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Development of Sorbers for the Recovery of Uranium from Seawater. 1. Assessment of Key Parameters and Screening Studies of Sorber Materials

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Abstract

At an average uranium content of 3.3 ppb the oceans can be considered as a very low-grade but practically unlimited source of uranium. Some essential chemical aspects of a large-scale sorptive recovery of uranium from seawater are discussed with special emphasis on required sorber properties such as high physical and chemical stability in seawater, fast and selective uptake of uranium, as well as a sufficient loading capacity. Systematic screening tests, including about 200 sorber materials on the basis of organic ion-exchange resins, identified cross-linked poly(acrylamidoximes) as the most promising candidate sorbers. Their uranium uptake closely approaches the uranium content of actually explored uranium ores.

I. INTRODUCTION

In view of the anticipated depletion of terrestrial uranium reserves, the possibility of recovering uranium from seawater has received increasing attention over the past two decades (*1–27*). Recently a topical meeting on the extraction of uranium from seawater allowed comparison of the pertinent activities of six different countries and documented the international state-of-the-art in this field (*28*).

Uranium occurs in the sea in a remarkably uniform distribution at a concentration of only 3.3 mg/m^3 (*29–31*). Russian workers report even somewhat lower values, especially for the Pacific Ocean (*32*), but the method of analysis does not seem appropriate and the preliminary results need further confirmation. The total volume of the oceans is estimated to be 1.39×10^{18} m^3, representing a total uranium content of 4.5×10^9 tons which is almost a thousandfold larger than the reasonably assured and estimated terrestrial resources in the cost range up to \$50/lb U_3O_8 (*33*). The recovery of uranium is claimed (*19*) to be restricted to the well-mixed surface layers of the oceans [upper 100 m (*19*)]. However, since these surface layers still contain as much as some 10^8 tons of uranium (*19*), a suitable extraction technology would make accessible a source of uranium which may be considered as practically unlimited with respect to uranium demand in the forseeable future.

The main uranium species in seawater is the very stable anionic tricarbonato-uranyl complex $[UO_2(CO_3)_3]^{4-}$ (*2, 34*). Marine uranium displays no detectable deviation from the normal terrestrial U-235/U-238 isotope ratio (*4, 5, 35*).

In order to extract economically significant amounts of uranium, enormous volumes of seawater must be processed, at least some 10^8 m^3 for 1 ton of uranium (see Section II-A). For such a large-scale recovery of uranium from seawater, many suggested methods of concentration (e.g., solvent extraction, ion flotation, coprecipitation) must be discarded for economic reasons or environmental impact considerations (*24*).

Only sorptive accumulation by the use of a suitable sorber seems to be feasible. Among various inorganic (*3, 24, 36–40*) and organic (*3, 24, 41–47*) sorber materials which have been tested in the past 20 years, hydrous titanium oxide combines a relatively high uranium capacity with a low solubility in seawater. Experimental work using this sorber, which was first developed by AERE, U.K. (*3, 4, 48*), is currently under way in Japan (*12–14, 49–54*), France (*55, 56*), and Germany (*22, 23, 57*). Some activity has been reported in Finland (*58*), the People's Republic of China (*59*), Russia (*60*), and India (*61*).

The most striking disadvantage of hydrous titanium oxide is its low mechanical resistance against attrition, resulting in a breakdown of sorber particles during operation in a fluidized bed, and all attempts to produce stronger materials involve a serious loss in sorption capacity (*48*). Cross-linked organic polymer lattices are expected to exhibit a better physical performance than hydrous metal oxides, and ion-selective complexing groups may be attached to such matrices by known chemical procedures.

It is the objective of the present and the following papers to summarize the work which has been done at the Nuclear Research Centre of Jülich on the development of more suitable sorber materials for the recovery of uranium from seawater on the basis of ion-exchange resins which meet the criteria of high physical and chemical stability against seawater, fast and selective uptake of uranium, and a sufficient loading capacity.

II. CRITERIA FOR SORBER SELECTION

A. General Properties

The problems pertaining to the development of a suitable recovery system are due to the very low concentration and the chemical form of uranium as well as to the large excess of competing ions such as calcium and magnesium in seawater. These facts place stringent requirements on the properties of potential sorbers.

Seawater is a low-grade source of uranium (Fig. 1), 3×10^8 m^3 contain only 1 ton of uranium, and the volumes of seawater to be processed in a commercially realistic plant will be enormous. Consequently, the separation process must be able to operate at the normal chemical composition (pH, salinity) of seawater. Any addition of reagents or removal of interfering constituents prior to the recovery of uranium must be discarded. These restrictions especially preclude any direct or indirect acidification of seawater. The addition of about 0.6 mg of hydrogen ions is necessary to neutralize 1 L of seawater to depress its pH from $pH = 8.3$ to $pH \approx 7$ (Fig. 2). However, in a projected extraction plant which will treat at least 3×10^8 m^3 of seawater per day for the extraction of 1 ton of uranium, the same weak degree of acidification would require the daily consumption of as much as about 9000 tons of pure sulfuric acid or some 18,000 m^3 of concentrated hydrochloric acid.

The sorber must be available in large quantities and at low cost. Its performance should not deteriorate in service; that is, it should be virtually insoluble in seawater and eluants, and highly resistant against physical, chemical, and biological degradation in order to permit long-term recycling procedures and to avoid contamination of the oceans. Further, since most of the uranium is sorbed only on the surface of the sorber particles (*62*), any loss due to attrition would represent a serious uranium loss.

The performance of the sorber must be suitable for bringing it into contact with large volumes of seawater in order to minimize the energy that will be necessarily consumed in processing such enormous volumes of seawater. Therefore the energy used for contacting the sorber with seawater should only be an insignificant fraction of the energy that would be generated by the marine uranium in a typical LWR, that is 2 GWd(e) per ton of natural

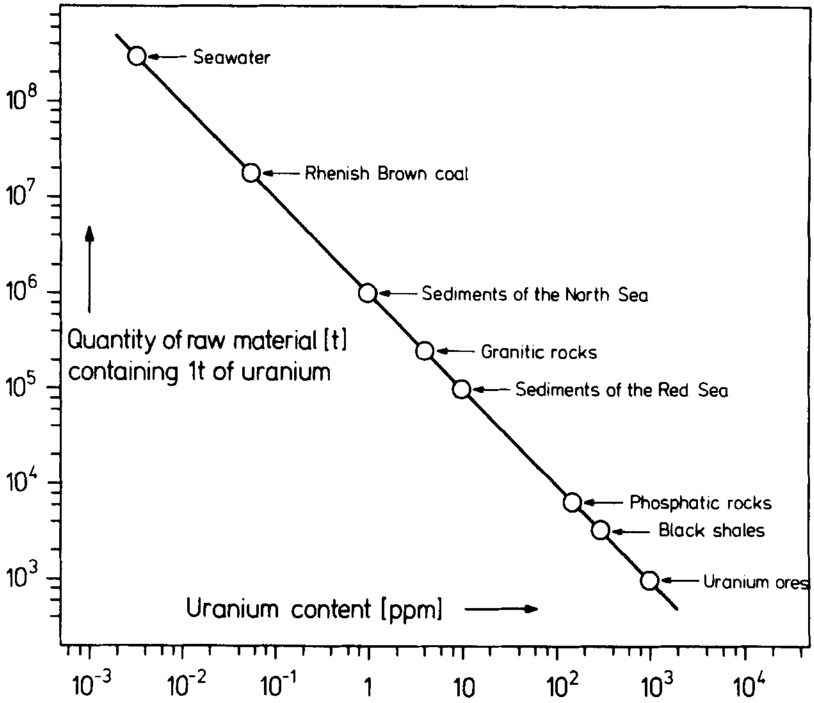


FIG. 1. Uranium content of classic and low grade uranium ores.

uranium (*63–65*) or 570 J ≈ 0.00016 kWh per 3.3 μg of natural uranium contained in 1 L of seawater.

B. Kinetics

Most imperative requirements pertain to the loading kinetics. The sorber should exhibit a rapid rate of uranium uptake in order to minimize the sorber inventory.

The amount of sorber material M_s (tons of dry sorber) which is needed is determined by the output or production rate P (tons of uranium per day) of the projected recovery plant by the uranium loading b of the sorber (ppm of uranium per cycle based upon the dry weight) and by the duration T (days per cycle) of a complete sorption-elution cycle:

$$M_s = P\frac{T}{b} \times 10^6 \qquad (1)$$

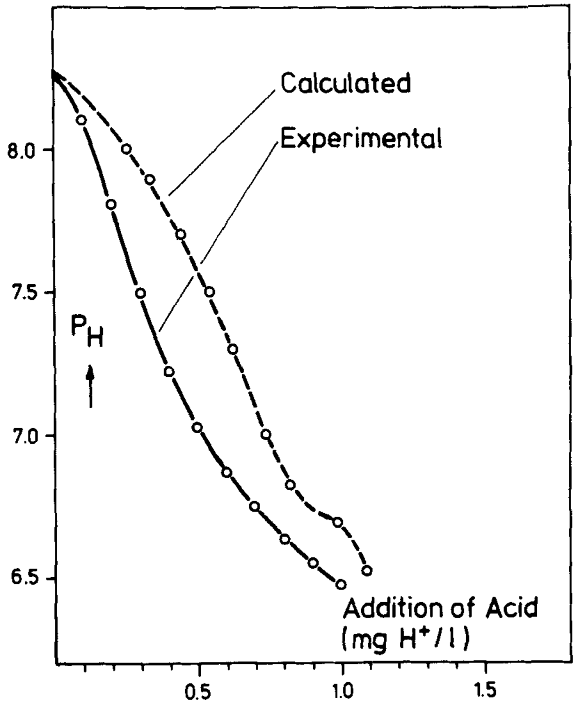


FIG. 2. Titration of seawater with 10^{-2} *M* HCl. The upper curve was calculated from the dissociation equilibria of carbonic acid in natural seawater of 35% salinity at 20° (*78*).

Since the entire period T is composed of both the time T_a which is needed for loading the sorber and the time T_e required for prewashing, elution, and postwashing:

$$T = T_a + T_e \tag{2}$$

the sorber inventory will depend on both the rate of uranium uptake a (ppm of uranium sorbed per day):

$$a = b/T_a \tag{3}$$

and the rate of uranium elution e (ppm of uranium eluted per day, 100% elution efficiency assumed):

$$e = b/T_e \tag{4}$$

according to

$$M_s = P\left(\frac{1}{a} + \frac{1}{e}\right) \times 10^6 \tag{5}$$

which may be approximated by

$$M_s = P\frac{1}{a} \times 10^6 \tag{6}$$

if the elution and washing steps proceed very rapidly as compared to the period of sorption. In such cases the quantity of sorber and the dimension of the recovery plant turn out to be inversely proportional to the rate of uranium uptake a, once the output of the plant has been fixed. However, the simplified Eq. (6) will not apply to very fast reacting sorbers for which $a \geq e$.

The accumulation rate a as defined by Eq. (3) measures the quantity of uranium M_u (g) retained per day of sorption and per ton of sorber:

$$a = \frac{b}{T_a} = \frac{M_u}{T_a M_s} \tag{7}$$

The total amount of uranium M_u/T_a which is sorbed per day is directly related to the volume v (m^3/d) of seawater processed per day, to the sorption efficiency η ($0 \leq \eta \leq 1$), and to the concentration of uranium in seawater (0.0033 g/m^3):

$$M_u/T_a = 0.0033\eta v \tag{8}$$

the time of contact τ (s) between the sorber and seawater is defined by

$$\tau = \frac{V - V_s}{v} \times 24 \times 3600 \tag{9}$$

where V (m^3) denotes the total volume of the sorber bed and V_s (m^3) the volume of the wet sorber. Assuming macroporous properties of the sorbing material, that is, minor volume changes during drying, V_s may be calculated from M_s and the apparent density γ_{dr} of the dry sorber (g/mL of dry sorber):

$$V_s = M_s/\gamma_{dr} \tag{10}$$

Defining

$$\gamma_B = M_s/V \tag{11}$$

(g of dry sorber/mL of sorber bed) as a measure of the concentration of the sorber in the working recovery bed and inserting Eqs. (8)–(11) in Eq. (7) leads to the function

$$a = 285\frac{\eta}{\tau}\left(\frac{1}{\gamma_B} - \frac{1}{\gamma_{dr}}\right) \tag{12}$$

which directly correlates the rate a of uranium uptake with the fundamental parameters η, τ, γ_B, and γ_{dr}. A suitable sorber should combine a high sorption efficiency per unit of contact time with a high apparent density. The relation $a \sim 1/\gamma_B$ points to some kinetic superiority of fluidized systems over packed bed designs where γ_B would equal the bulk density of the dry sorber, but it must be realized that too low values of γ_B will lead to a serious drop in sorption efficiency on account of decreasing sorption probability and to an unfavorable increase of the contact time τ, since the flow rate of seawater is limited by γ_{dr}. The optimum set of parameters η, τ, and γ_B must be determined by experiement.

C. Loading Capacity and Elution

The uranium loading b of the sorber should be high in order to ensure favorable process economics. The operating costs of a uranium from seawater plant will be roughly proportional to the product of the sorber inventory M_s as a measure of the quantities of washing water and elution solutions consumed per cycle (*21*) and the number z of complete sorption–elution cycles per year, which is

$$M_s z = \frac{PT \times 10^6}{b}\,\frac{360}{T}$$

inversely proportional to the uranium loading b. Furthermore, a high uranium concentration on the loaded sorber will reduce the necessity of additional concentration and purification steps.

The elution of the sorbed uranium must 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. Finally, elution must signify preferential desorption of uranium; the selectivity of the elution process should be equal to or exceed the selectivity of the uranium uptake by the sorber.

III. SCREENING STUDIES

A. Experimental

A wide range of commercially available ion-exchange resins (Table 1) containing strongly and weakly acidic and basic as well as chelating functional groups were tested in our laboratories with respect to their uranium uptake from natural seawater by means of batch and column experiments. On the laboratory scale the quantity corresponding to 1 g of dry resin was either shaken with 1 L of unspiked seawater (3.3 μg U/L) for 2 h or packed in a small column of 8 mm in diameter and contacted with seawater at a flow rate of 0.5 L/h $\approx$ 0.3 cm/s. Larger scale experiments comprising about 100 g of resin fluidized in 1–2 L columns were performed in collaboration with GKSS (Forschungszentrum Geesthacht GmbH) and UEB (Uranerzbergbau GmbH Bonn) on the island of Heligoland (Biologische Anstalt Helgoland) in the German North Sea and in a test plant located in the Gulf Stream near Miami (Light House Fowey Rocks). The linear velocity of seawater flowing through the columns varied from 0.3 to 1.5 cm/s, resulting in roughly 24–110 s contact times of the seawater with the sorbers.

A method for the rapid determination of uranium in natural and depleted seawater was developed using silica gel as an analytical tool to preconcentrate uranium for subsequent fluorometric analysis; in the range of 0.1–10/ μg/L the error turned out to be less than 10% (*66, 67*). Long-term matrix stability tests including both cross-linked polystyrene and polyacrylic lattices were run in the test plant at Fowey Rocks.

Resins not commercially available (Table 2) and incorporating various functional groups known to form powerful complexes with uranyl ions were prepared either via suspension polymerization of suitable monomeric substances in the presence of cross-linking agents or via functionalization of polymeric matrices by chemical reactions such as diazotation or Friedel-Crafts acylation. The functional groups were selected according to their ability to displace carbonate ions (*68*), leading to more or less drastic

TABLE I

Uranium Uptake of Some Representative Ion-Exchange Resins

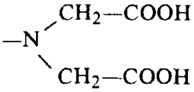
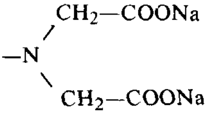
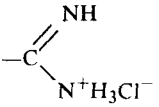
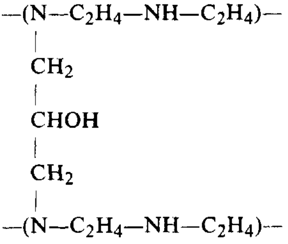
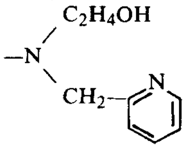
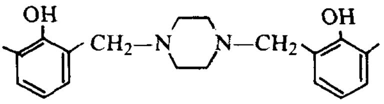
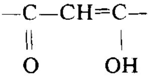
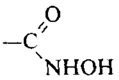
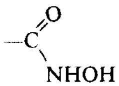
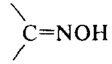
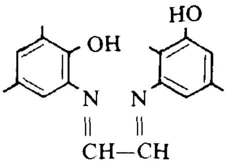
Resin	Matrix	Functional group	Uranium uptake (ppm)
IRC 84 (Rohm + Hass)	Cross-linked poly(acrylic acid)	$-COOH$	22.0
IRC 75 (Rohm + Hass)	Cross-linked poly(methacrylic acid)	$-COOH$	29.0
Ag11 A8 (Bio-Rad)	Cross-linked poly(styrene-acrylic acid)	$-COOH$ $-N^+(CH_3)_3Cl^-$	3.0
Chelex 100 (Bio-Rad)	Cross-linked polystyrene	 $-\mathrm{N}\begin{smallmatrix}\diagup \mathrm{CH_2-COOH}\\ \diagdown \mathrm{CH_2-COOH}\end{smallmatrix}$	3.5
TP 207 (Bayer)	Cross-linked polystyrene	 $-\mathrm{N}\begin{smallmatrix}\diagup \mathrm{CH_2-COONa}\\ \diagdown \mathrm{CH_2-COONa}\end{smallmatrix}$	3.0
Srafion (Ayalon, Haifa)	Cross-linked polystyrene	 $-\mathrm{C}\begin{smallmatrix}\diagup\!\!\diagup \mathrm{NH}\\ \diagdown \mathrm{N^+H_3Cl^-}\end{smallmatrix}$	2.3
ES 467 (Dia-Prosim)	Cross-linked polystyrene	$-CH_2-NH-CH_2-PO_3Na_2$	45
CR 20 (Mitsubishi)	Cross-linked polystyrene	$-CH_2-NH-(C_2H_4NH)_n-H$	1.0
CR 40 (Mitsubishi)	Cross-linked polyethyleneimine	 $\begin{array}{l}-(\mathrm{N-C_2H_4-NH-C_2H_4})-\\ \;\;\vert\\ \;\;\mathrm{CH_2}\\ \;\;\vert\\ \;\;\mathrm{CHOH}\\ \;\;\vert\\ \;\;\mathrm{CH_2}\\ \;\;\vert\\ -(\mathrm{N-C_2H_4-NH-C_2H_4})-\end{array}$	2.6
XFS 4195 (Dow)	Cross-linked polystyrene	Picolylamine	4.1
XFS 4196 (Dow)	Cross-linked polystyrene		3.6
Sirorez-Cu (ICI, Australia)	Mannich polycondensate of phenol, formaldehyde, and piperazine		0.8

TABLE 2

Uranium Uptake of Selected Functionalized Resins

Functional group	Starting materials	Main functionalization reactions	Uranium uptake (ppm)
 $-\underset{O}{\underset{\|}{C}}-CH=\underset{OH}{\underset{\mid}{C}}-$	Poly(vinyl alcohol)	CrO_3 oxidation (*74*)	0
	Poly(methylacrylate), macroporous	NH_2OH treatment	2
	Polystyrene, macroporous	Diazotation, coupling with *o*-$(OH)C_6H_4$ $(CONHOH)$	4
	Polystyrene macroporous	Friedel-Crafts with *o*-$(OH)C_6H_4$ $(COCHBrCH_3)$, NH_2OH treatment (*75*)	3
	2,4,6-Triaminophenol glyoxal	Polycondensation (*76*)	45
$-CH_2-(NH-CH_2)_3-NH_2$	Cross-linked chlormethylated polystyrene	Condensation with triethylenetetramine (*77*)	0.8

changes (Fig. 3) in the visible adsorption spectrum of the $[UO_2(CO_3)_3]^{4-}$ complex. The following classes of compounds proved to be effective: 1,3-diketones, *o*-hydroxyazoaromatics, *o*-diaminoaromatics, *o*-dihydroxyaromatics, dithiocarbamates, hydroxylamines, oximes, hydroxamic acids, and amidoximes.

The degrees of functionalization and cross-linking of the resins were deduced from elementary analysis and infrared spectroscopy. Specific surface areas were obtained from BET measurements; pore volumes and pore size distributions were determined by mercury porosimetry. Polarographic investigations yielded valuable informations on the chemical stability of the sorbers against elution solutions like hydrochloric acid or aqueous ammonium carbonate. A more detailed description of these physicochemical

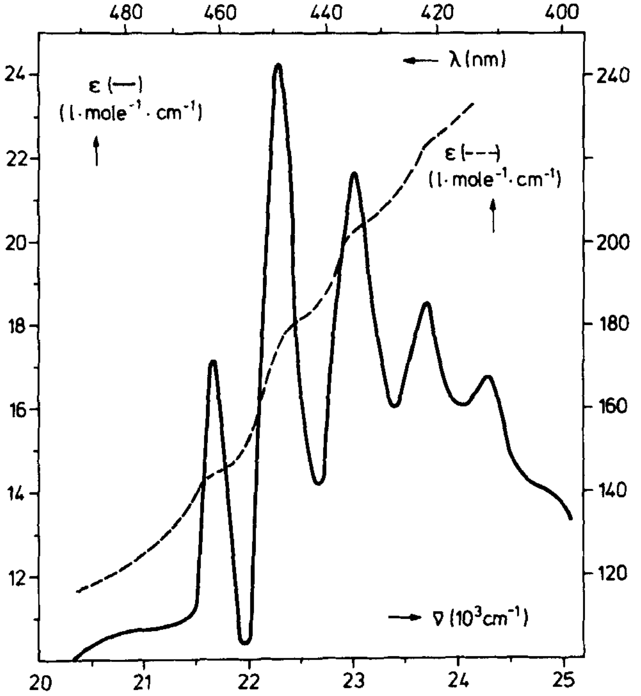


FIG. 3. Solution spectrum of $[UO_2(CO_3)_3]^{4-}$ (3×10^{-3} *M* in water) before (full line) and after (dotted line) adding of benzamidoxime (3×10^{-2} *M*). Note that the left-hand ordinate scale applies to the full line spectrum whereas the right-hand ordinate scale applies to the dotted line spectrum.

methods of sorber quality control will be given in the next paper of this series (*62*) which will be exclusively devoted to successful sorbers.

B. Results and Discussion

Owing to the relatively high carbonate concentration in seawater (3×10^4 mg/m^3), uranium predominantly occurs as the $[UO_2(CO_3)_4]^{4-}$ complex anion, the structure (*69*) of which is shown in Fig. 4. The uranium atom is eight coordinate, the linear UO_2^{2+} group being equatorially surrounded by an irregular hexagon of six oxygen atoms from three bidentate carbonate groups. The complex anion is one of the largest inorganic species occurring in sea water: in the equatorial plane the ionic radius amounts to 4.85 Å. Uranyl-

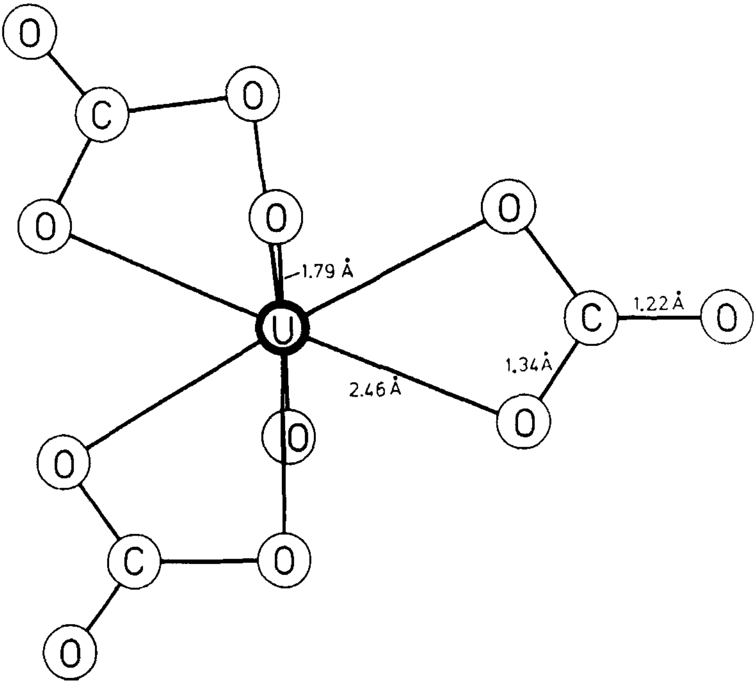


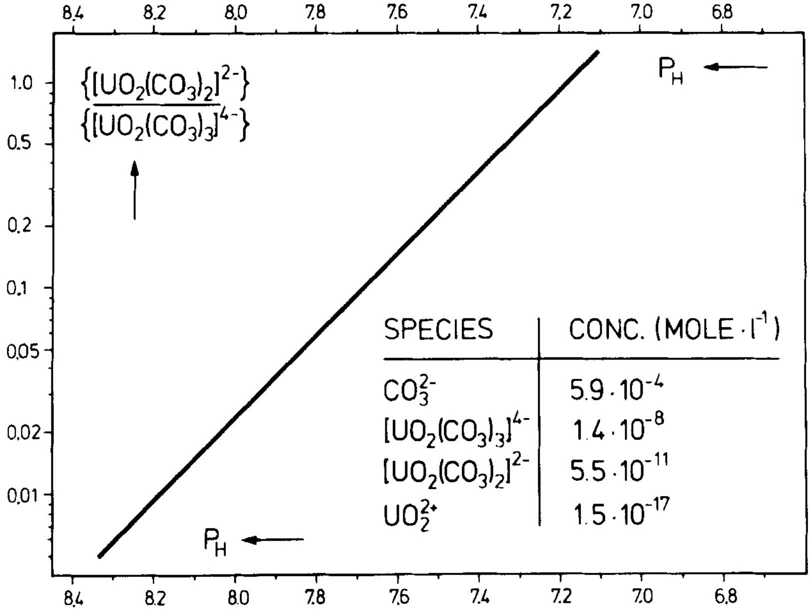
FIG. 4. The structure of the complex anion $[UO_2(CO_3)_3]^{4-}$ (from Ref. *69*).

tricarbonate is thermodynamically an extremely stable complex; the overall formation and stepwise formation constants amount to log $\beta_3 = 22.6$ (*24*) and log $k_3 = 5.41$ (*70*), respectively.

Commercially available anion-exchange resins were found to be insufficiently selective to extract $[UO_2(CO_3)_3]^{4-}$ in the presence of the large excess of competing anions in seawater such as Cl^- (19.4×10^6 mg/m^3), SO_4^{2-} (2.7×10^6 mg/m^3), and HCO_3^- (0.14×10^6 mg/m^3).

Weakly acidic cation exchangers like Rohm and Hass IRC 75 turned out to be more effective. However, the selective sorption of uranium via cation exchange probably necessitates that at least one of the equatorial CO_3^{2-} groups of uranyltricarbonate is replaced by some functional group of the resin. The concentration ratio of uranyldicarbonate $[UO_2(CO_3)_2]^{2-}$ and uranyltricarbonate $[UO_2(CO_3)_3]^{4-}$ is strongly pH-dependent (Fig. 5): it is <0.01 at the normal pH of seawater of 8.3, but both species can be calculated to occur in nearly equal concentrations at pH ≈ 7 (*71*).

Most of the numerous cation exchangers and complexing resins which were tested are able to adsorb uranium from seawater at pH values lower



SPECIES	CONC. (MOLE $\cdot l^{-1}$)
CO_3^{2-}	$5.9 \cdot 10^{-4}$
$[UO_2(CO_3)_3]^{4-}$	$1.4 \cdot 10^{-8}$
$[UO_2(CO_3)_2]^{2-}$	$5.5 \cdot 10^{-11}$
UO_2^{2+}	$1.5 \cdot 10^{-17}$

FIG. 5. The concentration ratio of uranyldicarbonate and uranyltricarbonate as a function of pH, calculated from the stepwise formation constant k_3 of $[UO_2(CO_3)_3]^{4-}$ (*70*) and the dissociation equilibria of carbonic acid in natural seawater (*78*). The quoted concentrations of CO_3^{2-} and uranyl species refer to natural seawater and are taken from Ref. *34*.

than 7, but they show a distinct decrease in uranium uptake with increasing pH (*71*) during successive contacting of 1 g of the resin with 1 L of seawater (Fig. 6). Note that the mentioned decrease is minimal in the case of hydrous titanium oxide. Therefore it can be postulated that in most cases the acidic character of the sorbers leads to a cleavage of $[UO_2(CO_3)_3]^{4-}$, thereby releasing UO_2^{2+} ions which in a second step are retained by the functional groups of the sorber. Such materials are not suitable for a large-scale recovery of uranium, since any acidification—direct or indirect—of the enormous volumes of seawater to be processed must be rejected for ecologic and economic reasons. A successful sorber should be capable of operating at the normal pH of seawater, its functional groups must be able to compete with carbonate in complexing uranyl ions at pH 8, and—as in the case of hydrous titanium oxide (*36, 37, 71, 72*)—the sorption must proceed via direct ligand exchange without previous decomposition of the $[UO_2(CO_2)_3]^{4-}$ complex by hydrogen ions.

Among 200 materials tested, only so-called poly(acrylamidoximes) were found to meet these requirements. These resins are generally obtained from

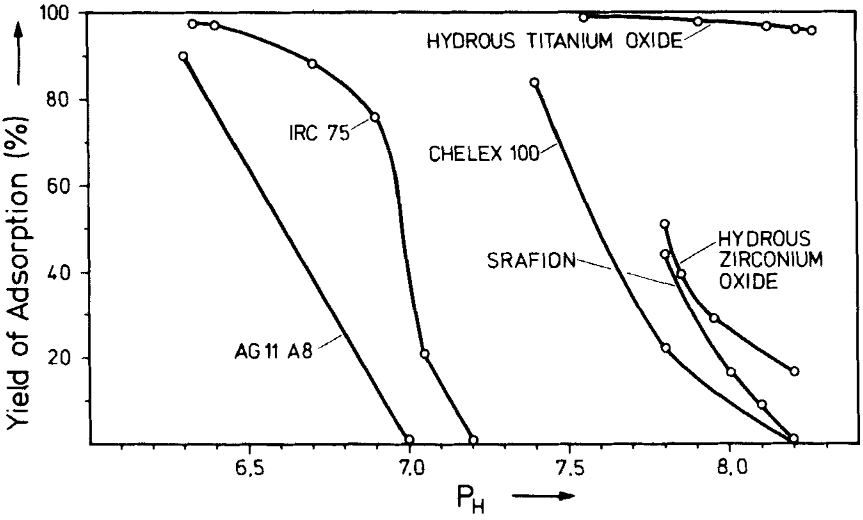


FIG. 6. Decrease in uranium uptake and increase of pH during successive contacting of 1 g of sorber with 1 L of seawater.

cross-linked poly(acrylonitriles) by treatment with solutions of hydroxylamine. Depending on the method of manufacture, these resins yield uranium loadings ranging from some hundred to some thousand ppm (*27*, *73*) which roughly equals the average uranium content of actually explored uranium ores (Fig. 1). Their synthesis, properties, and applications to the recovery of uranium from seawater will be discussed in detail in the next paper.

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REFERENCES

1. R. V. Davies, J. Kennedy, R. W. McIlroy, R. Spence, and K. M. Hill, *Nature, 203*, 1110 (1964).
2. J. Kennedy, *Rep. AERE-R 5023* (1965).
3. R. V. Davies, J. Kennedy, J. W. A. Peckett, B. K. Robinson, and R. J. W. Streeton, *Rep. AERE-R 5024* (1965).

4. N. J. Keen, *J. Br. Nucl. Energy Soc., 7,* 178 (1968).
5. N. J. Keen, *Indian East. Eng., 112,* 337 (1970).
6. G. I. W. Llewelyn, *Atom (London), 238,* 214 (1976).
7. N. J. Keen, *Chem. Ind.,* p. 579 (1977).
8. M. Kanno, *Rep. IAEA-CN-36/161* (1977).
9. N. Ogata, *Genshiryoku Kogyo, 24,* 27 (1978).
10. H. Miyazaki, *Nippon Kikai Gakkaishi, 81,* 475 (1978).
11. K. Sugasaka, *Kagaku Gijutsushi Mol, 18,* 25 (1980).
12. *Atoms in Japan,* p. 27 (August 1980).
13. M. Kanno and K. Saito, *NEUT Res. Rep. 80-08* (1980).
14. Research Committee, *Energy Dev. Jpn., 3,* 67 (1980).
15. H. Miyazaki, *Kobunshi Tokyo, 30, 193 (1981).*
16. M. Kanno, *Yukagaku Tokyo, 30,* 376 (1981).
17. C. Bettinali and F. Pantanetti, *Rep. IAEA-AG/33-4* (1976).
18. L. Baracco, S. Degetto, A. Marani, and U. Croatto, *Chim. Ind., 63,* 257 (1981).
19. M. R. Rodman, L. I. Gordon, A. C. T. Chen, M. H. Campbell, and J. E. Binney, *Rep. XN-RT-14* (1979).
20. M. H. Campbell, J. M. Frame, N. D. Dudey, G. R. Kiel, V. Mesec, F. W. Woodfield, S. E. Binney, M. R. Jante, R. C. Anderson, and G. T. Clark, *Rep. XN-RT-15* (1979).
21. F. R. Best, *Rep. MIT-EL-80-001* (1980).
22. H. G. Bals, *Rep. UR 1366* (1976).
23. H. G. Bals, *Metall, 33,* 401 (1979).
24. K. Schwochau, L. Astheimer, H. -J. Schenk, and J. Schmitz, *Rep. Jül-1415* (1977).
25. K. Schwochau, *Nachr. Chem. Tech. Lab., 27,* 563 (1979).
26. K. Schwochau, L. Astheimer, H. -J. Schenk, and E. G. Witte, *Chem. -Ing. -Tech., 51,* A706 (1979).
27. E. G. Witte, L. Astheimer, H. -J. Schenk, and K. Schwochau, *Ber Bunsenges. Phys. Chem., 83,* 1121 (1979).
28. F. R. Best and M. J. Driscoll (eds.), *Rep. MIT-EL-80-031* (1980).
29. R. Spence, *Talanta, 15,* 1307 (1968).
30. J. D. Wilson, R. K. Webster, G. W. C. Milner, G. A. Barnett, and A. A. Smales, *Anal. Chim. Acta, 23,* 505 (1960).
31. Y. Miyake, Y. Sugimura, and M. Mayeda, *J. Oceanogr. Soc. Jpn., 26,* 123 (1970).
32. D. S. Nikolaev, E. I. Efimova, and V. M. Drozhzhin, *Izot. Issled. Prir. Vod.,* p. 157 (1979).
33. *Uranium Resources, Production and Demand,* A Joint Report by the OECD Nuclear Energy Agency and the International Atomic Energy Agency, December 1979.
34. N. Ogata, N. Inoue, and H. Kakihana, *Nippon Genshiryoku Gakkaishi, 13,* 566 (1971).
35. P. DeBièvre, K. H. Linse, and K. Schwochau, To Be Published.
36. K. Schwochau, L. Astheimer, H. -J. Schenk, *Proc. 26th IUPAC Congr., Tokyo,* September 4–10, 1977, 8J103, p. 486.
37. K. Schwochau, L. Astheimer, H. -J. Schenk, and E. G. Witte, *Proc. 20th Int. Conf. Coord. Chem.,* Calcutta, December 10–14, 1979, p. 363.
38. N. Ogata and H. Kakihana, *Nippon Genshiryoku Gakkaishi, 11,* 82 (1969).
39. Y. Shigetomi, T. Kojima, and H. Kamba, *Ibid., 20,* 789 (1978).
40. D. Gregg and F. Wang, p. 243 of Ref. *28.*
41. L. Astheimer, H. -J. Schenk, and K. Schwochau, *Chem. Ztg., 101,* 544 (1977).
42. E. Koglin, H. -J. Schenk, and K. Schwochau, *Appl. Spectrosc., 32,* 486 (1978).
43. H. Denzinger, Ch. Schnell, D. Heitkamp, and K. Wagener, p. 95 of Ref. *28.*
44. I. Tabushi and Y. Kobuke, p. 71 of Ref. *28.*

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

46. R. A. A. Muzzarelli, F. Tanfani, and S. Mariotti, p. 124 of Ref. *28.*

47. B. L. Averbach, p. 135 of Ref. *28.*

48. E. W. Hooper, N. J. Keen, and G. I. W. Llewelyn, p. 37 of Ref. *28.*

49. H. Yamashita, *Nippon Kagaku Kaishi, 8,* 1057 (1978).

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

51. H. Yamashita, Y. Ozawa, F. Nakajima, and T. Murata, *Ibid., 53,* 3050 (1980).

52. N. Ogata, *Chem. Today, Tokyo, 112,* 16 (1980).

53. M. Kanno, p. 47 of Ref. *28.*

54. *Atoms in Japan,* p. 26 (July 1981).

55. V. Ziegler, *Rev. Energ., 309,* 586 (1978)

56. N. Jaffrezic-Renauld. H. Poirier-Andrade, and D. H. Tang, *J. Chromatogr., 201,* 187 (1980).

57. J. Bitte, M. I. Fremery, and H. G. Bals, p. 167 of Ref. *28.*

58. O. J. Heinonen, *Radiochem. Radioanal. Lett., 43,* 293 (1980).

59. M. Kanno, *Atoms Jpn.,* p. 9 (February 1979).

60. Y. P. Novikov, V. M. Komarevskii, and B. F. Myasoedov, *Radiokhimiya, 20,* 870 (1978).

61. V. N. Sastry, G. R. Doshi, T. M. Krishnamoorthy, and T. P. Sarma, *Indian J. Mar. Sci., 6,* 55 (1977).

62. L. Astheimer, H. -J. Schenk, E. G. Witte, and K. Schwochau, To Be Published.

63. A. D. Kelmers, p. 15 of Ref. *28.*

64. P. H. Koske, *Uranium Nucl. Energy, 4,* 111 (1979).

65. E. Bertel and V. Ziegler, *Rev. Gen. Nucl.,* p. 15 (1981).

66. A. Putral and K. Schwochau, German Patent 2,720,867 (1979).

67. A. Putral and K. Schwochau, *Fresenius Z. Anal. Chem., 291,* 210 (1978).

68. E. Koglin, H. -J. Schenk, and K. Schwochau, *Spectrochim. Acta, 35A,* 641 (1979).

69. R. Graziani, S. Bombieri, and E. Forsellini, *J. Chem. Soc., Dalton Trans.,* p. 2059 (1972).

70. C. Tsymbal, *Rep. CEA-R-3476* (1969).

71. H. -J. Schenk, E. Koglin, L. Astheimer, E. G. Witte, and K. Schwochau, *Proc. XIXth Intern. Conf. Coord. Chem.,* Prague, September 4–8, 1978, p. II 107.

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

73. K. Schwochau, L. Astheimer, H. -J. Schenk, and E. G. Witte, *Z. Naturforsch. b,* In Press.

74. S. Marmor and G. Kidane, *Polym. Bull., 1,* 239 (1978).

75. B. V. Dombrowskij, M. I. Shebchuk, and V. P. Kravets, *Zh. Obshch. Khim., 32,* 2278 (1962).

76. E. Bayer and H. Fiedler, *Angew. Chem., 72,* 921 (1960).

77. G. M. Orf, Thesis, Iowa State University of Science and Technology, Ames, Iowa, 1977; University Microfilms Order No. 78-05,960.

78. G. Skirrow, *Chemical Oceanography,* Vol. 2, 2nd ed. (J. P. Riley and G. Skirrow, eds.), Academic, London, 1975, pp. 39, 174, 176.

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