

AQUACULTURE OF URANIUM IN SEAWATER BY A FABRIC-ADSORBENT SUBMERGED SYSTEM

NORIAKI SEKO, AKIO KATAKAI, SHIN HASEGAWA, MASAO TAMADA,*
NOBORU KASAI, HAYATO TAKEDA, and TAKANOBU SUGO

Japan Atomic Energy Research Institute
Takasaki Radiation Chemistry Research Establishment
1233 Watanuki, Takasaki, Gunma 370-1292, Japan

KYOICHI SAITO Chiba University, Department of Materials Technology
1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

KEYWORDS: radiation-induced graft polymerization, uranium-specific fabric submerged system, seawater

Received September 11, 2002

Accepted for Publication April 11, 2003

The total amount of uranium dissolved in seawater at a uniform concentration of 3 mg U/m³ in the world's oceans is 4.5 billion tons. An adsorption method using polymeric adsorbents capable of specifically recovering uranium from seawater is reported to be economically feasible. A uranium-specific nonwoven fabric was used as the adsorbent packed in an adsorption cage 16 m² in cross-sectional area and 16 cm in height. We submerged three adsorption cages in the Pacific Ocean at a depth of 20 m at 7 km offshore of Japan. The three adsorption cages consisted of stacks of 52 000 sheets of the uranium-specific non-woven fabric with a total mass of 350 kg. The total amount of uranium recovered by the nonwoven fabric was >1 kg in terms of yellow cake during a total submer-sion time of 240 days in the ocean.

I. BACKGROUND

Uranium is dissolved in seawater at a uniform concentration of 3 mg U/m³ in the world's oceans: The molar concentration of uranium of 1.4×10^{-8} M in seawater is three parts of one billion of that of chloride. The total amount of uranium in seawater is 4.5 billion tons, which is much larger than that of uranium in terrestrial ores. A predominant species of uranium in seawater is determined to be uranyl tricarbonate ion,^{1,2} UO₂(CO₃)₃⁴⁻. Uranium is essential for managing existing atomic power plants. For example, Japan has consumed ~10 000 tons of uranium per year as fuel for atomic power plants.

The adsorption method using solid materials was determined to be more feasible and environmentally friendly than

other methods such as solvent extraction, floatation, and precipitation. Davies et al.³ in 1964 suggested the recovery of uranium from seawater using an adsorption column charged with hydrous titanium oxide. Seawater was forced to flow upward through the adsorption column using a pump. Sparingly soluble metal oxides were screened in terms of adsorption rate, and from these, hydrous titanium oxide was determined to be a promising adsorbent specific for uranium in seawater.⁴

A polymeric adsorbent capable of recovering uranium from seawater was prepared in the early 1980s by Egawa and Harada⁵ and Astheimer et al.⁶ The preparation scheme termed amidoximation was relatively simple: a cyano group (—CN) of the polymers, such as acrylonitrile-divinylbenzene copolymer, was allowed to react with hydroxylamine (NH₂OH) to form an amidoxime group (—C=N(OH)NH₂) as a chelate-forming group with the uranyl ion (UO₂²⁺) in seawater.⁷ A commercially available acrylonitrile fiber was readily converted into the amidoxime fiber capable of recovering uranium from seawater by amidoximation. The National Institute of Advanced Industrial Science and Technology (Shikoku) has been extensively developing an amidoxime-fiber bundle, which is packed in the adsorption bed.⁸

The possible uranium recovery system is composed of a combination of the adsorbent, i.e., bead or fiber, and the driving force for transporting the seawater, i.e., pump or current flow. To study the fundamental adsorption characteristics of uranium in seawater, seawater was forced to flow through the adsorbent-packed bed by controlling both the flow rate and temperature of seawater at prescribed values.^{9,10} From a feasibility study, the recovery system using the ocean current and wave is reported to be advantageous over that using a pump.^{11,12}

II. PREPARATION OF FABRIC ADSORBENT

A nonwoven fabric is used as a packing material for an adsorption cage submerged in the ocean. Acrylonitrile

*E-mail: tamada@taka.jaeri.go.jp

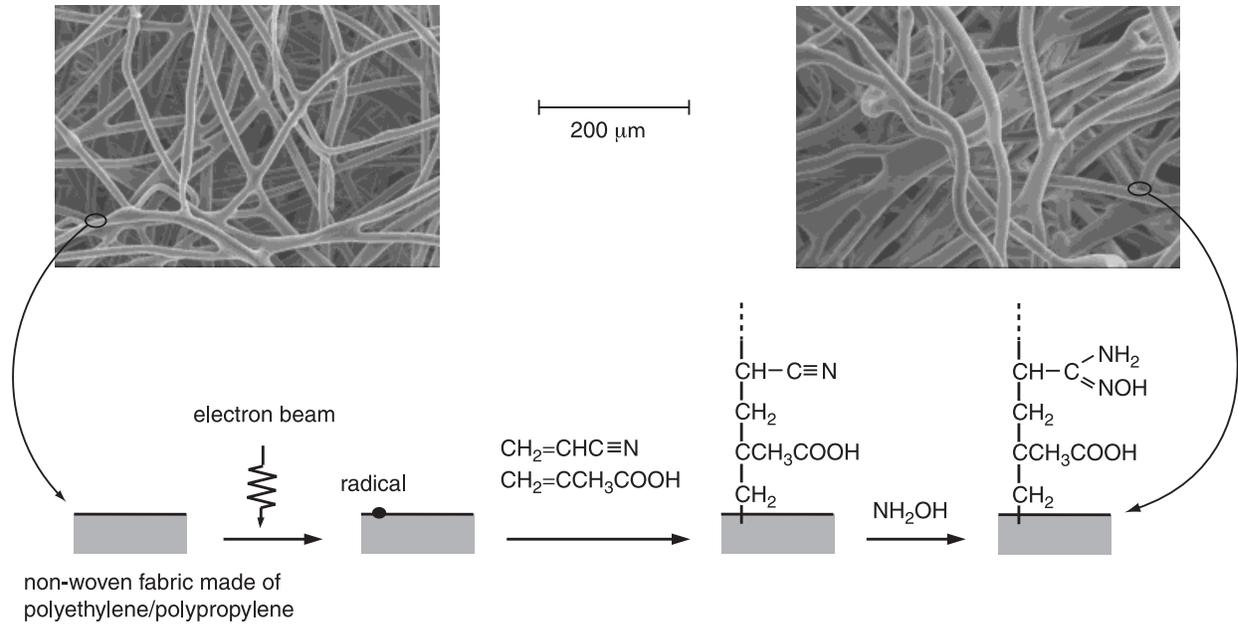


Fig. 1. The preparation scheme of polymeric adsorbent in nonwoven fabric form containing an amidoxime group capable of forming a complex with uranyl tricarbonate ion as predominant species of uranium dissolved in seawater. A sheet of the nonwoven fabric made of polyethylene/polypropylene was irradiated with an electron beam to produce radicals. A cyano-group-containing vinyl monomer, acrylonitrile, was grafted with a hydrophilic monomer onto the irradiated nonwoven fabric. Subsequently, the cyano group of the grafted polymer chain was converted into an amidoxime group by reacting with hydroxylamine.

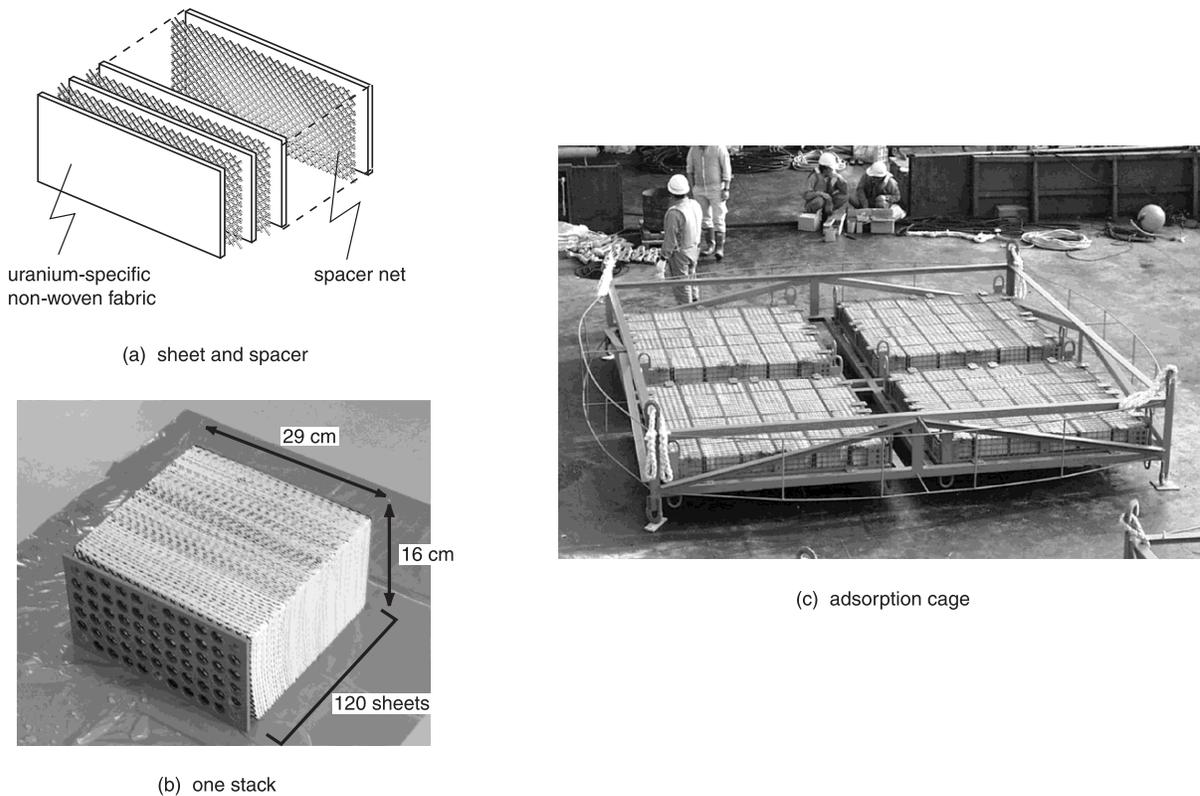


Fig. 2. Stacks of uranium-specific nonwoven fabric in adsorption cages. One hundred twenty sheets of the uranium-specific nonwoven fabric of 29-cm length, 16-cm width, and 0.2-mm thickness were assembled in parallel to the spacer nets to form a stack. One hundred forty-four stacks were packed in one adsorption cage.

($\text{CH}_2=\text{CHCN}$) was grafted onto the nonwoven fabric made of polyethylene/polypropylene by radiation-induced graft polymerization,¹³ and subsequently, the produced cyano group of the grafted polymer chain was converted into the amidoxime group.¹⁴ Cograft polymerization of hydrophilic monomer or methacrylic acid ($\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$) with acrylonitrile onto the nonwoven fabric was effective in improving the adsorption rate of uranium onto the resulting amidoxime adsorbent in seawater (Fig. 1). Acrylonitrile has a precursor group or a cyano group of the amidoxime group that specifically captures uranyl species, whereas methacrylic acid enhances micropore formation for uranyl species diffusion into the adsorbent; therefore, a balance between the amidoxime group and the hydrophilic group in producing the amidoxime adsorbents was required to yield a maximum adsorption rate of uranium.^{15,16}

III. URANIUM ADSORPTION IN SUBMERSION SYSTEM

We submerged adsorption cages for uranium recovery in the Pacific Ocean at 7 km offshore from Sekine-Hama in Aomori Prefecture, Japan ($141^\circ 18.0'E$, $41^\circ 24.4'N$). The sea depth at the submersion site was ~ 40 m. The adsorption cage, 16 m^2 in cross-sectional area and 16 cm in height, consisted of 144 stacks of the amidoxime adsorbent in the form of nonwoven fabric. Each stack consisted of 120 sheets of the nonwoven

fabric of 29-cm length, 16-cm width, and 0.2-mm thickness, with 59 sheets of spacer nets (Fig. 2). The stacks were regularly packed into the adsorption cages in the direction parallel to the perpendicular axis of the adsorption cages. Three adsorption cages, connected in series with four ropes, were submerged in seawater with a span of 1.5 m by a floating frame that was stabilized by four buoys suspended by four 40-ton anchors placed on the seafloor (Fig. 3). The total mass of the nonwoven fabric packed into the three adsorption cages was 350 kg in the dry state. The frame was designed to endure the following ocean conditions: wind strength, 30 m/s; tidal current, 1.03 m/s; and wave height, 10 m.

Seawater rapidly invades sheets of the spacer nets upward and downward induced by the wave motion and slowly penetrates sheets of the nonwoven fabric. In addition, the tidal motion stirs seawater horizontally between the adsorption cages. Uranium species in the bulk of seawater are transported to the amidoxime group of the polymer chain grafted onto the nonwoven fabric via both convective and diffusional mass-transfer processes.

The uranium recovery experiment was performed from autumn of 1999 to autumn of 2001. The adsorption cages were pulled out from the seawater by using a crane ship every 20 to 40 days. Thirteen to sixteen stacks were taken out of the adsorption cage to elute uranium adsorbed onto the nonwoven fabric with 0.5 M hydrochloric acid. The stacks were returned to the adsorption cages after elution and used for subsequent

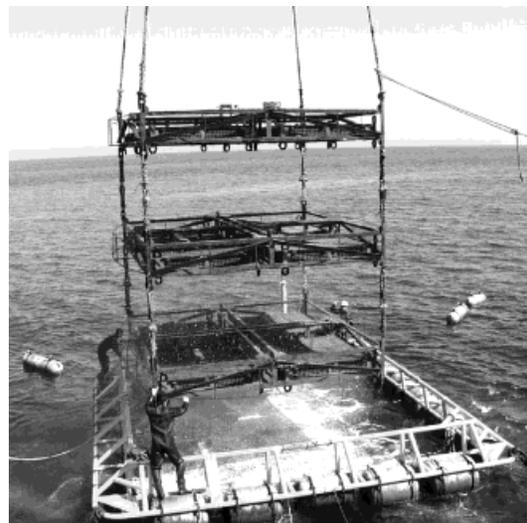
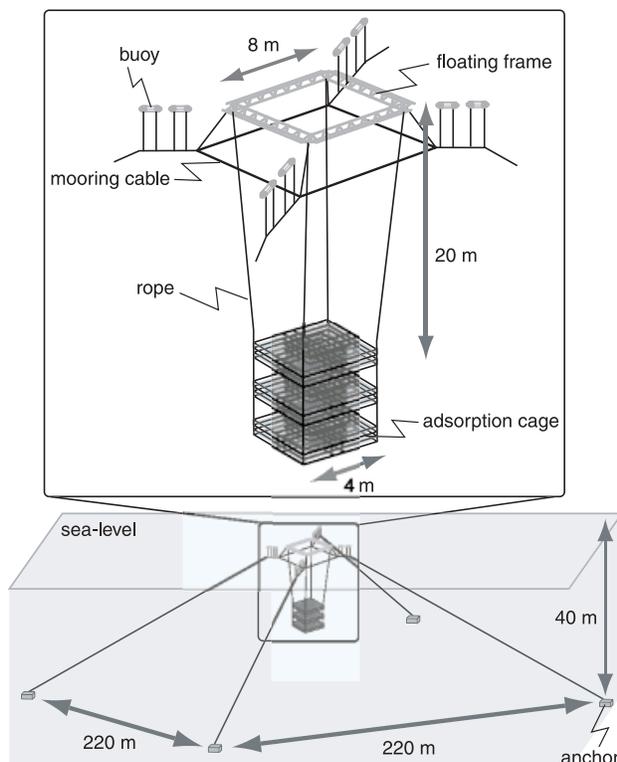


Fig. 3. A submerged system of adsorption cages for uranium recovery from seawater. A 64-m^2 floating frame made of stainless steel was stabilized by the mooring cables and buoys suspended by four anchors placed onto the seafloor. The frame hung three adsorption cages, which were connected in series with four ropes. The top cage was submerged at a depth of 20 m, and the span between cages was 1.5 m.

TABLE I
Amount of Uranium Recovered from the Adsorption Cages Charged with Nonwoven Fabric Adsorbent

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	20	144	12 to 13	47	0.016
28 June to 8 Aug	40	144	13 to 22	66	0.011
8 Aug to 7 Sep	30	144	22 to 24	101	0.023
7 Sep to 28 Sep	20	144	22 to 24	76	0.026
28 Sep to 19 Oct	20	144	18 to 22	77	0.027
2001					
15 Jun to 17 Jul	30	216	13 to 18	95	0.015
15 Jun to 20 Aug	60	72	13 to 20	48	0.011
15 Jun to 21 Sep	90	72	13 to 19	120	0.019
18 Jul to 20 Aug	30	216	18 to 20	119	0.018
18 Jul to 21 Sep	60	144	18 to 19	150	0.017
20 Aug to 21 Sep	30	216	19 to 20	118	0.018
Total		1800		1083	

^aAmount in terms of yellow cake.

submersion. The amount of uranium recovered by the total number of stacks in the adsorption cage was evaluated by linear multiplication of that eluted from the sampled stacks of the nonwoven fabric.

The amount of uranium adsorbed onto the amidoxime adsorbent during each submersion period and the apparent adsorption rate defined by dividing the amount of adsorbed uranium by the submersion period and stack number are summarized in Table I, as well as the seawater temperature. The variation of the apparent adsorption rate will be due to seawater temperature, the wave and tidal motions of the adsorption cages in seawater, and the elution history of the amidoxime adsorbent.

Throughout the uranium recovery experiment, the total amount of uranium recovered by the 350-kg nonwoven fabric was >1 kg in terms of yellow cake during a total submersion time of 240 days in the ocean; uranium ores with ~0.3% uranium were aquacultured in the Pacific Ocean.

Biofouling was observed on the surface of the stacks. Biofouling includes adhesion and subsequent growth of marine microorganisms and algae; however, most of these marine microorganisms were removed by immersing the stacks in fresh water after the stacks were taken out from the adsorption cage. The drastic decrease in ionic strength induced the detachment of these marine microorganisms from the surface of the stacks.

Projects on uranium recovery from seawater have been carried out for two decades in Japan from a laboratory scale to an offshore plant scale; extensive development of high-performance adsorbents and feasibility studies of the recovery system led to the development of an ocean-current/wave-utilizing system using the submerged adsorption cage charged with stacks of the nonwoven fabric capable of specifically recovering uranium.

REFERENCES

1. K. SAITO and T. MIYAUCHI, "Chemical Forms of Uranium in Artificial Seawater," *J. Nucl. Sci. Technol.*, **19**, 145 (1982).
2. K. SAITO and T. MIYAUCHI, "Diffusivity of Uranium in Artificial Seawater," *Kagaku Kogaku Ronbunshu*, **7**, 545 (1981).
3. R. V. DAVIES, J. KENNEDY, R. W. MCILOY, R. SPENCE, and K. M. Hill, "Extraction of Uranium from Seawater," *Nature*, **203**, 1110 (1964).
4. N. OGATA, "Review on Recovery of Uranium from Seawater," *Bull. Soc. Sea Water Sci. Japan*, **34**, 3 (1980).
5. H. EGAWA and H. HARADA, "Recovery of Uranium from Seawater by Using Chelating Resins Containing Amidoxime Groups," *Nippon Kagaku Kaishi*, 958 (1979).
6. L. ASTHEIMER, H. J. SCHENK, E. G. WITTE, and K. SCHWOCHAU, "Development of Sorbers for the Recovery of Uranium from Seawater. Part 2," *Sep. Sci. Technol.*, **18**, 307 (1983).
7. T. HIROTSU, S. KATOH, K. SUGASAKA, M. SENO, and T. ITAGAKI, "Adsorption Equilibrium of Uranium from Aqueous [UO₂(CO₃)₃]⁴⁻ Solutions on a Polymer Bearing Amidoxime Groups," *J. Chem. Soc. Dalton Trans.*, **9**, 1983 (1986).
8. T. HIROTSU, "Recovery of Trace Metals from Seawater," *Bull. Soc. Sea Water Sci. Japan*, **55**, 223 (2001).
9. K. SAITO, K. UEZU, T. HORI, S. FURUSAKI, T. SUGO, and J. OKAMOTO, "Recovery of Uranium from Seawater Using Amidoxime Hollow Fibers," *AIChE J.*, **34**, 411 (1988).

10. T. TAKEDA, K. SAITO, K. UEZU, S. FURUSAKI, T. SUGO, and J. OKAMOTO, "Adsorption and Elution in Hollow-Fiber-Packed Bed for Recovery of Uranium from Seawater," *Ind. Eng. Chem. Res.*, **30**, 185 (1991).
11. H. NOBUKAWA, M. TAKAGI, M. KOBAYASHI, H. NAKAGAWA, J. SAKAKIBARA, and N. TAKAGI, "Development of Floating Type-Extraction System of Uranium from Seawater Using Seawater Current and Wave Power. 1," *J. Shipbuild. Soc. Japan*, **165**, 281 (1989).
12. H. NOBUKAWA, M. KITAMURA, M. KOBAYASHI, H. NAKAGAWA, N. TAKAGI, and M. TAMEHIRO, "Development of Floating Type-Extraction System of Uranium from Seawater Using Seawater Current and Wave Power. 3," *J. Shipbuild. Soc. Japan*, **172**, 519 (1992).
13. A. KATAKAI, N. SEKO, T. KAWAKAMI, K. SAITO, and T. SUGO, "Adsorption of Uranium in Seawater Using Amidoxime Adsorbents Prepared by Radiation-Induced Cograftering," *Nippon Genshiryoku Gakkaishi*, **40**, 878 (1998).
14. K. SAITO, T. YAMAGUCHI, K. UEZU, S. FURUSAKI, T. SUGO, and J. OKAMOTO, "Optimum Preparation Conditions of Amidoxime Hollow Fiber Synthesized by Radiation-Induced Grafting," *Appl. Polym. Sci.*, **39**, 2153 (1990).
15. T. KAWAI, K. SAITO, K. SUGITA, T. KAWAKAMI, A. KANNO, A. KATAKAI, N. SEKO, and T. SUGO, "Preparation of Hydrophilic Amidoxime Fibers by Cograftering Acrylonitrile and Methacrylic Acid from Optimized Composition," *Radiat. Phys. Chem.*, **59**, 405 (2000).
16. T. KAWAI, K. SAITO, K. SUGITA, A. KATAKAI, N. SEKO, T. SUGO, J. KANNO, and T. KAWAKAMI, "Comparison of Amidoxime Adsorbents Prepared by Cograftering Methacrylic Acid and 2-Hydroxyl Ethyl Methacrylate with Acrylonitrile onto Polyethylene," *Ind. Eng. Chem. Res.*, **39**, 2910 (2000).

Noriaki Seko (BS, 1994, and MS, 1996, applied chemistry, Kanagawa University, Japan) is employed by Japan Atomic Energy Research Institute. His background includes functional materials and radiation chemistry.

Akio Katakai is employed by Japan Atomic Energy Research Institute. His background includes materials design for separation and environmental purification by radiation-induced graft polymerization.

Shin Hasegawa (BS, chemistry, 1993, and MS, materials engineering, 1995, Gunma University, Japan) is employed by Japan Atomic Energy Research Institute. His background includes radiation chemistry, synthesized gel, pyrolysis of polymer, and graft polymerization.

Masao Tamada (BS, applied chemistry, Osaka Prefecture University, Japan, 1978; MS, radiation chemistry, 1980, and PhD, engineering, 1988, Osaka University, Japan) is a principal scientist of environment functional material with Japan Atomic Energy Research Institute. His background includes surface modification of polymer and radiation chemistry of polymer.

Noboru Kasai (BS, mechanical engineering, Gunma University, 1976) is employed by Japan Atomic Energy Research Institute. His background includes radiation processing of organic materials.

Hayato Takeda (BS, chemical engineering, Muroran Institute of Technology, 1968) is employed by Japan Atomic Energy Research Institute. His background includes regulation for nuclear fuel and planning of equipment.

Takanobu Sugo is employed by Japan Atomic Energy Research Institute, and he is also a president of Environment Purification Research Company. His background includes radiation-induced graft polymerization and its applications.

Kyoichi Saito (BS, applied chemistry, Waseda University, Japan, 1977; MS, chemical engineering, 1979, and PhD, engineering, 1984, University of Tokyo, Japan) is an associate professor at Chiba University. His background includes materials design for separation and reaction by radiation-induced graft polymerization.