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REVIEW

Present Status of Study on Extraction of Uranium from Sea Water

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The growth rate of the energy demand in the world has been lowered recently, however, the essenciality of the development of nuclear power generation has not been changed. Because of the limited resources of terrestrial uranium, the techniques of the extraction of uranium from sea water as the practically unlimited resources of uranium have been developed in Japan and other countries like F.R. Germany, Sweden, United States and others. Many fundamental results in the above field have been accumulated as well as some design studies and cost estimations have been conducted. In the last October, the International Meeting on Recovery of Uranium from Seawater was held in Japan organized by AESJ and IAEA. At this time moment, the up-to-date status of the studies including the selection of the chemical processes, development of adsorbents, design studies and cost estimations will be reviewed.

KEYWORDS: uranium, sea water, extraction, hydrous titanium oxide, adsorption, polyacrylamidoxime, macrocyclic hexadentate, conceptual design, contactor system, cost estimation

I. INTRODUCTION

The growth rate of the energy demand in the world has been lowered recently, however, the essenciality of the development of nuclear power generation has not been changed because of maldistribution of the fossil energy resources, their ultimate shortage and the harmful effect of their burnings upon the environment. According to the estimation by the IAEA/OECD, some inversions between uranium demand and supply are predicted at the years between 2000 and 2020 depending upon the projected growth rate curves and the possibility of the introduction of the fast breeder reactors. Therefore, some incentive exists to examine the possibility of obtaining the required uranium from the sea. This review attempts to describe the present status of study on extracting uranium from sea water and identifies the problems in satisfactorily designing and operating the demonstration plant.

II. URANIUM DEMAND AND RESOURCES

According to the report of the IAEA/OECD, "Uranium-Resources, Production and Demand" (Feb. 1982), several different future growth rates of uranium demand were projected depending on the different reactor strategies. These results are shown in **Fig. 1**. These data do not include that of USSR, Eastern Europe nor China. The maximum attainable production capacity of uranium shown in Fig. 1 was based on the all reasonably

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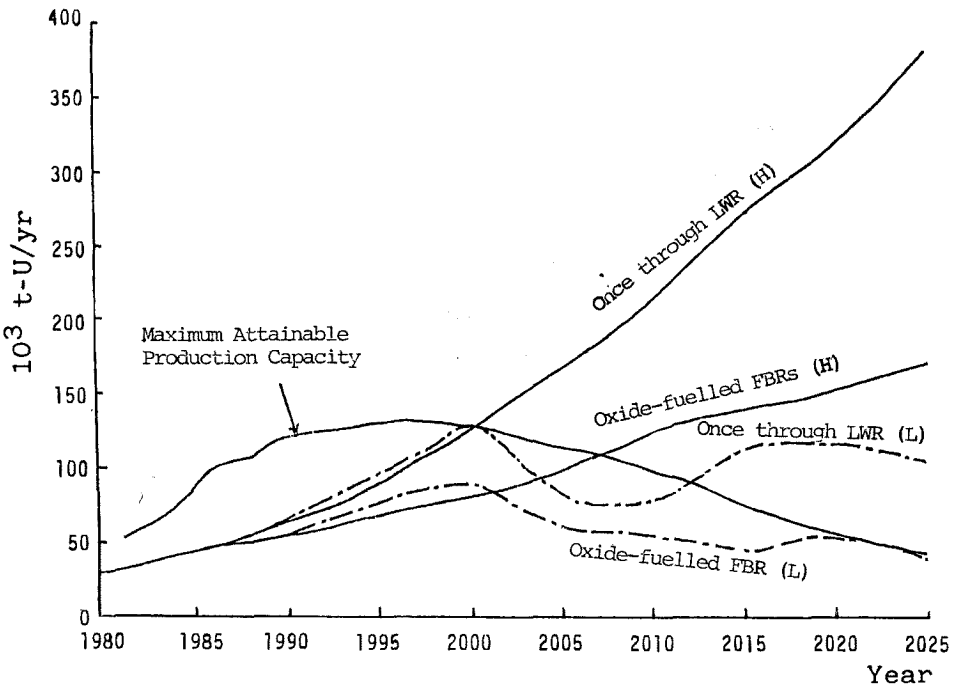


Fig. 1 Annual world uranium supply and demand

assured and estimated additional resources including phosphate ores. The maximum annual production rate would be reached between 1995 and 2000. The growth rate curves of "once through LWR" show the cases of the use of the conventional light water reactor without plutonium recycle. The *H* and *L* denote the high growth projection and low growth projection, respectively. "With oxide-fuelled FBR's" curves show the cases of the use of the plutonium-uranium mixed oxide fuels by fast breeder reactors. In the cases of "once through LWR", the inversions between uranium demand and production rate will occur at the year between 2000 and 2007, however, in the cases of "with oxide-fueled FBR's", the inversions will be delayed to the year between 2012 and 2020. In the former cases, some additional uranium production based on the other resources than known conventional resources will be required by the turn of the century. These facts have intrigued many investigators to extract uranium from the practically unlimited resources of uranium in sea water.

III. VARIOUS KINDS OF EXTRACTION PROCESSES

The uranium in the sea water is in a strongly complexed form at extreme dilution in the presence of relatively high concentrations of such other ions as sodium, magnesium, calcium, bromine and others, hence, it is considerably difficult to extract uranium from sea water economically. Various chemical processes have been considered and investigated. Among them, some coagulation and coprecipitation methods were investigated in Japan[(1)~(3)], but the long precipitation times involved in this process are not suitable for treating the large volume of sea water within the possibly short time. Adsorption methods with hydrous titanium oxide were much investigated[(4)~(6)] and are still considered to be one of the most promising methods. Some details will be described later. The PbS or galena showed some good adsorption capacity[(7)(8)], however, later it was found that it was difficult to keep the surface of PbS fresh without any oxide layers which deteriorate the adsorption capacity.

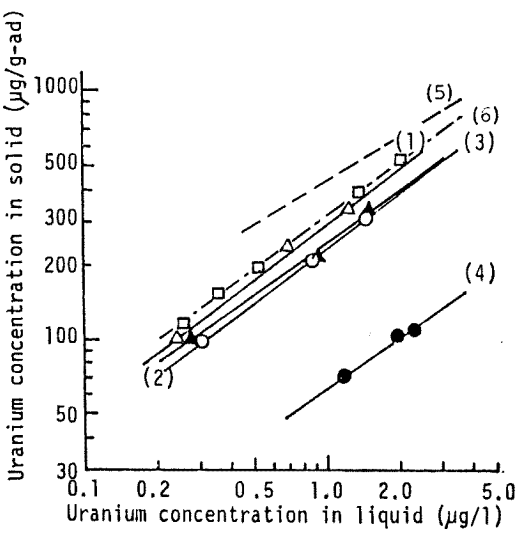
In initial stage, resorcinol arsonic acid resin showed a good uranium uptake, but it was later found that its capacity was deteriorated in sea water[7]. Recently, various kinds of chelating resins[9]~[11], macrocyclic hexadentate compounds[12] and other organic adsorbents have been developed. These adsorbents are also thought to be one of the promising methods.

Some flotation methods have been investigated[13][14], however, these methods are not suitable because of the fact that smaller froths are needed to attain high recovery but they take more time to float up to the sea surface. Solvent extraction, although feasible, any suitable solvent has not been found because solvent losses by entrainment and solubility would make it prohibitive economically and environmentally. In the Nuclear Research Center Jülich, the extraction of uranium with mutated and selected algae was investigated[15]. The uranium recoveries from sea water by use of such biological substances as chlorella and streptomyces were investigated[16]~[18], and recently, the researchers tested such other biological substances as acid polysaccharides (pectic acid, alginic acid *etc.*), phosphorylated polysaccharides (chitin phosphate, chitosan phosphate, cellulose phosphate *etc.*) and polyphenolic pigments (alizarin, quercetin *etc.*) The results of the recovery of uranium using immobilized chlorella and streptomyces, immobilized tannins were reported at the International Meeting on Recovery of Uranium from Seawater (IMRUS-1983) which was held in Tokyo, October 17~19, 1983. However, there are some problems of contacting microorganism with sea water and their collections.

IV. DEVELOPMENT OF ADSORBENTS

As for the inorganic adsorbents, many hydroxides, oxides, sulfides *etc.* of such metals as titanium, aluminum, magnesium and others were tested, however, hydrous titanium oxide has given the best results[4][5]. Various kinds of preparation processes of hydrous titanium oxide including neutralization method, urea method and thermal decomposition method have been investigated, and the urea method gave the best adsorption capacities and stabilities. Adsorption equilibrium curves of various hydrous titanium oxides are illustrated in **Fig. 2**[19], curves (1), (2), (3) and (4) are taken from the report to the Metal Mining Agency of Japan (MMAJ) prepared by Tokuyama Soda Co.[19] The curves (5) and (6) are based on the data of Ogata[20] and Yamawaki[21] though the data of the curve (5) was taken at 30°C. The maximum equilibrated adsorption capacity of the fine powder of hydrous titanium oxide prepared by the urea method has reached 660 μg/g dry adsorber at 25°C which is equivalent to about 1,600 μg/g Ti.

To improve the mechanical strength and avoid the blockage of the adsorbent filled bed, some granulation tests including pressing and crushing, screw extrusion and agitation granulation, were carried out. The



(1) Urea method: A (Tokuyama Soda Co.)
(2) 〃 B (〃)
(3) Neutralization: C (〃)
(4) 〃 D (〃)
(5) Ogata[20]
(6) Kanno[21]

Fig. 2 Adsorption equilibrium curves of various hydrous titanium oxides

uranium adsorption curves by fixed-bed columns for two different average particle sizes obtained in the MMAJ project (determined by Tokuyama Soda Co.) are shown in **Fig. 3**[19]. The granular adsorbent was made by only pressing and crushing. Recently, the granulation processes of hydrous titanium oxide with hydrophilic organic binder were developed in Tokuyama Soda Co. and Asahi Chem. Ind. Co. either by the contract with the MMAJ. Some typical results of uranium adsorption curves of granulated hydrous titanium oxide with organic binder according to the fixed-bed column tests are shown in **Fig. 4**[19]. These adsorbents have good adsorption capacity and high durability for attrition, therefore, some long-term column tests by fluidized-bed are under way.

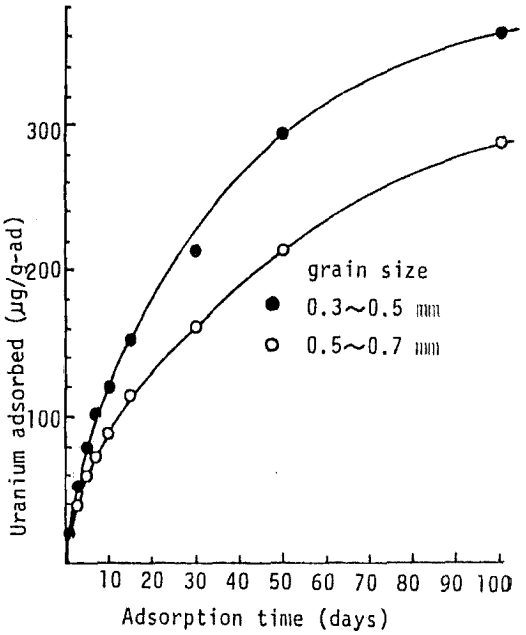


Fig. 3 Uranium adsorption curves by fixed-bed granular adsorbent made by pressing and crushing (Tokuyama Soda Co.)

Recently, the development of such organic adsorbents as polyacrylamidoxime resins[22]~[25], macroreticular chelating resins containing phosphino and/or phosphono groups[24], macrocyclic hexadentate resins[26]~[28] and others are noticeable. Some typical uranium uptake curves[23] of the polyacrylamidoxime are shown in **Fig. 5**. Some

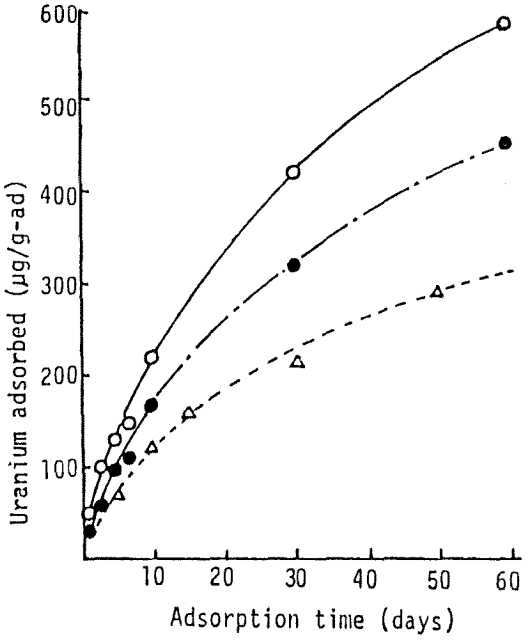


Fig. 4 Uranium adsorption curves of granulated hydrous titanium oxide with organic binder by fixed-bed (Asahi Chem. Ind. Co.)

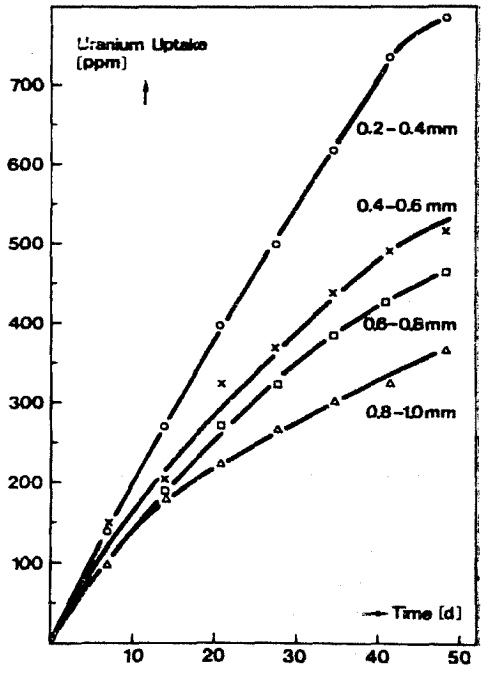
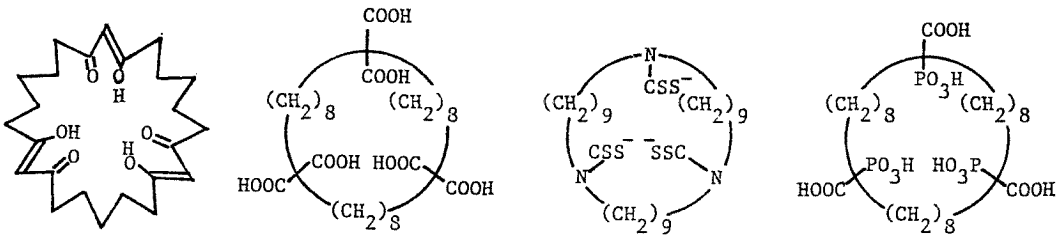


Fig. 5 Uranium adsorption curves of polyacrylamidoxime resin as a function of time and particle size

long-term recycling tests by using polyacrylamidoxime resin adsorbents and fluidized bed are being carried out in Japan[29] and F. R. Germany[23]. Tabushi *et al.*[26]~[28] in Kyoto University synthesized macrocyclic compounds having six coordinating atoms in a coplanarity by mimicking the crystallographic structure of uranyl complexes, including macrocyclic hexaketone, macrocyclic hexacarboxylic acids, polydithiocarbamates, macrocyclic triphosphonate and others. They demonstrated the effective uranium adsorption by using above compounds with artificial and natural sea water. The structural formula of these compounds are shown in **Fig. 6**.



(1) Macrocyclic hexaketone (2) Macrocyclic hexacarboxylic acid (3) Polydithiocarbamate (4) Macrocyclic triphosphonate

Fig. 6 Structural formula of macrocyclic hexadentates

Another noticeable development has been achieved with fibrous adsorbents. High uranium adsorption capacities of polyacrylamidoxime on the base of unit weight have been demonstrated by Schwochau[23], Sakane[30], Omichi[31] and others. Driscoll of MIT[32] reported some conceptual design of sea water contactor system with fiber-form adsorbents and cost calculations. The future attention must be paid to the fibrous adsorbents.

V. ADSORBENT/SEA WATER CONTACTOR SYSTEMS

To have a high quality adsorbent, we must contact the adsorbent with huge volumes of sea water to extract meaningful amounts of uranium due to its very low concentration of 3.3 $\mu g/l$ (3.3 ppb). If we assume 100% recovery, 3×10^{11} m^3/yr of sea water must be processed. For this purpose various kinds of contactor systems have been considered[33]~[36]. These include the tidal lagoon system, pumping and fixed-bed near-shore structure systems, flotation systems, magnetic adsorbent separation systems, off-shore floating systems and others.

The pumping and fixed-bed system was considered to be the most realistic because many experimentally proven conditions have been established and some conceptual designs were conducted by Taisei Corp. by the contract with the MMAJ. According to the first conceptual design on this bases, the total length of the facility reached 8.88 km, the initial adsorbent inventory was 25.19×10^4 t of hydrous titanium oxide, and the power requirement for the pumps was 67×10^4 kW where the number of pumps was 467 and its unit capacity was 80 m^3/s. Based on this conceptual design, a unit production cost of \$ 334/lb U_3O_8 (1976 dollars) was derived[37]. A second conceptual design and cost estimation was conducted using larger pumps with a capacity of 500 m^3/s. The pumps were arranged to be the breakwater type instead of the on-shore parallel type of the first design. Recovery ratio of the uranium extraction was also improved from 50 to 60%. The second conceptual design based on the pumping and fixed-bed system is illustrated in **Fig. 7**. This case resulted in some size reduction where the total length of the facility became 3.84 km, and the number

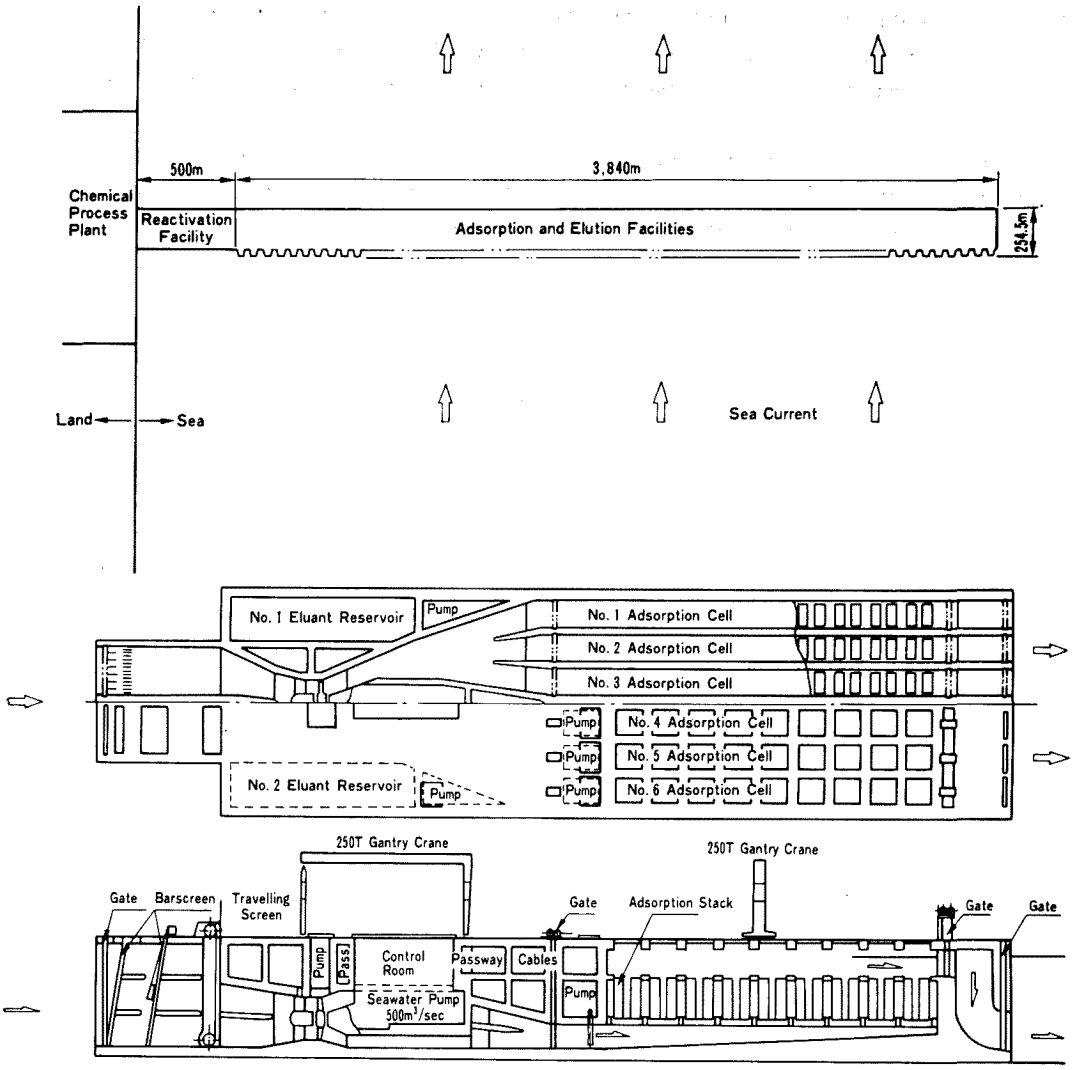


Fig. 7 Second conceptual design of pumping and fixed-bed system

of pumps was 60. Based on this conceptual design, a unit cost of \$ 223/lb U_3O_8 (1976 dollars) was obtained[37].

It has been recognized for some time that adsorption recovery and uranium concentration in the eluate have direct influences on the facility size and operating costs which will alter the overall production costs. There has been some experimental evidence to indicate that an adsorbent may be developed with an increased adsorption recovery and a high concentration of uranium in the eluate. Accordingly, a third set of cost estimations was completed with some basic condition changes where the adsorption recovery of 60% was increased to 80%, and the uranium concentration in the eluate was increased from 10 to 20 ppm. With these improvement, the necessary number of pumps was reduced to 45, and the total length of the facility became 2.95 km and the power requirement for the pumps was reduced to 52.4×10^4 kW. For this conceptual design, a unit cost of \$ 161/lb (1976 dollars) was calculated[37].

The concept of a direct sea current utilization system was also investigated in the

MMAJ. Marine structures containing many adsorption stacks are immersed in reasonably flat nearshore sea-beds to utilize the sea water current. The adsorption stacks are composed of three 5 m×5 m×5 m adsorption cubes with many parallel adsorption plates. These stacks are held in a single unit of 17.3 m width, 45 m height and 1.7 km length which is built on the sea-bed at a depth of about 35 m. The conceptual drawing was previously shown[38]. For a production rate of 1,000 t-U/yr, 30 sets of the unit structure were required. Based on this conceptual design, a unit cost of \$ 251/lb U_3O_8 (1976 dollars) was obtained. After further study, thin packed beds of adsorbent placed between two porous supporting plates appeared to be superior to the parallel adsorption plates previously considered. Due to the increased amount of adsorbent in a unit volume, the number of unit structures required was reduced to 20. With this improvement, a lower unit cost of \$ 177/lb U_3O_8 was obtained.

Recently, Driscoll[39] of MIT reported the system design of a sea water contactor unit resembling a fixed-leg off-shore oil production platform with the deck submerged. One unit rig of 200 ft in diameter has the uranium production capacity of 40 t and is equipped with 216 adsorption modules and low-head axial-flow pumps. The capacity of the pump was 32,000 GPM (26 kW). The module was composed of a cylindrical roll of spunbonded acrylamidoxime fiber sheet which has a loading rate of 700 ppm/d and a capacity of 5,000 ppm. Based on the conceptual design, the unit cost of uranium production was calculated to be \$ 140/lb U_3O_8 and after reducing the by-product credit due to molybdenum and vanadium production, the cost was estimated to be \$ 111/lb U_3O_8.

Bitte of Uranerzbergbau Co. who presented a paper concerning a conceptual design of a semi-submersible floating structure with fluidized beds attached with diffusors by using hydrous titanium oxide adsorbent[40], compared four different type concepts of floating structures for the recovery of uranium from sea water[41]. These include a self-propelled, semi-submersible catamaran concept, a moored semi-submersible catamaran concept, a ship concept with horizontal water intake and a ship concept with vertical water intake. As for the adsorbent, the former hydrous titanium oxide adsorbent was replaced by the polyacrylamidoxime resins. The minimum uranium production cost was obtained for the fourth concept and it was in the range of 200~300 \$/lb U_3O_8. The results show that the uranium costs below 150 \$/lb U_3O_8 can be achieved with longer adsorption periods and/or higher uptake rates by the adsorbents.

Koske of the University of Kiel cooperated with GKSS, proposed a new concept for the contact between sea water and adsorber granulate called "loop concept" and reported a conceptual design and cost estimations based on this concept[42]. The principle of the loop concept is illustrated in **Fig.** 8. The sea water flow enters the loop system through a diffusor like channel, which acts as a suction-pump and by which it is diverted downward. At the outlet of the diffusor it is mixed with the adsorber granulate coming from above. The direction of the sea water/granulate mixture is changed from downward to upward flow at the cone shaped bottom of

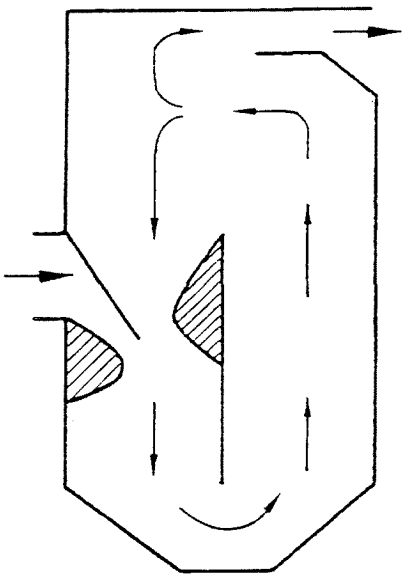


Fig. 8 Adsorber loop concept, principle flow scheme

the loop. After having arrived at the top the flow is slowed down and diverted horizontally, at the same time the granulate suspension is separated again, with the depleted sea water leaving at the top and the adsorber granulate collecting in the sedimentation cone from where it is, by gravity and suction, added to and mixed with the entering sea water agian. The conceptual design based on the loop concept was carried out. The sizes of the floating structure were 200 m in length and 40 m in width and the gross tonnage was 58,384 GRT. The annual uranium production rate of one unit structure was 20 t. Based on the above conceptual design, the uranium production costs of \$ 171~336 depending upon the sea water flow rate of 42~12.5 cm/s were estimated.

Forberg of Royal Institute of Technology, Sweden reported the improvement of their former wave-powered floating plant concept[43] by replacing the previous hydrous titanium oxide adsorbent with polyacrylamidoxime adsorbents both in the form of pellets and mats[44]. According to their conceptual design of the uranium extraction plant with annual production capacity of 600 t by using fluidized polyacrylamidoxime-pellet beds, the plant was composed of 26 floating units with a length of 426 m and a width of 65 m. In the case of the use of polyacrylamidoxime-mat adsorbents, the number of the units was reduced to 22. In the former case, the calculated uranium production cost ranged 130~340 \$/lb U_3O_8 for a real rate of discount interval of 4~15%. For the polyacrylamidoxime-mat concept, the cost ranged 90~200 \$/lb U_3O_8. For the "improved" polyacrylamidoxime-mat concept, the cost ranged 60~135 \$/lb U_3O_8.

VI. CONCLUSION

Instead of the research on the hydrous titanium oxide as the adsorbent for extracting uranium from sea water, the research on such organic resin adsorbents as acrylamidoxime has been very active. However, it seems to be difficult to evaluate which is better, considering the long-term adsorption and elution performances and the costs at the present stage. Further systematic studies of the adsorbents including hydrous titanium oxide and organic resin adsorbents as well as new types of organic and inorganic adsorbents are highly desirable.

As the contacting system of adsorbents with sea water, many different systems have been proposed and some cost estimations based on these systems have been reported also, however, any pertinent method for appraising these different types of contacting systems has not been established, and it is difficult to compare exactly the different types of contacting systems. Developments of any methods for comparing these different systems must be needed.

It is interesting to note that many different kinds of cost estimations almost lie in the range of \$ 150~350/lb U_3O_8, though they are based on much different technical and economical assumptions. For estimating more exact production costs, further design studies with using up-to-date adsorption and elution data and also some correct assessment of the economical conditions like construction period, rates of discount and others have to be assessed.

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