TITLE:

Recovery of Uranium from Sea Water. Current State of Technology and Requirements of Future Research

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51

Recovery of Uranium from Sea Water. Current State of Technology and Requirements of Future Research

By

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Abstract

The present status of technology for the recovery of uranium has been reviewed. Adsorbent qualities were discussed in terms of three important criteria: adsorption rate, equilibrium adsorption and chemical as well as physical stability. It was elucidated that a significant improvement of the adsorption rate is most important. Efforts were made to clarify factors influencing the adsorption rate. A method to treat a tremendous amount of sea water is of much importance as well. Pumping-up and direct use of sea currents were compared with each other. It has been emphasized that the active utilization of the various advantages of the latter method is crucial for the realization of the recovery project. The physical capability of the method was illustrated. Some composite systems with electric power generation plants were also discussed.

1. Introduction

Uranium has been one of the most promising possibilities for petroleum substitutes. It is important, especially for Japan, to make continuous efforts to secure a uranium supply by long-term purchase contracts, searching new ores in undeveloped areas and so on. At the same time, efforts to exploit our own uranium resources are certainly necessary. However, it is clear that we cannot expect large domestic ores in Japan. It should be noticed here that the predominant percentages of uranium resources are found in sea water rather than in ores.

In the world's oceans, ca. 4×10^9 tons of uranium are dissolved, while the ore resources available within a reasonable cost ($\leq$50$/1b, 1982) are limited to 2.3 $\times 10^6$ and 2.7×10^6 tons for the assured and estimated additional amounts, respectively[1]. It is interesting to compare them with the 5.3×10^6 tons which are brought to Japan simply by the Kuroshio current over a one year period[2]. Therefore, a successful recovery of uranium from sea water may reasonably be expected to provide an encouraging prospect not only to Japan, but to the world wide energy problem.

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These circumstances have aroused much attention to find recovery methods of sea uranium. Hydrous titania was the first adsorbent reported to bind a significant amount of uranyl ion directly from sea water[3]. Encouraged by its partial success, many inorganic as well as organic ligands have been investigated. Various methods other than adsorption have also been proposed, but recent investigations have been concentrated on the adsorbents of superior properties, polymers functionalized with macrocyclic compounds[4,5], dithiocarbamate[6], amidoxime[7,8] etc. These chelating resins put the recovery project very close to a practical application.

In addition to thorough studies on adsorbents, appropriate designs of the whole system are certainly important. The recovery plant will be of a tremendous scale, if one considers contributing to the energy problem to some extent. Without a smooth feedback of information between studies on the system and the adsorbents, the ultimate success will never be attained. Here we would like to discuss some problems of the system on the basis of the present status of adsorbent qualities. Special emphasis will be placed on a method for processing a huge amount of sea water.

2. Development of Absorbent

The discovery of hydrous titania and its partial success of uranium recovery from sea water have stimulated active investigations on various adsorbents of superior properties. A variety of characteristics are required to be satisfied in the ultimately applicable adsorbent, but the following three factors seem to be basically most important:

1. *Large adsorption rate*: This requirement has the greatest importance in order to minimize the contact time and hence the adsorbent volume, the equipment scale and finally the cost. The apparent adsorption rate is a result of many factors, namely liquid-to-particle mass transfer, intra-particle mass transfer and reaction rate. Therefore, the adsorption rate itself and the rate determining step are dependent on the size and the form of the adsorbents, the type of ligand and the method for contacting the adsorbent with sea water. It is necessary to separate the overall adsorption rate into influencing factors, to which appropriate improvements should be tried. Details will be discussed in the next section.

2. *Large equilibrium adsorption*: A larger value can reduce the number of recyclings of the adsorbent, although the adsorbent is usually subjected to an elution process long before the equilibrium adsorption is obtained. Such an unfavorable treatment is obliged again by a slow adsorption rate. A high differentiating factor from other metal ions contributes to a larger equilibrium adsorption.

3.   *Good chemical as well as physical stability*: The adsorbent is required to be resistant to a fairly rapid and long-term flow of sea water and to a repeated treatment of adsorption and elution.   Since the weight ratio of uranium recovered by the adsorbent is still small, any deterioration of properties, even partially, causes a large increase of the recovery cost.   Any adsorbent polluting environment is definitely rejected.

Figure 1 summarizes properties 1 and 2 of the new chelating resin recently obtained by us[6,10] in comparison with those of hydrous titania[9].
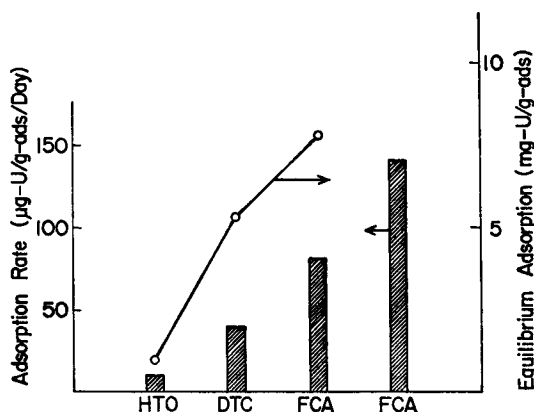

Fig. 1.   Adsorption rate and equilibrium adsorption of hydrous titania (HTO)[9], dithiocarbamate (DTC)[6], and fiber composite of amidoxime (FCA)[10].

2.1   Improvement of Adsorption Rate

As was illustrated in Figure 1, the adsorption rate has been improved much by the introduction of organic chelating resin.   In spite of this, we are still obliged to wander around the area of an adsorption rate less than 200 μg-U/g-adsorbent/ day.   One reason for not being able to cross the barrier seems to arise from the slow mass transfer at the phase boundary.   The flow, F [meq/cm^2 sec] at the phase boundary is expressed by Eq. (1):

$$F = D \frac{\Delta C}{\delta} \tag{1}$$

where D [cm^2/sec], ΔC [meq/cm^2] and δ [cm] denote the diffusion constant of uranyl ion in aqueous phase, the concentration difference between liquid and adsorbent phases and the thickness of the phase boundary, respectively.   In order to accelerate the process, it is definitely important to depress the thickness, δ of the layer by the employment of a faster flow rate of sea water.

One of the major reasons for the slow rate of adsorption comes also from a small intra-particle diffusion.   The diffusion process in a solid adsorbent is com-

plicated. The properties of the diffusing substance are evidently influential for permiability, but no information on the species is available now. Important variables include also a chemical structure of the adsorbent, hydrophilicity, the degrees and structure of cross-linking. It is characteristic that no operational parameters intervene in the rate processes. Thus, the improvement of this mass transport should be accomplished simply by the chemical modification of the influential factors above mentioned.

Another interesting point for explaining the slow adsorption is an extraordinary slow rate of the ligand exchange reaction. In order to bind a uranyl ion, at least one of the three carbonate ions is required to be exchanged by the ligand of the adsorbent. However, the rate constants measured recently[11] are exceptionally small even in a homogeneous solution. The acceleration of the kinetic process may be crucial to get an increased rate of the adsorption.

Elucidation of the rate determining step for each combination of an adsorbent and a system is certainly important to identify the point of improvement. At the same time, whatever the rate determining step is, the practical trials toward acceleration of the relevant processes are urgently required.

3. Contact Method of Adsorbent with Sea Water

Since the concentration of uranium is extremely low, it is necessary to treat a tremendous amount of sea water. There are basically two ideas for contacting an adsorbent with sea water: pumping-up and direct use of the sea current. Preliminary cost estimations have been undertaken for these two processes. The principal input data are summarized in Table 1[12~14]. Some of them are hypothetical, because not all relevant data were available on an experimental basis at that time.

Table 1. Principal Input Data for Cost Estimation of Uranium Recovery

	Pumping-up (MMAJ)[12,13]	Pumping-up (EXXON)[14]	Sea Current (MMAJ)[12,13]
Adsorbent	TiO_2	TiO_2	TiO_2
Annual uranium production (ton)	1000	1000	1000
Recovery of adsorption (%)	60	80	60
Linear flow rate (cm/sec)	1	0.35	
Adsorption rate (μg-U/g-ads/day)	20	21	12
Electricity for pumping (MW)	570		
Adsorbent bed area (10^5 m^2)	9.65	19	6.8
Cost ($/lb)	224~90	1437~740	

* MMAJ: Metal Mining Agency of Japan.

On the basis of this cost estimation, the pumping-up method was concluded to be more economical than the direct use of the sea current. In a system of the latter, 20 adsorption stacks (The total area is listed in the Table.) are claimed to be arranged in a zig-zag way leading to a large total occupation area (5.5 km × 5.5 km =3.0 × 10⁷ km²). However, this contributes to a sharp increase of the construction cost.

It should be noted here that the estimation basis sets adopt a slow adsorption with a high percentage of recovery. In the case of pumping-up, the high recovery yield is an essential condition, if one pays attention to the cost of pumping-up energy. In order to obtain much faster adsorption rates, it is indispensable to have a faster flow of sea water. However, it directly leads to higher costs of pumps of larger capacities and of pumping energy. As far as a constant percentage of recovery is maintained, the cost increase can be compensated by the increased rate of uranium adsorption. However, this does not mean a cost reduction. Furthermore, it is generally observed that the percentage of recovery is lowered by passing a faster flow of sea water. Therefore, the adoption of a much faster flow rate is not acceptable for the pumping-up method, from the comparison of the cost/performance relationship. These circumstances are never expected in the case of the direct use of the sea current.

Moreover, the above input data and comparison obviously overlook various important characteristics of the direct use of the sea current. The following points should be considered seriously.

1. *Flow rate is completely different for two cases*: As will be demonstrated in the following section, it is possible to use the sea current in the range 1–2 knots or at least 0.5–1 knots, which corresponds to 25–50 cm/sec. Compare the flow rate in the case of pumping-up: 1.0 or at most 1.3 cm/sec. A much faster flow (25–50 fold) is obtainable without any consumption of external energy.

2. *Faster flow gives a large rate of uranium adsorption*: As was suggested in an earlier section, one of the major resistances of adsorption originates with the slow mass transfer at the phase boundary of sea water and a solid adsorbent. This is lowered by the adoption of a faster flow rate. Recently, we have developed a new adsorbent of fiber material which can be passed through a rapid current of sea water[10]. Figure 2 shows the dependence of the adsorption rate on the flow rate. It clearly shows that the adsorption rate is increased much by a faster flow rate. It should be noted that the flow up to 50 cm/sec (1 knot) is most influential for an increase of the adsorption rate.

3. *Occupation surface area should be minimized by the use of sea depth*: The pumping-up method postulates a multi-layered fixed bed system. It is desirable to decrease
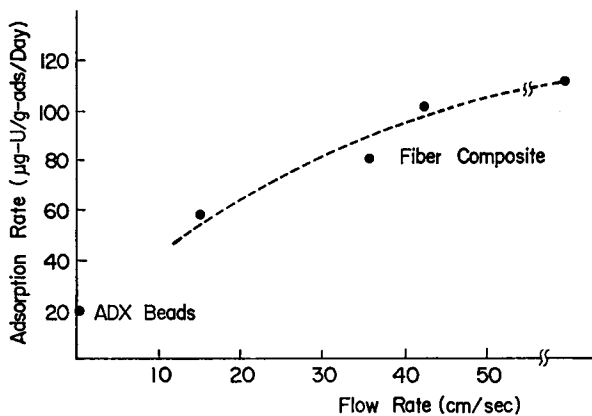
Fig. 2. Effect of flow rate on the adsorption rate[10]. (Adsorption
         rate was obtained by one day contact of 50 mg of polymer
         with 5 l of natural sea water.)

the occupation area by making a tall column. However, the capacity of the pump
must be compensated by the head of water. On the other hand, the direct use of
the sea current can utilize the sea depth to minimize the occupation area. The
huge occupation area in the Table 1 is a result of the complete neglect not only
of this factor, but of several advantages already discussed.

Without significant improvements of adsorption characteristics, especially the
adsorption rate, it is difficult to realize the uranium recovery project. We should
concentrate our efforts on this criterion. Based on the above discussions, we believe
that the system should directly use the sea current. Adsorbents should also be ad-
justed so as to be suitable for use in a rapid sea stream.

4. Direct Utilization of Sea Current

4.1 Consideration of Physical Capability

It is important to obtain knowledge about sea currents so as to design the
most suitable adsorbent as well as appropriate contact systems in a rapid flow of
sea water. Figure 3 illustrates the flow axis of Kuroshio.[15] The axis is always
fluctuating in the range shown in the Figure. The two most probable axes with
and without meander are illustrated by the thick and dotted lines, respectively.
The statistical distribution of the axis is also included in the Figure. Figure 4
shows contour diagrams of the scalar mean velocity[16].

The fastest flow with a stable continuation was obtained near Cape Shiono-
misaki, or far to the south of the South-West Islands (near Formosa). These
points are satisfactory in view of the flow rate, but it is required to make a solution
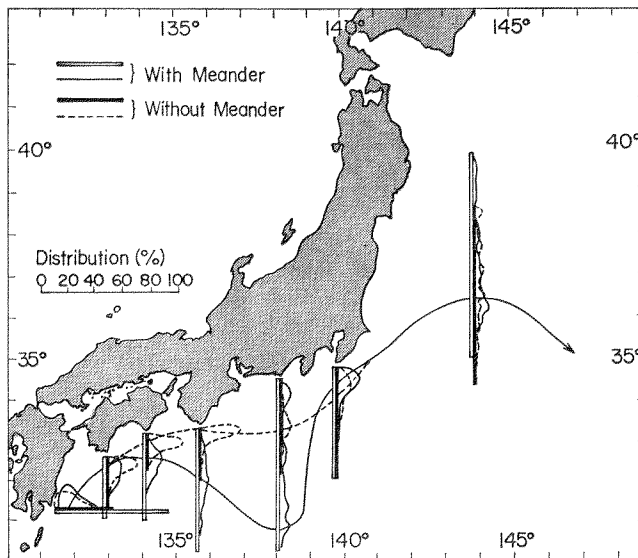for the mooring of the adsorption bed. The adsorption basement should be suita-

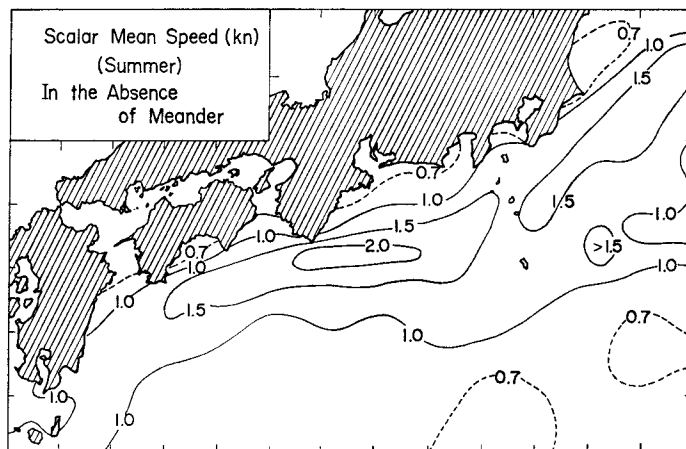Fig. 3.   Flow axes of Kuroshio with and without meander[15].

Fig. 4.   Scalar mean speed of Kuroshio in the absence of meander in summer season[16].

bly placed near land in order to avoid a transportation problem.   It is also advisable to choose a point where the depth is less than 50 m.   However, it is generally observed that a shallow sea has only a limited flow rate.   It is therefore very important to choose exceptional points satisfying these conflicting conditions.   Such conditions are required to be satisfied exactly in the project of a power generation plant by direct use of the sea current.   Possible points were already suggested, and in Figure 5 were illustrated flow-continuation curves at such four points[15].
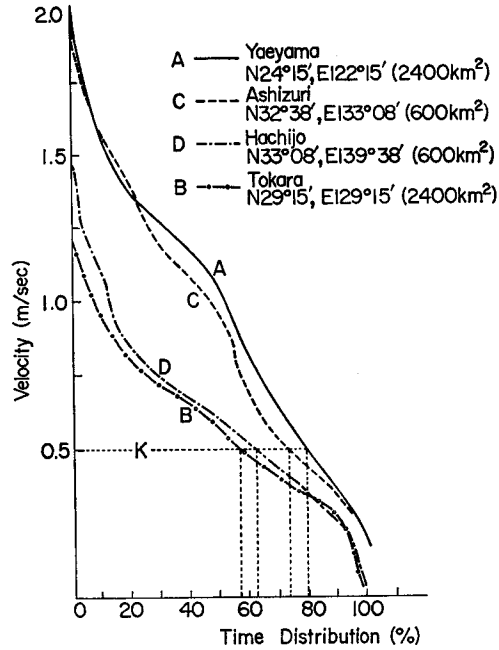
Fig. 5. Flow-continuation-curves at four points near the flow axis of Kuroshio[15].

The curves mean that an ordinate flow rate is obtainable for a percent period of the abscissa. For example, the K-line in the Figure means that a flow of 0.5 m/sec is assured for a 57, 63, 73, and 79% peroid at Tokara, Hachijo, Ashizuri, and Yaeyama areas, respectively. As is shown in this Figure, it is easy to choose several appropriate points which assure 0.5 knot (25 cm/sec) for 22 hrs (90%) within a one day period.

The head of water, h [mmAq] is related to the velocity, v [m/sec] by the simple Bernoulli theorem (2):

$$h = \gamma v^2/2g \qquad\qquad (2)$$

where γ [kg/m^3] and g [m/sec^2] mean the density of the sea water and the acceleration of gravity, respectively. If we put 0.5–1.0 knots for v, the head is limited only to 6.9–13.8 mmAq. Thus, the apparatus and the adsorbent are required to be completely free from any resistance for the flow of sea water.

4.2 Combination of Uranium Recovery with Power Generation Plant Utilizing Sea Current or Tidal Flow

Electric power generation plants are continuously trying to find possible ways to use the natural resources of energy. The use of sea currents or tidal flows can be bound together by common interests with the recovery project of uranium.

One of the most difficult problems for the power generation plant is the difficulty of transporting electricity from the basement in the middle of sea to the distant mainland. A composite system of power generation and uranium recovery plants may reasonably be expected to give a clear solution. Although it is difficult for the power generation plant to provide enough energy for pumping-up[13], it may be enough to maintain the secondary energy requirement for the uranium recovery process using a direct use of the sea current.

4.3 Utilization of Warm Drain Water from Nuclear or Thermal Power Generation Plant

Thermal as well as nuclear power generation plants produce daily a big amount of warm sea water used for cooling the equipment. This may change the natural environmental condition around the exhaust of the drain water. In order to avoid a drastic change of the environment around there, the drain is cooled down before the final exit by passing through long artificial installations. In other words, warm sea water is running with a high speed in the water route. Such a combination provides ideal chances for the recovery of uranium. The following considerations are based on our trial undertaken at the Second thermal power generation plant of the Kansai Electric Power Company, Himeji, Hyogo prefecture during the period 1981–1983.

The drained sea water amounts to 6.9×10^{10} ton/year when integrating over power generation plants capable of producing more than 2000 MW/h for 300 days/year. The total uranium is calculated to be ca. 200 ton/year. A similar calculation for plants of more than a 500 MW/h capacity gives 460 tons of uranium per year. Although the amount is limited, it is worthwhile to make serious considerations as a step to the real scale equipment.

The advantages of the process are as follows:
1. The flow rate is large, even larger than that of the sea current, since the usual flow rate is 3-4 knots. for the drain water.
2. High temperature helps the adsorption rate to a great extent.
3. There is no necessity to build large equipment for the adsorption.
4. Pre-treatment of the sea water to remove rubbish material, microorganisms etc. is already finished.

The following fastors add a small difficulty to the project:
1. Concentration of active chlorine is maintained at a certain level. A due consideration to avoid an oxidation of ligands is required.
2. The concentration of heavy metal ions is high, especially when zinc or iron is added from an external source to avoid electric corrosion or scaling.

References

1) OECD/IAEA: Uranium-Resources, Production and Demand, 213 (1982).
2) M.R. Rodman, L.I. Gordon, and A.C-T. Chen, XN-RT-14, Vol. 1 (1979).
3) R.V. Davies, J. Kennedy, R.W. McIloy, and K.M. Hill, Nature, **203**, 1110 (1964).
4) I. Tabushi, Y. Kobuke, and T. Nishiya, Nature, **280**, 665 (1979).
5) I. Tabushi, Y. Kobuke, K. Ando, M. Kishimoto, and E. Ohara, J. Am. Chem. Soc., **102**, 5947 (1980).
6) I. Tabushi, Y. Kobuke, N. Nakayama, T. Aoki, and A. Yoshizawa, I & EC Prod. Res. and Dev. in press (1984)
7) H. Egawa, H. Harada, J. Chem. Soc. Japan, 958 (1979).
8) K. Schwochau, L. Astheimer, H.-J. Schenk, and E.G. Witte, Z. Naturforsch. B: Anorg. Chem. Org. Chem., **37b**. 214 (1982).
9) Report from Research Committee on Extraction of Uranium from Sea Water, J. Atomic Energy Soc. Japan, **22**, 31 (1980).
10) I. Tabushi and Y. Kobuke, Proceedings of an International Meeting of Recovery of Uranium from Sea Water, Tokyo, Japan, Oct. 1983, p. 267.
11) I. Tabushi and A. Yoshizawa, Proceedings of an International Meeting of Recovery of Uranium from Sea Water, Tokyo, Japan, Oct. 1983, p. 261.
12) M. Kanno, J. Atomic Energy Soc. Japan, **19**, 586 (1977).
13) M. Kanno, Symposium on Recovery of Uranium from Sea Water, Miyazaki, Japan, Abstract p. 1, Dec. 1981.
14) M.H. Campbell et al., XN-RT-15, Vol. 1 (1979).
15) Association of Hydrography of Japan, Environmental Map—Sea Current Series (1979).
16) Report from a Committee of Investigation of Resources, Science and Technology Agency, " Stepwise Development and Utilization of Kinetic Energy of Kukoshio " (1979).