

Recent International R&D Activities in the Extraction of Uranium from Seawater

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Summary

A literature survey has been conducted to collect information on the International R&D activities in the extraction of uranium from seawater for the period from the 1960s till the year of 2010. The reported activities, on both the laboratory scale bench experiments and the large scale marine experiments, were summarized by country/region in this report. Among all countries where such activities have been reported, Japan has carried out the most advanced large scale marine experiments with the amidoxime-based system, and achieved the collection efficiency (1.5 g-U/kg-adsorbent for 30 days soaking in the ocean) that could justify the development of industrial scale marine systems to produce uranium from seawater at the price competitive with those from conventional uranium resources.

R&D opportunities are discussed for improving the system performance (selectivity for uranium, loading capacity, chemical stability and mechanical durability in the sorption-elution cycle, and sorption kinetics) and making the collection of uranium from seawater more economically competitive.

1. Background

The total amount of uranium resource in seawater is about 4.5 billion tons ($[U] \sim 3$ ppb, ocean volume $\sim 1.37 \times 10^9$ km 3), one thousand times of the amount of uranium in terrestrial ores. However, there are two major obstacles to using this virtually limitless reservoir as an economic source of uranium: 1) the uranium is in a strongly complexed form (carbonate complexes) at extreme dilution in the presence of relatively high concentrations of other ions; 2) it is a very difficult operation to bring any extraction agent into contact with very large volumes of seawater that would be involved. To be successful, the extractant must function efficiently at the seawater pH and ionic strength, and must be virtually insoluble (1).

2. R&D Activities by Country/Region

2.1 Japan

2.1.1 Earlier studies

The extraction of uranium from seawater was studied by the Japan Tobacco and Salt Corporation in the 1960s. Since then, the National Institute of Advanced Science and Technology (Shikoku), the University of Tokyo, Kyoto University and other research institutes have carried out laboratory experiments. In 1974, the Research Committee on Rare Resources from Seawater was organized in the Ministry of International Trade and Industry (MITI) to start overall study of uranium recovery from seawater. In 1975, the Metal Mining Agency of Japan participated in the project, and established a coordinating committee (2).

The earlier studies focused on evaluation of different methods (solvent extraction, ion exchange, flotation, biomass collection, adsorption), and development of adsorbents (hydrous TiO_2 , PbS) (3).

Solvent extraction, though feasible, is considered to be unsuitable for the extraction of uranium from seawater on a large scale, due to the requirements of complicated engineering setup/procedure and large amounts of chemicals and volatile solvents, and the problem of solvent loss by entrainment and dissolutin (3,4).

Ordinary organic ion exchange resins, such as the resorcinol arsenic acid formaldehyde or 8-hydroxyquinoline resin, show good uptake of uranium, but their rapid deterioration with aging makes them unsuitable for the extraction of uranium from seawater (3,4). Some macrocyclic polydentate ligands were studies to improve the selectivity (3,4), but no further development work was reported in the later literature for unclear reasons. For example, polymer-bound macrocyclic hexaketone (Figure 1) was found to be capable of extract uranyl ion from seawater (4). However, the study was not continued probably because the drawbacks such as slow kinetics and potential loss of the chelating agent precluded its further development.

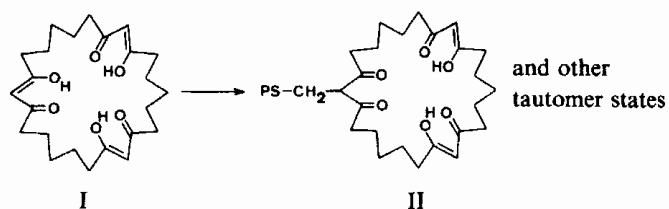


Figure 1. Hexaketone ligand for the complexation of U(VI) (3,4).

Several types of biological substances have been reported to be used for uranium extraction, including acid polysaccharides, phosphorylated polysaccharides (chitin phosphate, chitosan phosphate, cellulose phosphate). However, the adsorption capacity is low and there are problems of contacting microorganism with seawater and their collections (3,4).

The earlier studies indicated that hydrous TiO_2 was a promising adsorbent for the collection of uranium from seawater. From 1981 to 1988, the first experimental plant for collection of uranium from seawater with hydrous TiO_2 was operated by the Agency for Natural Resource and Energy (ANRE), MITI, and Metal Mining Agency of Japan. The reported adsorption ability of the hydrous titanium oxide, 0.1g-U/kg-adsorbent, was too low for practical applications and should be improved at least 10 times in order to make the process economical. Also, significant loss of the adsorbent in the process as well as the consumption of electricity for pumping seawater increased the collection cost. Additionally, the hydrous TiO_2 adsorbent is not mechanically strong enough for the wearing motion in the moving bed system.

2.1.2 Recent studies

Recent studies in Japan have been focused on the amidoxime-based adsorbent system. Both laboratory studies and marine experiments in the Pacific Ocean have been conducted. The laboratory studies cover the preparation of amidoxime-based adsorbents, the equilibrium of the uranium uptake, and the kinetics and mechanism of the extraction of uranium from seawater (4-16). Collection of uranium with chitosan-resin and biomass such as algae was also performed (17,18). The marine experiments were

performed by using two types of collection systems: the stack system and the braid system (19,20).

Laboratory studies

R&D activities on the laboratory scale were carried out in Japan to develop absorbents for practical applications to the seawater system and three types of amidoxime-based adsorbents were developed (19):

- I. Amidoxime-based polymer beads: polymer beads having cyano groups were first synthesized, and then converted to amidoxime groups by reacting with hydroxylamine. The beads type adsorbent needs a package for feasible handing and for effective contact between adsorbent and seawater.
- II. Amidoxime-based fiber prepared by a chemical route: This type of amidoxime fiber materials, developed by the National Institute of Advanced Science and Technology, was prepared by reacting commercially available acrylonitrile fiber with hydroxylamine. The adsorbents can utilize the ocean current and the wave motion when it is moored in the sea. However, because the amidoxime groups were imparted evenly in the fiber and the intrinsic mechanical strength of fiber was lost after amidoximation, the amidoxime fiber prepared by the chemical route is not mechanically strong enough for mooring in the seawater.
- III. Amidoxime-based fiber prepared by radiation-induced graft polymerization: As shown in Figure 2, polyethylene was irradiated with electron beam and acrylonitrile was grafted onto polyethylene non-woven fabrics. Subsequently, the cyano group of the grafted polymer chain was converted into the amidoxime group. This grafting led the production of adsorbent having enough mechanical strength and high capacity of uranium adsorbent.

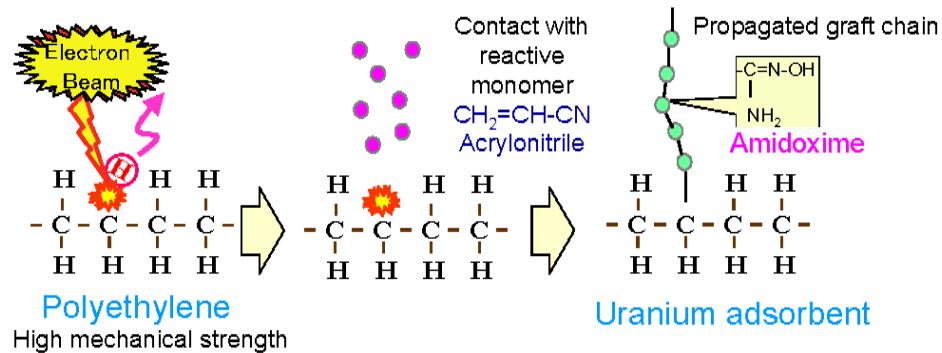


Figure 2. Amidoxime-based fiber prepared by radiation-induced graft polymerization (19).

The adsorption of uranium and other metals by the amidoxime-based fiber from seawater is shown in Table 1.

Table 1. Selectivity of the amidoxime adsorbent (19).

Elements	Concentration in seawater ^a [μ g/L]	Concentration in adsorbent ^b [μ g/g-ad]	Distribution coefficient (b/1000a)
Na	1.08×10^7	618.5	0.057
K	3.80×10^5	45.9	0.12
Al	2	86.94	4.35×10^3
Pb	0.03	108.82	3.62×10^6
Ti	1	1.49	1.49×10^3
Fe	2	414.44	2.07×10^5
Co	0.05	23.57	4.71×10^5
Ni	1.7	78.17	4.60×10^4
U	3.2	63.72	1.99×10^4

Adsorption conditions: 0.2g adsorbent 25°C, 3L/min seawater, and 7 days.

Marine experiments

Type III of the amidoxime-based fiber was used in the marine experiments in Japan. Two types of marine experiments have been carried out: (1) uranium collection system using amidoxime adsorbent stacks (19,20); (2) uranium collection system using amidoxime braid adsorbent (19).

The stack collection system. The results of the marine experiments using the stack collection system are summarized in two references (19,20). The collection system is shown in Figure 3. It is composed of a floating frame and adsorption beds. The floating frame was stabilized with ropes connecting to four 40 t-anchors placed on the sea bottom. Three square adsorption beds, 16 m² in cross-sectional area and 30 cm in height, can each pack 144 adsorbent stacks. The adsorbent stacks were assembled by 120 sheets of adsorbent fabrics (0.2 cm thick, 16 cm wide and 29 cm long) alternately with spacer nets and hanged in seawater from the floating frame in the sea depth of 20 m. The frame was designed to endure the following ocean weather conditions: wind strength of 30 m/s, tidal current of 1.0 m/s, and wave height of 10 m.

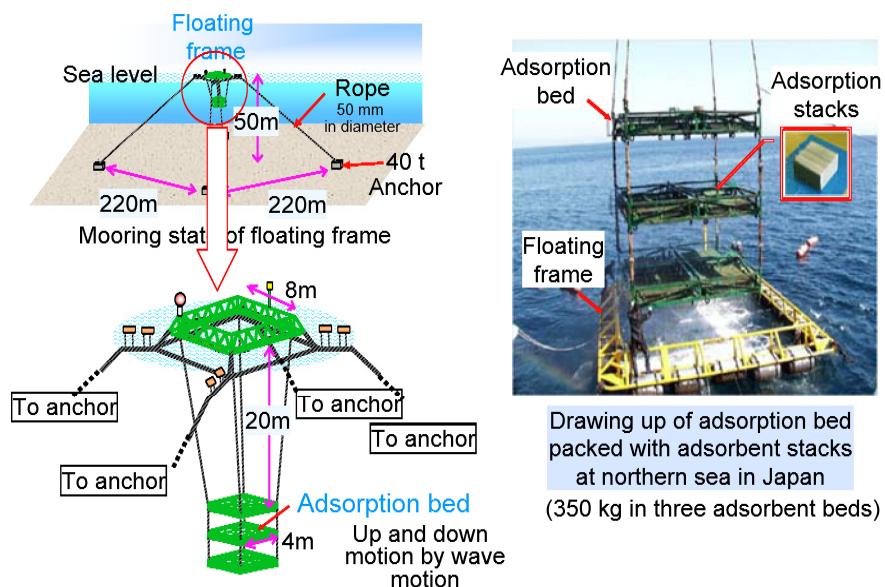


Figure 3. Collection of uranium from seawater using the adsorbent stacks (19).

The uranium collection experiment using absorbent stacks was performed in the Pacific Ocean at 7 km offshore from Mustu-Sekine in Aomori prefecture of Japan from 1999 to 2001. The sea depth of this site was approximately 40 m. Adsorbed uranium on adsorbent fabric was fractionally eluted by 0.5 M hydrochloric acid. The average uptake of uranium was 0.5 g-U/kg-ad for 30 days' soaking. Total amount of uranium collected by this demonstration reached roughly one kilogram in terms of yellow cake during a total submersion time of 240 days in the ocean. Detailed data of the uranium uptake are shown in Table 2.

Table 2. Uranium uptake in the marine experiments using the stack system (20).

Submersion Period	Submersion Time (day)	Number of Stacks	Seawater Temperature (°C)	Amount of U Adsorbed ^a (g)	Apparent Adsorbent Rate [g/(day·stack)]
1999 29 Sep to 20 Oct	20	144	19 to 21	66	0.023
2000 8 Jun to 28 Jun 28 June to 8 Aug 8 Aug to 7 Sep 7 Sep to 28 Sep 28 Sep to 19 Oct	20 40 30 20 20	144 144 144 144 144	12 to 13 13 to 22 22 to 24 22 to 24 18 to 22	47 66 101 76 77	0.016 0.011 0.023 0.026 0.027
2001 15 Jun to 17 Jul 15 Jun to 20 Aug 15 Jun to 21 Sep 18 Jul to 20 Aug 18 Jul to 21 Sep 20 Aug to 21 Sep	30 60 90 30 60 30	216 72 72 216 144 216	13 to 18 13 to 20 13 to 19 18 to 20 18 to 19 19 to 20	95 48 120 119 150 118	0.015 0.011 0.019 0.018 0.017 0.018
Total		1800		1083	

^aAmount in terms of yellow cake.

The variation of the apparent adsorption rate (the last column of Table 2) is supposed to be due to the difference in seawater temperature, the wave and tidal motions of the adsorption cages, and the elution history of the amidoxime adsorbent (20).

Data in Table 2 may suggest that the uranium adsorption is correlated with the temperature of seawater and the warming of seawater enhances the chemical adsorption of uranium on the adsorbent (19). It is not clear whether the temperature effect on the sorption, if it is confirmed, is due to the thermodynamics or kinetics of the sorption.

One problem with the stack collection system was biofouling on the surface of the stacks. Biofouling included adhesion and subsequent growth of marine microorganisms and algae. By immersing the stacks in fresh water after the stacks were taken out from the adsorption cage, most of the marine microorganisms could be removed because the drastic decrease in the ionic strength induced the detachment of these marine microorganisms from the surface of the stacks.

Another drawback of the stack collection system is the high collection cost. It is estimated that, if the floating frame and the adsorption beds can be deleted, the total cost could be reduced by 40% (19).

The braid collection system. The braid collection system was developed to reduce the total collection cost and was evaluated in marine experiments in the sea of Okinawa area of Japan. A schematic image of the braid adsorbent is shown in Figure 4.

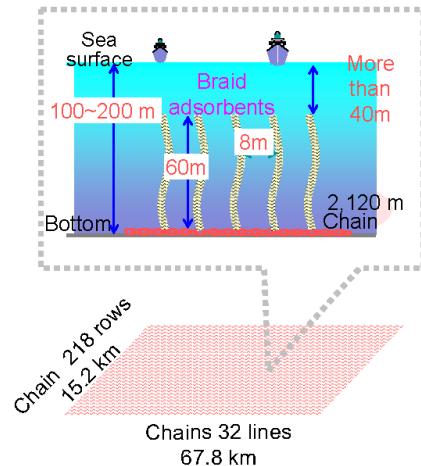


Figure 4. Schematic image of the braid collection system (19).

After the braid adsorbent was thrown into the sea, it simultaneously stood on the sea bottom. When collected, it was cut off from the anchor using wireless operation. The braid adsorbent that appeared on the sea surface was recovered by fishing boat.

Figure 5 shows that the uranium uptake by the braid system was 1.5 g-U/kg-ad for 30 days' soaking at 30 °C in the Okinawa area (10 °C higher than that of Mutsu area for the stack experiments). Taking into consideration of the difference in temperature, the adsorption ability of the braid system appeared to be 2 times that of the stack system, probably owing to the better contact between seawater and the braid adsorbent.

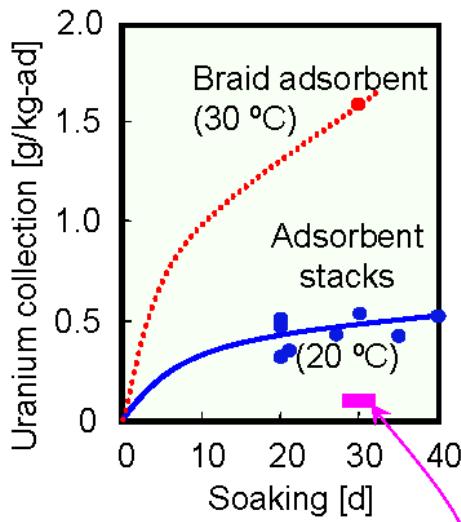


Figure 5. Comparison of uranium collection by different collection systems: red dotted line – braid; blue solid line – stacks; arrow pointed magenta rectangle – hydrous TiO_2 (19).

Cost estimation. The uranium collection cost includes processes of adsorbent production, uranium collection, and purification. A rough estimate was made for the amidoxime-based braid collection system, based on the following assumptions:

- The adsorption ability is 4 g-U/kg-ad for 60 days' soaking. This is the highest ability observed in the Okinawa experiment.
- 1,000 km² sea area near the Japan Current is covered by the braid adsorbents (60 m length, with the internal spacing of 8 m) at the depth from 100 m to 200 m.
- Uranium is collected on the scale of 1,200 t-U/y.
- The braid adsorbents can be repeatedly used without deteriorating performance. In the laboratory experiment, the repetition of 8 times was achieved.

The estimated collection cost is 32,000 yen/kg-U with the currently confirmed repetition use of 8 times. If the repetition is 18 times, the collection cost will be expected to be 25,000 yen/kg-U.

2.1.3 Current status

Efforts are being made to secure funding to construct the large scale uranium collection farm, carry out new marine experiments in large scale, and promote the industrialization process. The farm will cover nearly 400 square miles (~ 1000 km²) that would meet one-sixth of Japan's annual uranium requirements (21).

The marine experimental equipments have already been dismantled. The uranium adsorbents are soaked into tanks of seawater and adsorption data are continuously collected. Up to the time of preparing this summary report, the required funding for the large scale farm has not been obtained (22).

2.2 India

2.2.1 Laboratory studies

Laboratory studies are conducted by two groups in BARC (Bhabha Atomic Research Centre, Mumbai, India), one group in the Radiochemistry Division, and the other in the Desalination Division). The studies are focused on the amidoxime based absorbent systems, in the forms of membranes (23) or hydrogels (24). Other systems with resin or magnetic particles grafted with ligands (such as amidoxime or calixarene) are also proposed (25). The work reported by the group in the Desalination Division was carried out under the specific collaboration agreement between the BARC and the CEA (Commissariat à l'Energie Atomique of France).

The amidoximated macroporous membranes (AO membranes, 2 cm x 1 cm x 2 mm) were prepared by post irradiation grafting of acrylonitrile (AN) onto thermally bonded non-woven matrix of poly(propylene) sheet using electron beams. These precursor membranes were reacted with hydroxylamine to convert AN to AO groups, and conditioned by treating them with 2.5% KOH at 80°C for 1 h. The expected functional group density based on the degree of AN grafting (125 wt.%) and its subsequent conversion to AO groups (80%) was found to be 7.8×10^{-3} mol/g. In the batch experiments with ²³³U spiked in seawater, (96±3)% of the ²³³U was sorbed by the membrane. The comparison of the expected functional group density and uranium uptake capacity seems to suggest that UO_2^{2+} forms a complex with AO groups in 1:4 proportion (Figure 6) (23).

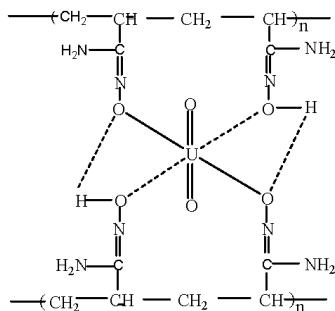


Figure 6. Proposed structure of the 1:4 UO_2^{2+} /Amidoxime complex (23).

In the batch experiments with the membrane, the equilibrium time for sorption saturation was about 200 min. The long equilibrium time could be due to the diffusion of uranium species in the membrane matrix and the reaction kinetics involved in the dissociation of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ (26) and subsequent complexation of UO_2^{2+} with the AO groups in the membrane. However, the data obtained in this work are not sufficient to identify the rate determining step.

The uranium could be quantitatively desorbed (>90%) from the AO membrane in Na_2CO_3 and mineral acids like HCl in the equilibration times of 60 min and 40 min, respectively. Alkaline conditioning was found to be necessary for reuse of the membrane equilibrated with acid. However, AO membranes equilibrated with Na_2CO_3 could be reused without any conditioning for uranium sorption (23).

In the batch experiments with the cross-linked AO-based hydrogels, the hydrogels were prepared with AO and different acidic (acrylic acid (AA), methacrylic acid (MAA), ethylene glycol methacrylate phosphate (EGMP), 2-acrylamido-2-methyl-1-propane sulfonate (AMPS)) and basic (3-(acrylamido propyl)trimethylammonium chloride (APTAC)) co-monomers by UV-initiated bulk polymerization. The objectives are to test the effect of the hydrogel composition on the selectivity and the rate of the sorption of uranium from seawater (24).

The results indicated that the presence of weak acid co-monomer like MAA with AO enhances the selectivity as well as the kinetics of U(VI) sorption from seawater. The kinetics of uptake of U(VI) from seawater was found to be highly dependent on the proportion of MAA and AO in the hydrogel. The presence of a strong acid ($-\text{SO}_3\text{H}$) or strong base ($-\text{N}^+(\text{CH}_3)_3$) as a co-monomer with AO retards the overall kinetics involved in the U(VI) sorption from seawater. Among the hydrogels under investigation, EGMP hydrogel sorbed U(VI) quantitatively from seawater as well aqueous feed containing high acid concentration. The advantages of EGMP-hydrogel would be as follows: (i) one step synthesis using a single monomer, no hydroxylamine and alkali treatment are required; (ii) unlike acrylonitrile, EGMP is neither volatile nor toxic; (iii) EGMP is readily polymerizable; (iv) under identical seawater conditions, the profile of U(VI) sorption kinetics is faster in EGMP hydrogel as compared to AO and AO/acid co-monomer hydrogels; and (v) EGMP hydrogel can be used for preconcentration of U(VI) from the seawater as well as aqueous feed having high acidity (24).

2.2.2 Engineering/pilot plant studies

Under a collaborative project between BARC and CEA, work was conducted to extract uranium from the concentrated brine rejected by desalination plants in BARC (25,27). An

R&D program called RUSWapp (Recovery of Uranium from Sea Water pilot programme) in BARC was initiated (27).

The effluent rejected from the desalination plant contains a number of materials and is a source for many chemicals. Recovery of some of the rare and valuable elements (including uranium) from the rejected brine of the desalination plant helps to make the desalination plant more environment-friendly and reduce the cost of desalinated water.

The present scenario under RUSWapp is to use AO based polymers. Three methods have been proposed: 1) Resin grafted with calixarene (Figure 7): this method could have the advantage of very high selectivity. Its performances, especially for large-scale extraction, still need further R&D and optimization; 2) Magnetic separations using magnetic particles grafted with calixarene or AO ligands: this method could have the advantages of high selectivity, easy separation and high degree of material recovery. However, it is still in an early developmental stage; 3) Canal system with braid AO adsorbents: this method, similar to that developed in Japan, appears to be selective and feasible in conjunction with existing technology (25).

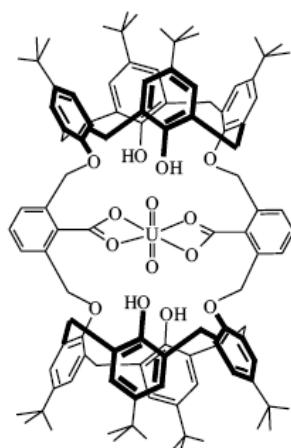


Figure 7. UO_2^{2+} -calixarene complex (25).

In the studies with the braid AO adsorbents, experimental data concerning the effect of immersion depth, degree of alkalization, bio and dirt fouling and tidal wave velocity on uranium sorption efficiency were collected at four locations:

- CIRUS Jetty head
- Kalapakkam, near seawater intake tunnel
- Tarapur 1&2 Seawater intake and outfall canals
- Andaman & Nicobar Islands

A total of about 800 μg of U was collected in 5 campaigns from CIRUS Jettyhead, about 1.8 mg from TAPS seawater intake and outfall canals and around 200 μg from Andaman & Nicobar Islands. The specific collection was found to be from 60 to 160 $\mu\text{g/g}$ of PAO in 12 to 24 days. In comparison, Japanese researchers reported an equilibrium value of 1000 $\mu\text{g/g}$ of PAO in 52 days at 25°C under laboratory conditions. It was observed that vanadium also gets collected on the adsorbent (27).

The BARC 2006-2007 report (27) mentions that a pilot plant facility for 100 grams U per year (RUSWapp100) is under installation (Figure 8). Information on the current status of the pilot plant is not available.



Figure 8. Pilot plant facility (under construction) for uranium recovery from seawater (27).

2.3 China

Studies on the extraction of uranium from seawater were initiated in mid-1970's (28). The research activities were mainly conducted in the institutes for research in oceanic sciences or environmental protection, and focused on testing absorbents and understanding the kinetics and mechanism of absorption (29-32). No work on the engineering setup or pilot-plant tests for the extraction of uranium from seawater has been found in the literature.

Hydrous titanium oxide, aluminum hydroxide, and organic resins were among the absorbents tested in late 1970's – early 1980's. More recently, studies with polyacrylamidoxime (33) and chitin (34) for the extraction of uranium from seawater have been discussed in the literature.

Chitin ($C_8H_{13}NO_5)_n$ (Figure 9) is a cellulose-like biopolymer consisting predominantly of unbranched chains of β -(1,4)-2-acetamido-2-deoxy-D-glucose (also named N-acetyl-D-glucosamine) residues. It is found in fungi, yeasts, marine invertebrates and arthropods, where it is a principal component in the exoskeletons. Chitin may be regarded as a derivative of cellulose, in which the C-2 hydroxyl groups have been replaced by acetamido residues. It forms colored complexes with a variety of metal ions and can be used to extract novel metals. For example, its phosphate derivatives could extract uranium from seawater (up to 2.6 mg U/L) and the sorbed uranium can be eluted with dilute phosphoric acid (34). The deacetylated form of chitin, chitosan, has been used to enrich uranium from seawater in other countries (17).

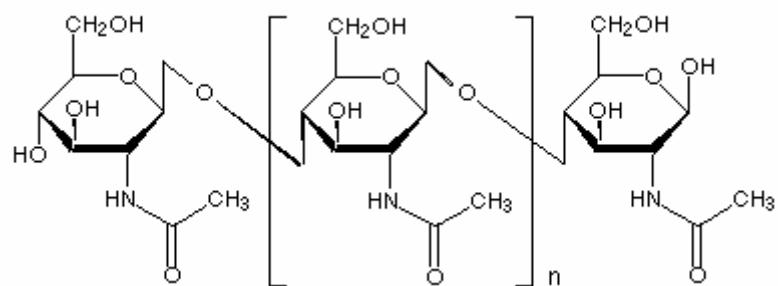


Figure 9. Chitin (its deacetylated form is called chitosan).

2.4 European Countries

2.4.1 Overview

Research activities on the extraction of uranium from seawater from a number of European countries are reported in the literature, including Finland (35), France (36-39), Germany (40-58), Greece (59), Italy (60-64), Poland (65), Sweden, and UK (1,66-71). Among the European countries, Germany by far has the largest number of publications and patents on this subject.

As seen in the activities carried out in Japan and other countries, earlier studies (before 1981-1982) in Europe were focused on using hydrous titanium oxide as the sorbents. A number of patents were filed in 1975 – 1984, mostly on the methods and apparatus for the recovery of uranium from seawater based on the sorption by titanate and biomass (72-84). The sorption by titanate looked promising at that time so that the design and layout of an industrial plant were discussed (44,48,54). However, the low mechanical resistance of hydrous titanate materials against attrition resulted in breakdown of the sorbent particles during operation in a fluidized bed. All attempts to produce stronger materials involved serious loss in sorption capacity (48). These disadvantages precluded the further development of the titanate process.

2.4.2 Studies on amidoxime in Germany

In earlier 1980s, systematic screening studies of about 200 adsorbents for collection of uranium from seawater were conducted in the Jülich Nuclear Research Centre in Germany. The sorbent materials, including cross-linked resins with different functional groups, were tested on both laboratory scale and large field scale with seawater (3 ppb U). The field tests were conducted using 100 g adsorbent materials fluidized in 1-2 L columns on the island of Heligoland 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 time of the seawater with the sorbents (48).

The screening tests indicated that cross-linked poly(acrylamidoximes) were the most promising candidate adsorbents for the extraction of uranium from seawater. The uranium loading on poly(acrylamidoximes) ranged from hundreds to 3000 ppm, which roughly equals to the uranium content of actually explored uranium ores, while most of other materials tested had the uranium loading in the range of a few ppm. Besides, the cross-linked poly(acrylamidoximes) materials were found to have desired properties such as high physical and chemical stability in seawater, as well as fast and selective uptake of uranium (52,53).

The sorbed uranium could be eluted from the cross-linked poly(acrylamidoximes) resin by 1 M HCl. It was observed that the uranium uptake of the resin decreased with increasing number of sorption-elution cycles. At a loss rate in sorption efficiency of 6% per cycle, the uranium uptake would fall to 50% of its original value after 11 sorption-elution cycles. Such a rapid breakdown in sorbent performance would very unfavorably affect the process economics. The Jülich studies suggested that two types of functional groups formed during the preparation of the cross-linked resin, an open-chain diamidoxime (Figure 10) and a cyclic imide dioxime (Figure 10). The open-chain diamidoxime was found to be rather stable in HCl whereas the cyclic imide dioxime turned out to be distinctively more unstable by a factor of 25. On the other hand, the cyclic imide dioxime is expected to be more effective for complexing UO_2^{2+} in the competition

with CO_3^{2-} because it can afford a tridentate coordination (Figure 10). The stronger complexing ability and higher instability of the cyclic imide dioxime are probably the reason for the deteriorating performance of the poly(acrylamidoximes) resin during repeated sorption-elution cycles (53).

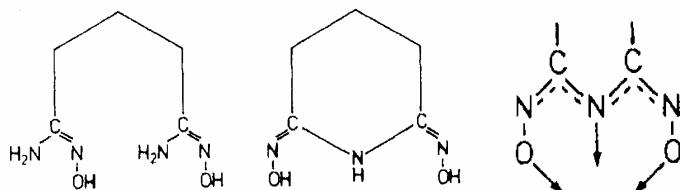


Figure 10. Open-chain diamidoxime (left), cyclic imide dioxime (center) and its coordination mode (right) (53).

No further R&D activities in Germany since 1990 on the collection of uranium from seawater by amidoxime-based systems have been found in the literature by this survey.

3. R&D Opportunities

To make the collection of uranium from seawater more economically competitive, the performance of the collection systems, in terms of selectivity, loading capacity, chemical stability and mechanical durability, as well as the sorption kinetics, must be further improved.

3.1 Understanding the Coordination Modes, the Sorption Mechanism and Kinetics at the Molecular Level

Though the amidoxime system has been demonstrated to be significantly better in performance for the extraction of uranium from seawater, the nature of the uranium/amidoxime complex, and the extraction mechanism and kinetics are not clearly illustrated. A better understanding of the coordination modes, the sorption mechanism and kinetics is the key to improving the extraction efficiency.

For example, the amidoxime group $-\text{C}(\text{NH}_2)\text{NOH}$ is expected to form a chelate complex with metal ions via the N atom of the amino group ($-\text{C}(\text{NH}_2)$) and the O atom of the deprotonated $-\text{C}(\text{NO}^-)$ group. Crystal structures of the amidoxime complexes with transition metals (Co, Ni, Cu, Pb and Pt) have confirmed the formation of such chelate complexes (57). However, in the crystal structure of two amidoxime complexes with UO_2^{2+} , the amidoxime ligand was found to be monodentate. As shown in Figure 11, the O atom of the deprotonated $-\text{C}(\text{NO}^-)$ group coordinates to UO_2^{2+} but the N atom of the amino group ($-\text{C}(\text{NH}_2)$) does not (Figure 11) (57).

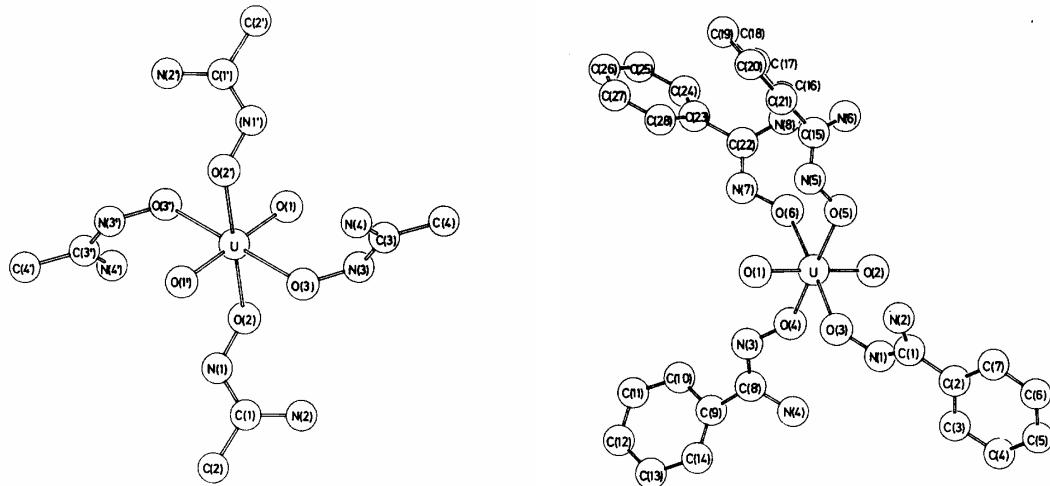


Figure 11. $[\text{UO}_2(\text{acetamidoxime})_4]^{2+}$ (left) and $[\text{UO}_2(\text{benzamidoxime})_4]^{2+}$ (left) (57).

The difference in the coordination modes between the transition metals and the uranyl ion may suggest that the softer donor (N) has the higher affinity to transition metals with higher covalency. Such difference should be further investigated and fundamental understanding of the effect could help to design or select ligands with higher selectivity for uranium. Besides, it is unclear how the amidoxime ligands function when grafted on the polyethylene fiber. Studies with spectroscopic techniques (IR, XAS, etc.) could provide insight into the coordination modes of amidoxime complexes with uranium.

Because the dominant uranyl species in seawater are the carbonato complexes (26), the amidoxime must compete with and replace the carbonate groups in the sorption process. Literature reports suggest that the dissociation of the tricarbonato uranyl complex ($\text{UO}_2(\text{CO}_3)_3^{4-}$) is the rate-determining step (85). However, further systematic studies are needed to evaluate the earlier conclusion.

3.2 Developing Ligands to Improve the Selectivity

The amidoxime-based fiber extracts uranium, as well as transition metals including Pb, Fe, Co and Ni. In fact, the distribution coefficients for the transition metals are all higher than that for UO_2^{2+} (19). R&D work should be conducted to evaluate other ligands that could have higher selectivity for UO_2^{2+} .

Based on the hypothesis that the softer N donor might be more affinitive toward transition metals than uranyl, ligands with catechol units might have higher affinity toward uranyl than the transition metals. Also, grafting the fibers with ligands such as iminodiacetic acid (IDA) and its derivatives (*N*-methyl-IDA, dipicolinic acid) may also lead to adsorbents with stronger affinity to uranyl since these tri-dentate ligands could coordinate with uranyl in its equatorial plane without much pre-organization energy.

Grafted polymers with amine-type ligands may also show high efficiency. In a recent study using graft polymerization with amine-type (e.g., ethylenediamine), a distribution coefficient of 2×10^6 for uranyl was observed (6).

Calixarene ligands with catechol units and calyx[4]resorcinarene-hydroxamic acids have shown high selectivity toward uranyl (86-89). In particular, if the calixarene ligand (as

shown in Figure 7) could be designed so that, in addition to the equatorial coordination with UO_2^{2+} , hydrogen bonding could form between the ligand and the axial oxygen(s) of the UO_2^{2+} ion, additional binding strength and selectivity toward uranyl might be achieved.

Engineered biological materials could also be tailored to have high affinity toward uranyl. In a recent study (90), a uranyl-responsive DNA-binding protein was prepared by reengineering the nickel(II)-responsive NikR protein. In the design, the square-planar coordination geometry of the Ni^{2+} ion in NikR was used as the starting point to construct an equatorial coordination plane for the uranyl core. To achieve a favorable uranyl coordination environment, His76 and Cys95 were mutated to aspartic acid (H76D C95D), which can coordinate either in a monodentate or a bidentate fashion. To accommodate the uranyl oxo groups, Val72 was mutated to serine (V72S), which has the potential to form a hydrogen bond to one of the oxo groups of the uranyl cation (Figure 12). Such studies, in a long run, may lead to the preparation of biomaterials with engineered protein for specific collection of uranium from seawater, or for environmental remediation purposes.

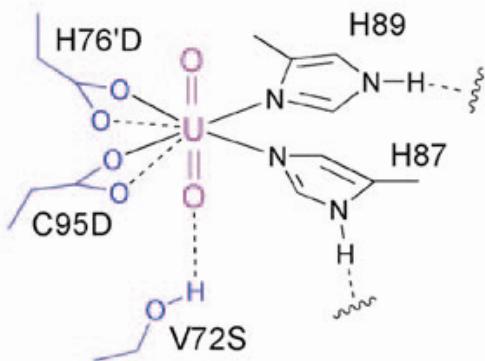


Figure 12. Engineered NikR protein for selective binding of UO_2^{2+} (90).

It should be emphasized that, to be applicable to the extraction of uranium from seawater, the ligands should be robust and simple, easy and less costly to make on a large scale, and have a fast sorption rate. A balance between these properties and the selectivity must be achieved.

3.3 Developing New Materials to Improve the Chemical Stability, Mechanical Durability, and the Sorption Kinetics of the Sorbents

To make the collection of uranium from seawater economically competitive, the sorbents must be stable and durable during repeated sorption/elution cycles. One of the major reasons for the failure of the TiO_2 sorption systems is the serious loss of the material in the collection process. The performance of the amioxime-based sorbents was also found to deteriorate after repeated use – successful reuse for 8 times has been achieved but a repetition of 18 times could reduce the collection cost by more than 20% (19).

Better techniques for functionalizing the fiber materials could increase the density as well as the binding strength of the ligands on the fiber. In addition, improved synthetic routes could help to prepare the sorbents with higher yield of the preferred configuration to allow uranyl chelate complex formation (e.g., the cyclic imide dioximes in Figure 10). Besides, if the cyclic dioximes are indeed the preferred configuration, means to protect them from breaking down in acidic elution could significantly increase the reusability of the amidoxime-based sorbents.

Though the non-woven polyethylene fiber has been used in marine experiments with some success, its hydrophobicity might adversely affect the sorption rate of ionic species such as uranium ($\text{UO}_2(\text{CO}_3)_3^{4-}$, etc.). Previous studies aiming at improving the sorption kinetics include the preparation of hydrophilic amidoxime fibers by co-grafting multiple ligands (9), the preparation of hydrogels containing various acidic ligands (24) and the use of cellulose or cellulose-like materials (e.g., chitosan Figure 9) (17). The rapid advances of nanotechnology in recent years are expected to help develop novel materials for applications in the collection of uranium in seawater.

Use of biomass for the collection of uranium is another area that should be investigated. Previous studies have shown that the concentration factor of biomass such as algae for uranium in seawater is about 200 (18), which is too low for practical applications. Development of Innovative biomaterials with engineered protein (such as that shown in Figure 12 could significantly increase the concentration factor and make bio-collection practical.

3.4 Developing Innovative Elution Processes to Improve the Elution Efficiency and Minimize Loss of Sorbents

The loss and deterioration of sorbents in the elution process (e.g, with 1 M HCl for the amidoxime-based systems) is a significant factor that limits the economical competitiveness of current collection systems. Innovative elution processes should be studied. For example, application of supercritical fluid CO_2 extraction of uranium from sorbents loaded with uranium is an area worth investigating.

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