}$ of seawater. But whereas the time of contact is roughly inversely proportional to the flow rate of seawater [2]

$$\tau \sim (\dot{V}_{sw})^{-1}$$

the function

$$\eta / \gamma_B = \mathrm{f}(\dot{V}_{sw})$$

must be derived from experiments. Our results (Fig. 3) suggest the ratio η/γ_B

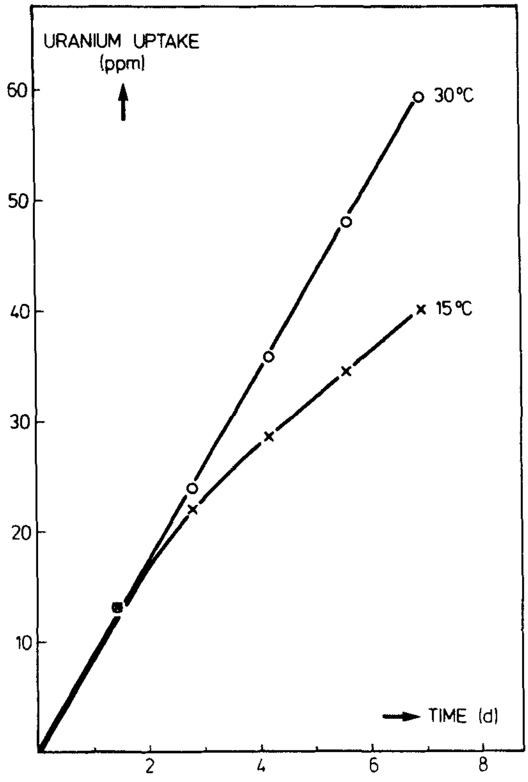


FIG. 2. Uranium uptake of the Duolite ES 346 resin at 15 and 30°C. Cylindrical columns, 8 mm in diameter; 5 mL of resin; particle size, 0.8–1.2 mm; upward flow rate of seawater, 0.5 L/h. The uranium uptake of the resin was calculated from the uranium concentration of the depleted seawater.

to be independent on $\dot{V}_{sw}$ in the measured range of 7 L/h (0.08 cm/s) to 160 L/h (1.84 cm/s) since the sorption rates are found to increase almost linearly with increasing flow rate of seawater.

In a fluidized system the flow rates of seawater are limited by the low apparent density of the resin and the size of the resin particles (Stokes' law). In order to maintain stable fluidized beds over longer periods of sorption, the long-term loading experiments (Fig. 4) were not run at the maximum but at somewhat lower flow rates of seawater as indicated by the arrows in Fig. 3. Under these conditions the sorber beds were uniformly fluidized up to a height of 44 cm which corresponds to a swelling of the sorber bed by a factor of 4.35. The uranium uptake of the Duolite ES 346 resin as a function of time and particle size is illustrated in Fig. 4; sorber bed characteristics are

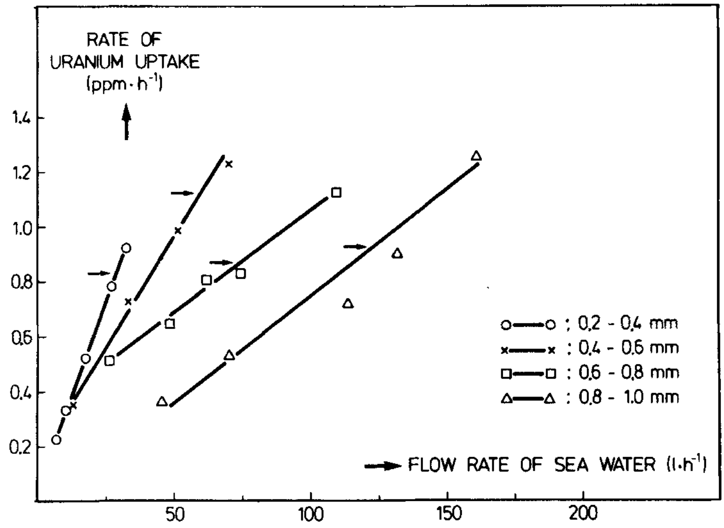


FIG. 3. Rate of uranium uptake of the Duolite ES 346 resin as a function of particle size and flow rate of seawater. Columns and sorbers inventory as described in Table 2. The uranium uptake was directly determined by uranium analysis of resin samples (5 mL per measurement). The arrows indicate the working conditions for long-term loading experiments.

collected in Table 2. The uranium loadings obtained after a sorption period of 49 d are not yet saturation values since the sorption efficiencies still amount to 29% (bead diameter: 0.2–0.4 mm), 9% (0.4–0.6 mm), 10% (0.6–0.8 mm), and 6% (0.8–1.0 mm).

The uranium loading measured after 49 d of sorption is found to decrease with increasing resin particle size. The roughly inverse relation, uranium uptake ≈ (particle radius)$^{-1}$ suggests that the sorption of uranium is essentially limited to the external surface of the resin particles, since the total external surface S_E per sorber inventory can be calculated from

$$S_E = \frac{\text{total volume of sorber inventory}}{\text{mean volume of a sorber particle}} \times \text{mean surface of a sorber particle}$$

which is

$$S_E \approx (\text{mean particle radius})^{-1}$$

assuming spherical particles. This is confirmed by electron microprobe analysis of uranium-loaded resin beads demonstrating the uranium accu-

TABLE 2
Uranium Uptake of the Duolite ES 346 Complexing Resin[a]

Sorber particle diameter (mm)	Flow rate of seawater $\dot{V}_{sw}$ (m^3/d)	Linear velocity of sea water[b] u (cm/s)	Time of contact τ (s)	Mean sorption efficiency η (%)	Uranium loading b (ppm)	Mean rate of uranium uptake a (ppm/d)
0.2–0.4	0.62	0.29	129	69.7	775	16
0.4–0.6	1.44	0.67	56	19.3	514	11
0.6–0.8	1.72	0.81	47	15.0	462	9
0.8–1.0	2.90	1.36	28	7.0	362	7

[a] Conical columns; tan $\alpha = 0.035$; lower diameter, 4.00 cm; upper diameter, 7.36 cm; height, 48 cm; sorber inventory, 250 mL of each fraction; swelling factor, 4.35; period of sorption, 49 d; 28°C.

[b] The linear velocity of seawater refers to the mean cross-section of the fluidized beds

$$\bar{F} = \frac{V_{\text{Fluid}}}{H_{\text{Fluid}}} = \frac{1088}{44} = 24.7 \text{ cm}^2$$

the sorber beds being fluidized up to a height of 44 cm.

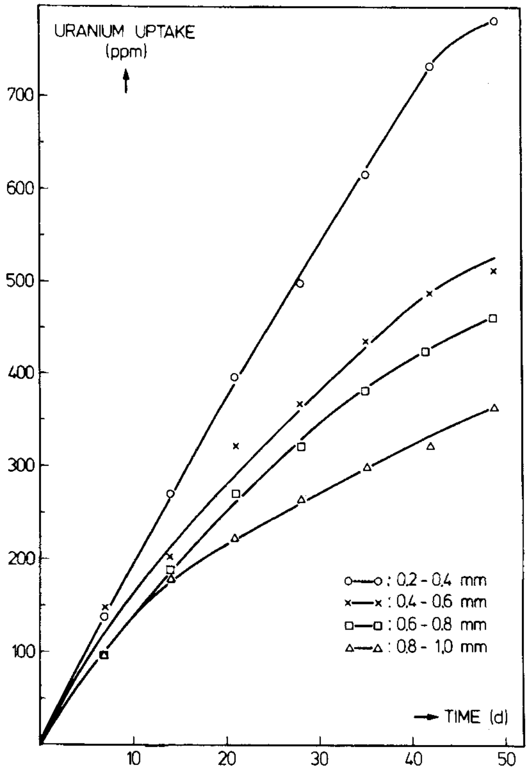


FIG. 4. Uranium uptake of the Duolite ES 346 resin as a function of time and particle size. Columns, sorber inventory, and working conditions as indicated in Table 2.

mulation to be restricted to a narrow surface layer which represents only some 10% of the bead diameter.

The participation of polymers with complexing functionalities in the sorption process drastically affects the kinetic behavior of the system as compared to classical ion-exchange. This is mainly due to the intrinsic need of the ions involved to diffuse through the polymer lattice in order to reach the active sites where the complexation reactions take place. The macroporous structure of the Duolite ES 346 resin already reduces the paths of diffusion in the polymer beads; however, for complexation to occur at as many sites as possible, the ions to be retained must still diffuse through the micropores of the polymer. Obviously the microporous structure of the resin is well adapted to smaller cations such as copper(II) which visually displays a remarkably uniform distribution all over the entire resin beads volume, but it seems to be less adapted to the large uranyl tricarbonate ion, the equatorial diameter of which amounts to almost 10 Å (*40*). A polymer lattice facilitating the diffusion of the $[UO_2(CO_3)_3]^{4-}$ ion may be produced by reducing the length of the polymer chains (*41*). Furthermore, reduced cross-linking and the incorporation of special cross-linkers and comonomers will result in enhanced flexibility of the polymer framework. Insofar as the complexing behavior of the polymeric amidoxime may be compared to that of the corresponding monomeric acetamidoxime (*42*), it can be anticipated that the uranyl ion will be immobilized to a greater degree by the cooperative action of several functional groups. A flexible matrix will fulfill this requirement more easily than a rigid one unless the latter fortuitously possesses the correct spatial arrangement of groups; this, however, is highly unlikely.

Figure 5 shows the uranium uptake of a modified sample of Duolite ES 346 with an enhanced water regain of 2.70 g/g, an increased pore volume of 0.82 cm^3/g, and an increased BET surface of 150 m^2/g. After a loading period of 260 d the resin is not yet saturated, the rate of uranium uptake having decreased from an initial 30 ppm/d to an actual 6 ppm/d. The uranium loading of 3100 ppm = 0.31% (determined by direct uranium analysis of a resin sample) is sufficiently high and roughly equals the average uranium content of actually explored uranium ores. With respect to uranium capacity and selectivity, the resin is superior to hydrous titanium oxide (Table 3). Despite the higher uranium loading by one magnitude, the resin sample accumulates less calcium and sodium than hydrous titanium oxide and the concentration factor for magnesium is only 2 times higher than in the case of hydrous titanium oxide.

Elution of Uranium

The elution of the sorbed uranium should proceed rapidly and with high yield in order to maximize the overall efficiency of the recovery process which is measured by the effective concentration gain; that is, the concentration of uranium in the elution solution as compared to the initial concentration of uranium in seawater (*1, 2*). Among many potential eluting materials tested (acids, carbonates, complexing agents like hydroxylamine, thiocyanates, salicylates, oxalates, etc.), only mineral acids and aqueous solutions of alkaline and ammonium carbonates yielded measurable elution efficiencies. Whereas carbonates require higher concentrations and temperatures, mineral acids turn out to be quite effective at room temperature and at concentrations of 1 *M*. Hydrochloric acid, in particular, combines a relatively high uranium concentration in the collected eluates with a high

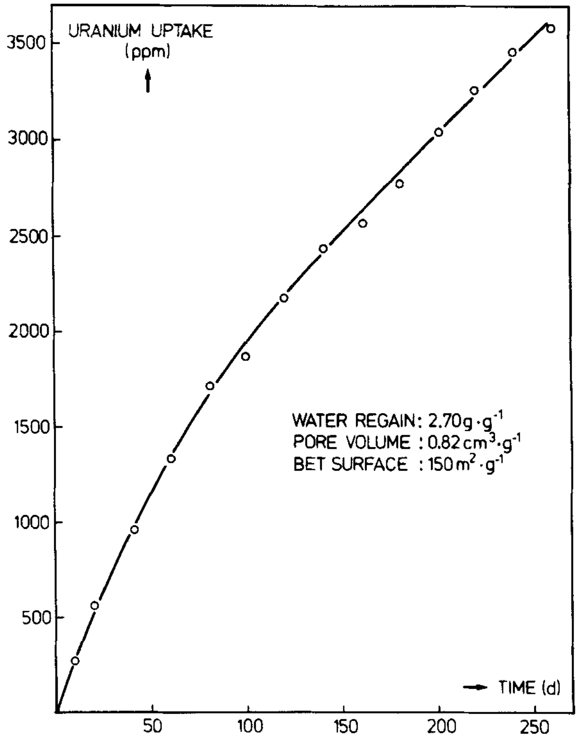


FIG. 5. Uranium uptake of a modified sample of Duolite ES 346 (3.70 g, particle size <0.4 mm). Column and working conditions as indicated in the caption of Fig. 2. Sorber inventory: quantity corresponding to 1 g of dry resin.

TABLE 3

Uranium Uptake and Selectivity of Hydrous Titanium Oxide (purchased from AERE, Harwell, U.K.) and The Duolite ES 346 Complexing Resin (modified sample)

Sorber	Uranium uptake (ppm)	Concentration factors[a]			
		U	Ca	Mg	Na
Hydrous titanium oxide	230	7.2×10^4	70.0	6.5	0.7
Modified Duolite ES 346	3100	9.7×10^5	31.8	12.8	0.3

[a] Ratios of metal concentrations in the loaded resin and metal concentrations in natural seawater.

integral elution efficiency of >90% with four bed volumes of the eluant (Fig. 6).

Large volumes of the eluant will be required for stripping the uranium from the sorber in a practical recovery system, e.g., 5×10^7 L for the elution of 1 t of uranium at an average uranium concentration of 20 ppm in the eluate. Consequently, any not easily recyclable eluant like hydrochloric acid should be as low in cost as possible; in particular, the application of more dilute acids is expected to reduce the costs of elution. Figure 7, however, illustrates that the elution efficiency decreases drastically with decreasing HCl concentration and amounts to only 60% for 0.5 *M* HCl.

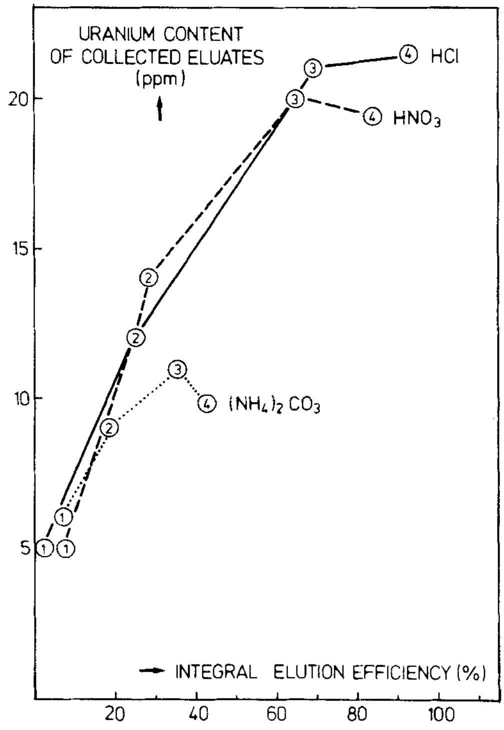


FIG. 6. Uranium content of collected eluates versus integral elution efficiency contours during successive elution of 5 mL of the resin (particle size, 0.8–1.2 mm; initial uranium loading, 266 ppm) with one bed volume (BV) of a 1-*M* solution of the quoted eluants; the encircled numbers refer to the numbers of BV; elution columns as described in the caption of Fig. 2; downward flow rate of the eluant, 4 BV/h; room temperature.

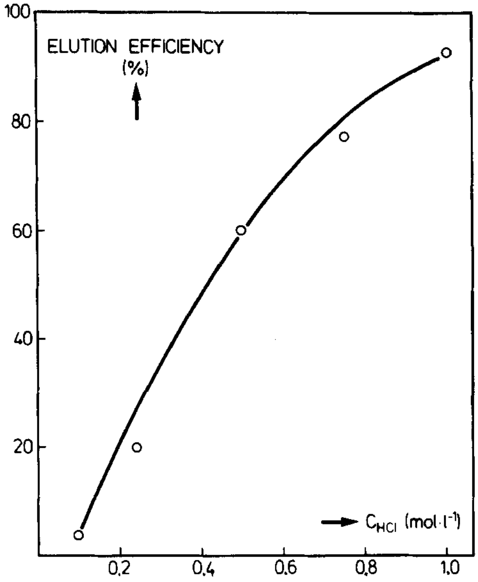


FIG. 7. Elution efficiency as a function of HCl concentration; total volume of eluates, 4 BV; sorber inventory and working conditions as indicated in the caption of Fig. 6.

The sorber inventory of a commercially realistic uranium from seawater plant will be enormous, e.g., 5 × 10^4 t of dry resin ≈ 10^8 L of supplied resin for the daily production of 1 t of uranium at a rate of uranium uptake of 20 ppm/d. Therefore the performance of the sorber should not deteriorate in service in order to permit long-term recycling procedures. Figure 8 demonstrates six loading-elution cycles which were carried out with the Duolite ES 346 resin in the standard form supplied using 1 *M* HCl as eluant. The uranium uptake is found to decrease from an initial 112 ppm to 75 ppm at the end, which corresponds to an average decrease of 6% per cycle as indicated by the dotted line. The decrease in sorption rate and capacity obviously reflects a certain instability of the resin functional groups in 1 *M* HCl. This could be confirmed by differential pulse polarographic measurements. The quantity of hydroxylamine released by hydrolytic cleavage of oxime bonds amounts to 1.3 mmol NH_2OH per gram of dry resin in 42 d of contact with 1 *M* HCl. Carbonate eluants which are less effective (Fig. 6) practically do not attack the resin functional groups.

These findings seriously question the very optimistic results issued by

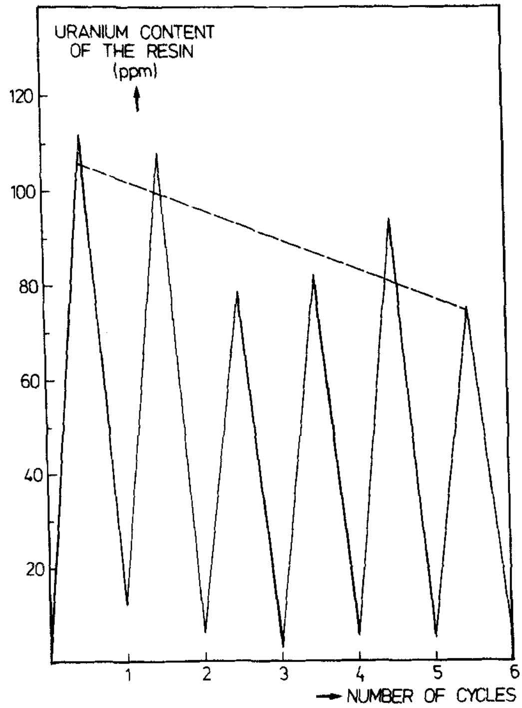


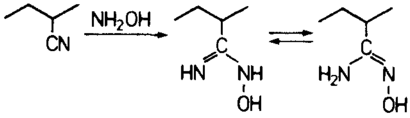
FIG. 8. Uranium loading-elution cycles with the Duolite ES 346 resin; sorber inventory, 250 mL; particle size, 0.5–0.6 mm; fluidized columns as described in Table 2. Loading: 15 m^3 of seawater in 10 d. Prewashing: 8 BV of H_2O. Elution: 6 BV of 1 *M* HCl in 1 h. Postwashing: 300 L of seawater. 8 BV of H_2O.

American (*18*) and Japanese research groups (*32–34*) reporting the ability of poly(acrylamidoxime) resins to withstand extremes in pH during several loading and elution cycles with no apparent loss in efficiency. This discrepancy probably arises from different washing procedures between subsequent elution and loading steps. In the Japanese papers the resin is said to be rinsed with water after each acid elution before being again exposed to seawater. From our experience the resin must first be neutralized with dilute aqueous sodium hydroxide (or seawater) and then washed with water to reconvert it to the neutral form; otherwise the remaining acidic character of the functional groups will lead to a slight acidification of the seawater, and the concomitant enhanced uranium uptake will compensate the hydrolytic loss of sorption capacity in the quoted loading ranges of 50–100 ppm of uranium.

OPEN-CHAIN AND CYCLIC URANIUM BINDING GROUPS IN HYDROXYLAMINE DERIVATIVES OF POLY(ACRYLONITRILES)

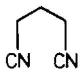
At a loss in efficiency rate of 6% per cycle the uranium uptake of the sorber would fall to 1/2 of its original value after 11 load–elute cycles. Such a rapid breakdown in sorber performance would very unfavorably affect the process economics, and for the Duolite ES 346 resin to be applied in a uranium from seawater recovery plant its uranium binding groups must be stabilized against acid eluants.

The stabilization of functional groups in a polymer lattice, however, presumes a detailed elucidation of the nature of these functional groups. The complexing ability of the Duolite ES 346 resin is attributed to amidoxime functionalities (*22,23*) produced by the action of hydroxylamine on macroporous poly(acrylonitrile):



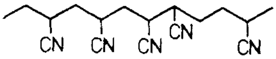
In the case of monomeric amidoximes, IR, NMR, and neutron diffraction results suggest the amino-oxime tautomer to be predominant over the intermediate hydroxy-amidine form (*4, 43–48, 57*).

Differential pulse polarographic and UV spectroscopic measurements which were carried out in our laboratories demonstrated simple compounds such as acetamidoxime to be stable in acid solutions over a period of 3 months. The obvious instability of poly(acrylamidoximes) should therefore arise from some configuration interactions between adjacent functional groups in the polymer lattice and for further investigations monomeric dinitriles like glutaronitrile

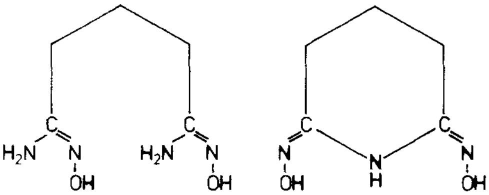


or succinonitrile

should be better monomeric representatives of poly(acrylonitrile)



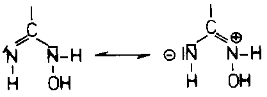
The addition of hydroxylamine to glutaronitrile is reported to afford simultaneously both an open-chain diamidoxime and a cyclic imide dioxime,



the yields of both products depending on the reaction conditions (*49, 50*). The cyclic imide dioxime is formed from glutaronitrile and hydroxylamine (molar ratio 1:2), probably via additive cyclisation of an intermediate monoamidoxime (*4*) in aqueous ethanol at 90°C in high yield. From glutaronitrile and hydroxylamine (molar ratio 1:1) at 60–70°C, the acyclic bis-amidoxime was obtained in low yield (*49, 50*).

In addition to these reported results, we found that the yield of the open-chain diamidoxime increases with decreasing temperature. The behavior of succinonitrile is very similar (*4*). Differential pulse polarographic measurements of 5×10^{-3} *M* solutions of the compounds in 1 *M* HCl revealed the open-chain diamidoxime to be rather stable in aqueous hydrochloric acid whereas the corresponding cyclic imide dioxime turned out to be distinctly more unstable by a factor of about 25.

These results give some evidence for the formation of cyclic structures during the reaction of hydroxylamine with poly(acrylonitrile) as postulated in Fig. 9. The addition of hydroxylamine probably results in the primary formation of a hydroxyamidine (1) which may readily be stabilized as the usual amidoxime tautomer (2). However, on account of the very nucleophilic nature of the imine nitrogen



the hydroxyamidine intermediate (1) can react with an adjacent nitrile group by intermolecular cyclization (3) leading either to "ladder" structures (4) which are known to be easily initiated in poly(acrylonitriles) by external nucleophiles (*51–54*) or to an imidine monoxime (5) which may add water or hydroxylamine to give the imide monoxime (6) or the corresponding imide dioxime (7). According to Refs. *4* and *55*, additional cyclization reactions between adjacent amidoxime groups by immediate splitting off one molecule of ammonia probably do not occur during the reaction of hydroxylamine with poly(acrylonitrile), but such reactions may take place to some extent in acid solutions as indicated by the slight instability of glutarodiamidoxime in 1 *M* HCl.

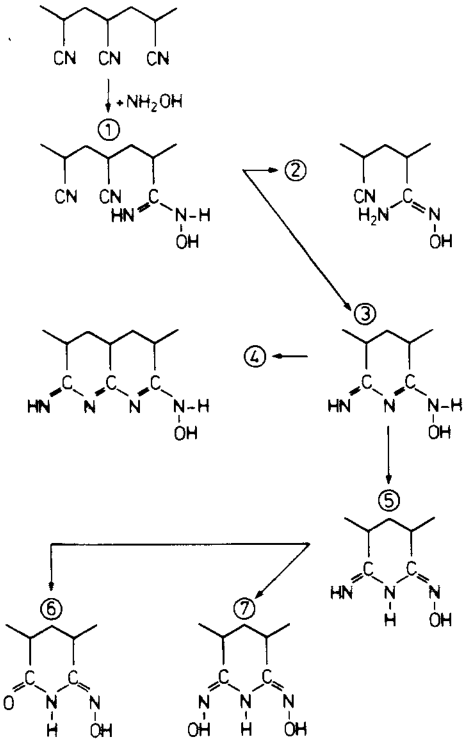


FIG. 9. Possible reactions of hydroxylamine with poly(acrylonitrile).

The simultaneous formation of open-chain and cyclic functionalities during the reaction of hydroxylamine with poly(acrylonitrile) will lower the nitrogen content of the final polymer as compared to pure poly(acrylamidoxime). This is actually observed. When a poly(acrylonitrile) containing about 19% of nitrogen or 13.5 mmol/g CN groups is reacted with hydroxylamine, the amidoxime polymer should contain about 26% of nitrogen. Actually the nitrogen content of poly(acrylamidoximes) never exceeds 19–21% although the reaction is complete as inferred from the disappearance of the $C \equiv N$ stretching mode in the infrared spectra.

Hence it may be postulated that so-called poly(acrylamidoximes) like the Duolite ES 346 resin will inevitably contain at least two types of functional groups: open-chain amidoximes and more or less hydrolyzed cyclic imidoximes. Whereas the detected instability of poly(acrylamidoximes) is most probably due to the occurrence of cyclic configurations, the complexing ability of the two kinds of functionalities cannot be easily deduced from the behavior of the corresponding monomeric representatives. In order to decide which kind of functional group is really able to compete with carbonate in complexing uranyl ions and is thus responsible for the excellent uptake of uranium from natural seawater, we synthezised resins which were functionalized by exclusion of configuration interactions unequivocally either with open-chain amidoxime or with cyclic imide dioxime groups.

COMPARATIVE INVESTIGATION OF AMIDOXIME AND IMIDE DIOXIME URANIUM BINDING RESINS

Experimental

Starting Polymers

The following matrices were used as polymeric backbones for functionalization reactions.

Poly(p-cyanostyrene). *p*-Cyanostyrene was obtained in good yield by a modified Wittig synthesis using aqueous formaldehyde and *p*-cyanobenzyl triphenylphosphonium bromide which was prepared from *p*-cyanobenzylbromide and triphenylphosphine (*56*). The copolymerization of *p*-cyanostyrene (90% by weight) and divinylbenzene (10%) was run in water suspension at 60°C (1 h), 70°C (1 h), 80°C (3 h), and 90°C (2 h), mainly in the presence of toluene or normal alkanes (50% by weight of the organic phase) as inert diluents and benzoyl peroxide (2% by weight of the organic phase) as initiator. The aqueous phase consisted of a 6% solution of Na_4SO_4 containing 1% $CaCO_3$ and 0.1% gelatine. The volume ratio of organic phase to aqueous phase was 1:2.5. The polymer beads were washed with dilute HCl, water, and methanol.

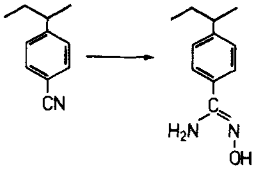
Chloromethylated Polystyrene. Commercial product (Bayer OC 1032).*

Poly(glycidyl Methacrylate). Macroporous copolymers of glycidyl methacrylate and cross-linking ethylene dimethacrylate were prepared according to procedures given by Švec (*58*, *64*) at 80°C in the presence of cyclohexanol and dodecanol as inert diluents and azodiisobutyronitrile as the free-radical generating compound.

Polyvinyl Alcohol. Commercial polyvinyl alcohol was insolubilized by cross-linking with epichlorhydrin according to Ref. *59*.

Functionalizations

Resin 1. Poly (*p*-cyanostyrene) was directly converted to the corresponding polymeric amidoxime by hydroxylamine treatment under standard conditions as follows: 1 g of the cyanopolymer was reacted for 16 h at 78°C with 100 mL of a 1 *M* ethanolic solution of NH_2OH obtained by neutralization of $NH_2OH \cdot HCl$ in ethanol with solid NaOH and separation of the precipitated NaCl.



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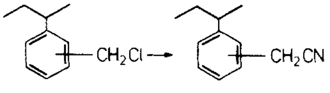
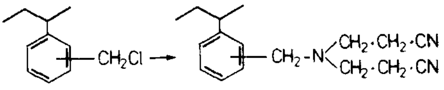
*The authors are indebted to the Bayer Company, Leverkusen, for a gift of this resin.

Resin 2. Poly(cyanomethylstyrene) was synthesized in high yield by reacting chloromethylated polystyrene (16.5% by weight of chlorine) with an excess of KCN in dimethylsulfoxide at 23°C for 48 h in a sealed container (*60*).



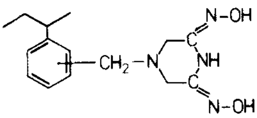
The polymeric nitrile was converted to the amidoxime as indicated above.

Resin 3. Chloromethylated polystyrene (3 g) was reacted with 3,3′-iminodipropionitrile (30 g) in 27 mL dioxane at 115°C during 20 h according to a modified procedure of Ref. 61.

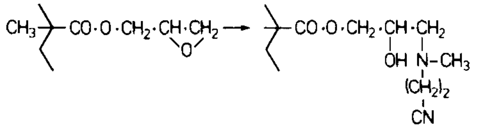


NH_2OH treatment of the polymeric dinitrile resulted in an open-chain bis-amidoxime.

Resin 4. Chloromethylated polystyrene (5 g) was functionalized with iminodiacetonitrile (23.4 g) in aqueous dimethylformamide (25 mL DMF, 2 mL H_2O) in the presence of NaI as catalyst at 47°C during 19 h in a modified procedure of Ref. *62*. NH_2OH treatment of the polymeric dinitrile yields a six-membered cyclic imide dioxime.

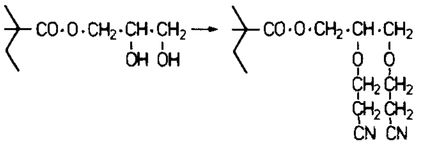


Resin 5. Poly(glycidylmethacrylate) (5.7 g) was reacted with 37 mL $CH_3 \cdot NH \cdot CH_2 \cdot CH_2 \cdot CN$ at 55°C for 8 h.



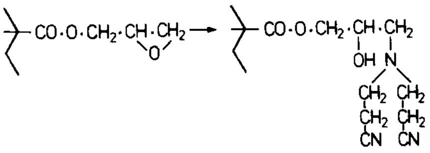
The polymeric nitrile was converted to the amidoxime as indicated above.

Resin 6. Poly(glycidylmethacrylate) (3.5 g) was hydrolyzed with 350 mL of 0.1 *M* H_2SO_4 and cyanoethylated (*63*) with 3.5 mL acrylonitrile in 50 mL of 10 *M* NaOH. The reaction product was extracted with dimethylformamide in order to remove residues of poly(acrylonitrile).



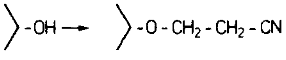
NH_2OH treatment of the polymeric dinitrile yields an open-chain bis-amidoxime.

Resin 7. Poly(glycidylmethacrylate) (7.4 g) was functionalized with 3,3′-iminodipropionitrile (20.4 g) at 105°C during 25 h.



NH_2OH treatment of the polymeric dinitrile affords an open-chain bis-amidoxime.

Resin 8. Cross-linked polyvinyl alcohol (5 g) was cyanoethylated with 30 g acrylonitrile in 40 mL of 10% NaOH at room temperature during 72 h.



The polymeric nitrile was converted to the amidoxime as indicated above.

Results and Discussion

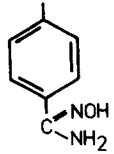
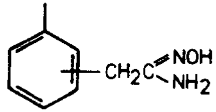
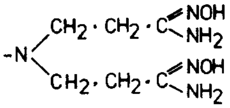
Table 4 comprises the functional groups and properties of some representative resins which we have synthesized and characterized by elemental analysis and IR spectroscopy. The functionalities are either of the open-chain amidoxime or of the cyclic imide dioxime type. Resins functionalized with monomeric dinitriles are found to yield cyclic imide dioximes upon NH_2OH treatment if the cyclization reaction gives rise to a six-membered ring of minimal strain energy. Iminodiacetonitrile (cf. Resin 4) closely resembles glutaronitrile.

The iminodiacetonitrile derivative of polystyrene contains 11% nitrogen or 2.6 mmol/g of functional groups $—N(CH_2CN)_2$; the nitrogen content of the resulting cyclic imide dioxime is then calculated to be 12.9%, whereas the corresponding open-chain bis-amidoxime should contain 15.5% N, the conversion of CN groups being complete. The experimental value of 12.8% (Resin 4 of Table 4) clearly is in favor of the ring structure. The infrared spectra of corresponding amidoxime and imide dioxime resins (Fig. 10) differ mainly in the ν(N—H) and $\delta(NH_2)$ regions. Whereas the spectra of the open-chain amidoxime resin (3) and of the monomeric acetamidoxime exhibit both the antisymmetric and symmetric stretching modes of the NH_2 group at 3480 and 3380 cm^{-1} respectively, only one broad N—H valency vibration is seen in the spectrum of the imide dioxime resin (4). The bending mode of the NH_2 group, which appears at 1585 cm^{-1} in the spectrum of Resin 3, is strongly reduced in the spectrum of Resin 4.

The resin derivatized with cyclic imide dioxime groups turns out to be unstable in 1 *M* HCl, the amount of hydroxylamine released by hydrolytic cleavage of oxime bonds being comparable to the quantity of hydroxylamine separated from Duolite ES 346 under similar conditions. These results give further experimental evidence that the observed instability of poly(acrylamidoximes) arises mainly from cyclic glutarimidoxime-like structures in the macromolecular lattice.

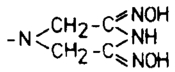
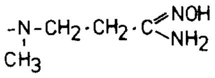
However, the seven amidoxime resins and the imide dioxime resin display no striking difference in uranium uptake from natural seawater, which is very moderate in all cases (Table 4). Polystyrene-based resins are known to be rather hydrophobic. But neither the partial substitution of divinylbenzene by

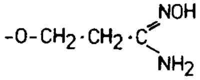
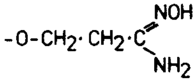
TABLE 4
Properties of Selected Amidoxime and Imide Dioxime Resins

No.	Functional group (starting matrix)	Nitrogen content (%)	Theoretical capacity (mmol/g)	Pore volume (cm^3/g)	Specific surface (m^2/g)	Behavior in 1 *M* HCl	Uranium uptake (ppm)
1	 (poly-p-cyanostyrene)	14.1	5.0	1.05	3.5	Stable	<5
2	 (chloromethylated polystyrene)	9.1	3.3	0.75	44.4	Stable	5
3	 (chloromethylated polystyrene)	13.9	2.0	0.75	44.4	Stable	<5

(*continued*)

TABLE 4 (continued)

No.	Functional group (starting matrix)	Nitrogen content (%)	Theoretical capacity (mmol/g)	Pore volume (cm^3/g)	Specific surface (m^2/g)	Behavior in 1 *M* HCl	Uranium uptake (ppm)
4	 (chloromethylated polystyrene)	12.8	2.3	0.75	44.4	Unstable	11
5	 (polyglycidyl methacrylate)	9.1	2.2	1.00	31.9	Stable	28

6	 $-O-CH_2\cdot CH_2\cdot C\begin{matrix}=NOH\\ NH_2\end{matrix}$ (polyglycidyl methacrylate)	8.4	3.0	1.00	31.9	Stable	5
7	Same as Resin 3 (polyglycidyl methacrylate)	11.7	1.7	0.97	44.1	Stable	12
8	 $-O-CH_2\cdot CH_2\cdot C\begin{matrix}=NOH\\ NH_2\end{matrix}$ (polyvinyl alcohol)	12.8	4.6	Gel-type		Stable	8

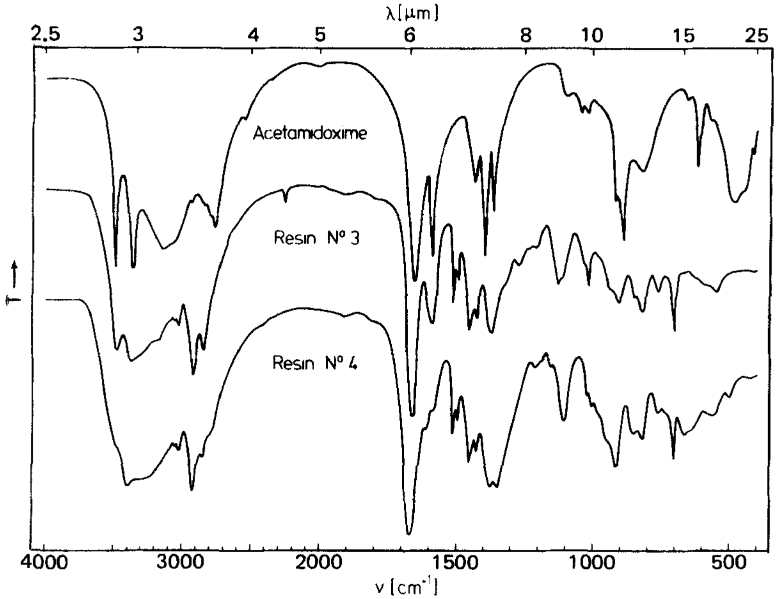
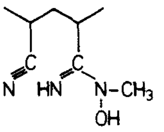


FIG. 10. Infrared spectra of acetamidoxime, Resin 3 and Resin 4.

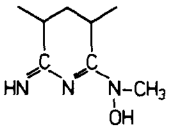
more hydrophilic cross-linking agents such as 1,5-hexadiene-3-ol or ethylenedimethacrylate nor the incorporation of comonomers with enhanced wettability such as acrylic acid or 2-butene-1,4-diol resulted in a substantially improved uptake of uranium from natural seawater. We believe that the poor performance of polystyrene as compared to polyacrylic resins is mainly due to the presence of benzene rings which partly clog the micropores of the polymer and thus block or strongly decelerate the diffusion of the voluminous uranyl tricarbonate anion in the macromolecular lattice. In the case of the more hydrophilic poly(glycidyl methacrylate) matrix, the very long side chains probably produce the same deceleration effect. This could be confirmed by experiments with acidified seawater of $pH = 3$ where uranium is present as the small UO_2^{2+} cation which will more easily diffuse even in partly obstructed micropores; under these conditions the uranium uptake of poly(styreneamidoximes) turned out to be excellent and comparable to the uranium uptake of the Duolite ES 346 resin.

The comparative investigation of amidoxime and imide dioxime resins identified the cyclic imidoxime structures as being responsible for the observed instability of poly(acrylamidoximes) in dilute acids, but allowed no discrimination to be made between open-chain amidoxime and cyclic imidoxime groups with respect to uranium uptake from natural seawater. All trials to produce poly(acrylamidoximes) containing exclusively amidoxime groups failed. The copolymerization of acrylonitrile with ethyl acrylate or other suitable monomers did not yield the desired copolymers of rigorously alternating composition. The exclusion of water (*65*) during the reaction of hydroxylamine with poly(acrylonitrile) did not lead to an enhanced formation of stable amidoxime groups as compared to the standard procedure.

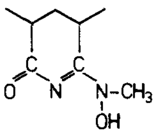
However, there is some experimental evidence that the instable cyclic structures in poly(acrylamidoximes) are responsible for the uptake of uranium from natural seawater. Substituting hydroxylamine by *N*-methylhydroxylamine in the reaction scheme of Fig. 9 will result in the intermediate formation of a *N*-methyl-*N*-hydroxyamidine

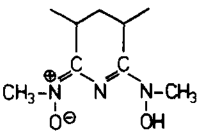


which cannot be transformed in an amidoxime isomer. But the inductive effect of the methyl group will increase the nucleophilic character of the imine nitrogen and initiate enhanced cyclizations



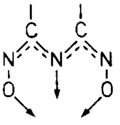
leading to functional groups such as (cf. 6 and 7 of Fig. 9)





with partly conjugated double bonds. Consequently the *N*-methylhydroxylamine derivatives of poly(acrylonitrile) are deep-orange to red in color and their infrared spectra inhibit two vibrations in the ν(C=N) region: the usual C=N stretching mode at 1655 cm^{-1} and a band at 1600 cm^{-1} which may be assigned to conjugated C=N bonds. Owing to the participation of polar structures, the N—O valency vibration is shifted to the somewhat higher value of 950 cm^{-1}.

The rate of uranium uptake of these substituted poly(acrylamidoximes) is enhanced by a factor of about 2 as compared to the Duolite ES 346 resin, supporting the assumption that cyclic imidoxime configurations are responsible for the unique performance of poly(acrylamidoximes) in accumulating uranium from natural seawater. Furthermore, it can easily be calculated that the geometry of tridentate ligands like



with one nitrogen and two oxygen atoms as binding sites agrees nicely with the arrangement of three coordinate oxygens in the equatorial plane of uranyl tricarbonate which is known to be a very stable complex.

CONCLUSIONS

Hydroxylamine derivatives of cross-linked poly(acrylonitriles), so-called poly(acrylamidoxime) resins, are able to accumulate uranium from natural seawater by a concentration factor of $>10^6$ which corresponds to a uranium loading of more than 3000 ppm. With respect to loading capacity and selectivity, the resins are superior to hydrous titanium oxide. Uranium can be eluted by dilute mineral acids like 1 *M* HCl with an elution efficiency of more than 90%. However, the uranium uptake is found to decrease with an increasing number of sorption–elution cycles, reflecting a certain instability of the uranium-binding groups in acid eluants.

The resins simultaneously contain at least two types of functional groups: open-chain amidoxime groups, which, if isolated, are stable in 1 *M* HCl, and cyclic imidoxime groups, which are unstable in 1 *M* HCl. There is some experimental evidence that the excellent uptake of uranium from natural seawater is closely related to the presence of cyclic imidoxime structures in the polymer lattice. The stabilization of these groups against acid eluants by chemical or physical modifications of the polyacrylic matrix seems hardly feasible.

Current work within the present research project is mainly concerned with the further optimization of poly(acrylamidoximes) with special emphasis on improved sorption kinetics for compensating the hydrolytic loss of sorption capacity. The actual sorption rate is in the range of 5–30 ppm/d. A better rate of uranium uptake may be achieved by systematic investigation of the relationship between porosity and specific surface area of the macroporous resins on the one hand and polymerization conditions such as kind and concentration of cross-linkers, comonomers, inert solvents, initiators, and chain transfer agents on the other hand. The standard nitrile to amidoxime conversion needs to be modified as well. The sorption properties of optimized poly(acrylamidoximes), including fibrous materials, will be discussed in the next paper.

Acknowledgments

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