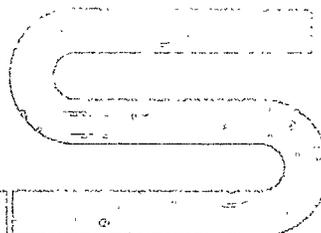


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Extraction of Uranium from Seawater

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1. INTRODUCTION

Requirements for energy resources in the world are expected to increase rapidly with its industrial progress. Especially, the country like Japan which has very rare resources of oil, coal, and natural gas etc. faces with very serious problem. Though many countries are developing their nuclear power generations, recent estimates of demand for uranium indicate an alarming shortage in known reserves of uranium as compared with world demand assuming an expanding thermal reactor programme. Without a significant breeder reactor capability known reserves will be exhausted by the turn of the century. There is, therefore, some incentive to examine the possibility of obtaining the required uranium from the sea. This view attempts to describe the present status of the research on the extraction of uranium from seawater and identify the problems to enable a demonstration plant to be satisfactorily designed and operated.

2. URANIUM DEMAND AND RESOURCES

According to the report of the IAEA Advisory Group Meeting on Fuel Cycle Demand, Supply and Cost Trends held in Vienna on 11-14 November 1975, the approximately 70 GWe of nuclear electric generating capacity installed around the world in 1975 was projected to increase to around 500 GWe by

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1985 and over 2000 GWe by the year 2000.

Based on the nuclear power growth projections and reactor characteristics, the fuel cycle requirements were calculated by various participants. These demand projections are summarized briefly in Table I to indicate the predicted magnitudes and growth rates. Present estimates of world uranium resources are shown in Table II. A comparison of these figures with the projected cumulative demand for uranium (Table I) highlighted a potentially serious problem. The reasonably assured reserves in the normally utilized lower price category are only sufficient to meet the demand through the late 1980s. Of perhaps equal significance, the total presently known and estimated resources at < 30\$/lb U₃O₈ will be exhausted by about 2000.

To meet this problem, one way is to develop fast breeder reactors which utilize plutonium as reactor fuels. The other way is to expand efforts on the exploration and the development of mining and milling technique of lower grade mineral deposits such as shales, granites, phosphates etc. Exploration throughout the world, however, is not increasing sufficiently for current growth rate prediction to be met. It is, therefore, worthwhile considering whether the largest known untapped source of uranium - the oceans - can be usefully employed to enable the shortfall in reserves to be overcome.

The Japanese requirement for uranium has been estimated to be 12,000 tonnes per annum by 1985 to support a thermal reactor programme of about 49 GWe capacity.

3. THE SEA AS A SOURCE OF URANIUM

Seawater is said to be a treasure house of not merely uranium, but also other mineral resources, for which Japan is depending upon overseas supply. For example, all the seawater of the world contains about in total 4,000 million tonnes of uranium, and in addition large quantities of other such valuable minerals as strontium, vanadium, lithium etc. In the case of uranium the concentration has been found to be practically constant at around 3×10^{-9} (3 ppb). The level of uranium is maintained at a steady level by sedimentation which is equally balanced by incoming river borne dissolved material.

Because of the low concentration of uranium in solution and the consequently enormous volumes of water which must be handled to extract useful amounts of uranium it would not be possible to consider any chemical pretreatment or control (for example, pH). Only filtration and, possibly, temperature increase by low grade heat, may be considered as physical pretreatment possibilities. On this basis the colloid flotation process described by Kim and Zeitlin [2] must be rejected as unworkable on the scale necessary to produce meaningful quantities of uranium.

4. THE EXTRACTION PROCESS

The uranium is said to occur in true solution as the

tricarboxylate complex, $\text{UO}_2(\text{CO}_3)_3^{4-}$. As it is in a strongly complexed form at extreme dilution in presence of relatively high concentrations of other ions, there are considerable difficulties to extract uranium from sea water economically.

First, various kinds of organic solvents and ion exchange resins were tested. An obvious step following the successful solvent extraction experiments with dibutyl phosphate was to incorporate functional groups of similar type in solid insoluble organic resin matrices. Resins containing mono- and di-basic phosphoric and phosphonic acids, hydroxyquinoline, kojic acid, salicylic acid, aminocarboxylic acid and amino-phosphoric acid functional groups were tested in England [3]. Among them most promising resin was a condensation product of formaldehyde and resorcinol arsonic acid. The uptake of uranium by this organic material was found to reach 1,000 $\mu\text{g/g}$ of dry H^+ form. Although the solubility shown by the original arsonic acid resin in sea water was largely overcome there still remained a steady loss of capacity which was traced to a slow hydrolytic attack on the carbon-arsonic bond. The suitability of synthetic ultramarine as an ion exchanger for the extraction of uranium in sea water was studied in Germany, but it needed to adjust the pH of the seawater to 5 from its ordinary value of 8 [4].

It has been noted that the deposition of uranium from carbonate-containing waters in the Goodsprings district of Nevada is attributed to adsorption by hydrated ferric oxide and basic zinc carbonate. This, coupled with the observation that ferruginous deposit in the filter on the inlet side of the seawater laboratory at Portland in England contained some uranium, led to the investigation of a number of inorganic materials as possible adsorbents. Basic zinc carbonate, titanium hydroxide (more correctly termed hydrous titanium oxide) and such lead compounds like lead sulphide and lead pyrophosphate were the only materials which exhibited an effective uptake in England [5]. Except titanium hydroxide, however, the materials were too soluble or unstable in sea water and eluting agents for further consideration.

Extraction of uranium from natural water was studied in Soviet Union [6]. Various types of minerals, rocks and artificial gels were tested as adsorbents as well as various ion-exchanging resins. As a result satisfactory capacity was shown by the gels of calcium phosphate, barium, alumogel, titanogel and bauxite. Application of uranium coprecipitation with various inorganic and organic coprecipitants were tested also. Adsorption of uranium with activated carbon [7], with anion exchange resin [8] and various adsorbents for extracting uranium and other metals from sea water [9] were studied in Soviet Union.

The coagulation method [10], coprecipitation method [11] and adsorption method [12] were investigated by Ogata in Japan. As the adsorbents, about fifty insoluble compounds of titanium, aluminium, magnesium, calcium, silicon, zinc, chromium, lead and tin were examined. The highest uptake capacity was obtained for titanium hydroxide. Different types of titanium hydroxide were tested [13], [14], and the effects of the homogeneity of the reaction, reaction temperature and pH were

determined. Titanium hydroxide prepared by neutralization of titanium sulphate with alkali solution showed a uranium uptake of 760 $\mu\text{g}/\text{Ti g}$, and titanium hydroxide prepared by thermal decomposition of titanium sulphate showed a uranium uptake of 1,550 $\mu\text{g}/\text{Ti g}$. The effect of granule radius of the titanium hydroxide in the range of 0.27-0.04 mm on the adsorption efficiency was determined by Kanno et al. [15]. Recovery of uranium by active carbon and metal hydroxide composite adsorbent was studied by Ninomiya et al. [16] and the uptake capacity of 500-600 $\mu\text{g}/\text{g}$ adsorbent was reported. Galena was found to be one of the effective uranium adsorbents from sea water in England [3] and according to the examination of uranium uptake in Japan, the capacity of about 550 $\mu\text{g}/\text{g}$ was obtained [17].

In Nuclear Research Center Juelich, Germany, the extraction of uranium using mutated and selected algae has been investigated [18]. The highest concentration ratio of 10^5 has been obtained on green algae which uranium concentration reached 0.03% in dry form. Recently, however, it was found that the aggregation property of green algae was not good enough for contact with sea water and collection compared with blue algae which concentration ratio was one order lower than green algae.

5. ADSORPTION AND ELUTION TEST

The MITI (Ministry of International Trade and Industry) of Japan has worked out a research program entitled "Studies on the Establishment of Comprehensive Recovery system of Rare Resources from Sea Water" since the 1975 fiscal year. The object is to extract uranium as well as other mineral resources such as Sr, V from sea water. This research, starting in the 1975 fiscal year, envisage a basic study of structures suitable for model plants in the initial year. This will be followed by the designing, construction, testing and comprehensive assessment of the test plant. Under the advice and leadership of the steering committee, planning and drafting of this research were entrusted to the MMAJ (Metal Mining Agency of Japan). The MMAJ made contracts with six private corporations, and the system design of the test plants, experimental tests of the adsorption and elution, the concentration and purification of the eluate and the research of plant sites have been carried out.

As the adsorbents, titanium hydroxide, activated carbon-titanium composite adsorbent and galena as well as phosphate ore, powdered bones, ultramarine, zinc carbonate, calcium phosphate, aluminium phosphate, hydrous silicate and hydraulic cement were tested. Furthermore, the development of some new types of adsorbents was tried on complexes using titanium and microfiber or porous resins. Among them, the highest capacity for recovering uranium was obtained on titanium hydroxide by thermal decomposition in the coexistence of dilute titanium sulfate and urea solution. The adsorption capacity was about 300 $\mu\text{g-U}/\text{g-dry adsorbent}$ at 25°C and about 500 $\mu\text{g-U}/\text{g-dry adsorbent}$ at 35°C in natural sea water using pulverized

adsorbents and adsorption isotherms.

To improve the mechanical strength of the titanium hydroxide adsorbents, some granulation tests including pressing and crushing, screw extrusion and agitating granulation were carried out. Favorable results were obtained by using ethylsilicate, portland cement and polyvinyl alcohol as a binder. As for elution, only the experiments with ammonium carbonate solution were carried out in the range of 20 to 60°C. The efficiency of elution was dependent strongly on temperature, and the efficiency at 60°C was shown three times greater than that at 20°C.

The long term tests were performed mainly with the adsorbent of granulated titanium hydroxide. The particle size distribution of the adsorbent was in the range of 0.5-2.0 mm. The column having a diameter of 10 cm and a length of 30-50 cm was used in 1975. The periods of the continuous tests were 15 to 50 days with the six adsorption and elution cycles as a maximum, and the linear velocity of the sea water was kept at 20-60 cm/min. The recovery of uranium throughout the adsorption and elution process was 10 to 20%, and the concentration of uranium in the eluate was about 7 ppm. Decrease of adsorption capacity of titanium hydroxide was observed after long term operation and acid elution with dilute hydrochloric acid was found to be effective to activate the adsorbent. Some strontium was found on the adsorbents of titanium hydroxide and it could not be eluted by ammonium carbonate solution and probably accumulated on adsorbent gradually.

6. CONCENTRATION AND PURIFICATION OF ELUATES

Purpose of the concentration process is to increase the concentration of uranium in the eluate (a few milligrams of U/l), which results from the primary adsorption and elution process, with high recovery to the extent that further refining should be feasible on the economical as well as technical bases. According to the operational examples currently adopted commercially, leached solutions with uranium concentration in the order of grams per liter are usually processed as a starting solution in the refining stage and, consequently, it will be necessary to increase the uranium concentration in the eluate from a few milligrams per liter to the order of grams per liter.

In order to increase uranium concentration keeping high uranium recovery, several methods such as ion exchange, chemical precipitation, adsorption, solvent extraction, flotation etc. could be considered as the possible methods of concentration. In 1975, ion exchange and flotation have been selected for experimental tests after prospective discussions.

For the ion exchange experiments, eighteen different kinds of ion exchange resins consisting of strong acid cation resins, strong base anion exchange resins, weak acid cation exchange resins and chelating ion exchange resins with different physical characteristics and different degrees of cross linking were tested. In order to know approximate uranium adsorption capacities, a few milliliters of each resin were soaked in

100 ml (50 mg U/l) of 0.05 M hydrochloric acid or 0.1 M ammonium carbonate solution and the solution was agitated for 100 minutes and then the residual uranium concentration of the solution was determined. As a result, for the hydrochloric acid solutions, four strong acid cation exchange resins showed high adsorption efficiencies ranging from 96% to 97%. For ammonium carbonate solutions, seven strong base anion exchange resins showed adsorption efficiency as high as 100%.

More precise adsorption experiments were performed with small-scale ion exchange columns. In the case of 0.05 M hydrochloric acid solution (50 mg U/l), strong acid ion exchange resins showed maximum loading of 95 mg U/ml-R and in the case of 0.1 M ammonium carbonate solution, strong base anion exchange resins showed maximum uranium loading of 98 mg U/ml-R. The concentration ratio defined as the ratio of uranium concentration of product solution to that of starting solution decreased with increase of uranium recovery. For example, 63%, 80% and 90% of uranium recovery corresponded with 300, 150 and 50 of the uranium concentration ratio, respectively. In the experiments with the simulated eluate consisted of U(11 mg/l), Na^+ , Cl^- , SO_4^{2-} and so forth in 0.1 M ammonium carbonate, the uranium loading was 76 mg U/ml-R.

In the ion flotation experiment, both cationic and anionic surfactants were tested and uranium recovery of more than 90% was obtained with moderate concentration ratio in sodium hydroxide solution, while in the acid or ammonium carbonate solution the tests gave rather poor results.

7. ENGINEERING OF LARGE SCALE HANDLING

Enormous volumes of sea water must be handled to extract uranium from sea water. For example, assuming the adsorption efficiency of 30%, $10^{12} \text{ m}^3 \text{ year}^{-1}$ ($3 \times 10^9 \text{ m}^3 \text{ day}^{-1}$) of sea water must be contacted with the adsorber to produce 1000 tonnes of uranium per annum. These figures are much larger than the capacity of desalination plants and the cooling water used in coastal power stations. It is desirable for the extraction plant to be sited so that it can be supplied with fresh uranium-bearing water by natural transport processes, superimposed on the tidal motion. Several sea water handling systems including tidal barrage scheme and pumped scheme have been reviewed by Haigh [19].

Initially, a tidal lagoon system, similar in principle to a tidal power scheme was examined for a hypothetical plant in the Menai Straits which consisted of two lagoons of about 50-60 km^2 each. The sea water flows into one on a rising tide to form an upper lagoon, and out of the other lower lagoon on the falling tide. The adsorber beds would be situated in the barrages separating the upper and lower lagoons. Due to the oceanographic survey by Haigh, the maximum potential for world uranium extraction at identified tidal power locations is the order of 2.5×10^4 tonnes/annum. This figure is not insignificant but it is still an order of magnitude below the anticipated world demand. It is therefore considered that such other scheme for sea water handling like a pumped scheme must

be found.

The feasibility of a pumped scheme may be examined in terms of "energy gain ratio", which is defined as the ratio of the energy content of the product to the energy cost of producing the fuel. The "energy gain ratio" of the tidal and pumped schemes are 11.7 and 6.4 respectively for the thermal reactor, assuming 2.2 m head loss [19] [20] [21]. No energy gain will be obtained for the head loss more than 25 m.

In the Japanese MMAJ programme, the conceptual design for two types of test plants, the "column type" which is equivalent to the pumped scheme and the "tidal type" was made based on the available information for construction of test plant in the near future. As for the "tidal type", slurry cell was adopted because of the insufficient head due to the only 2 meters of the Japanese tidal difference at the maximum. Both plants had the capacity of 10 Kg U/annum provisionally. As a result, there have been several problems awaiting solution, but there were no technically fatal problems. A number of alternative concepts for contacting seawater and adsorbent has been considered. Amongst these, the use of beds immersed in ocean current was considered to be important to make use of "Kuro Shio" current in the North Pacific Ocean. To realize this, however, there remains a number of technical problems.

8. COST ASSESSMENT

It is doubtful whether even tentative cost figures are worth producing at this stage. However, initially, Davies et al. [3] indicated that the Menai Site could produce uranium at a cost of about \$20 per lb of uranium oxide. A further estimate made in 1966 for a pumped flow scheme at Menai showed a cost of around \$40 per lb. Revision to 1974 prices indicates this would now be at least \$70 per lb. [19]. Hill suggested this in the region of \$100/lb U_3O_8 , based on Menai and a production of around 850 tonnes of uranium per annum [22].

The original Menai scheme was subjected to critical appraisal in 1967 in the United States by a team of workers at the Oak Ridge National Laboratory but the report was only released in 1974 [23]. Different assumptions from those made in the original study resulted in very much higher production cost figures being deduced, e.g. a minimum cost of about \$300/lb U at a production rate of about 500 tonnes U/year. In any way, there are too much uncertainties associated with the process to estimate the cost of uranium production from sea water.

9. CONCLUSION

(i) Though the process techniques developed on a small scale show the possibility of extraction of uranium from seawater under appropriate conditions, there are a number of uncertainties associated with the process. Extensive further research work would be necessary to reduce the uncertainties.

(ii) The most promising extraction system at present is

that based on pumped flow of sea water. A rough energy accounting exercise indicates that a considerable gain might be achieved through extraction of uranium from sea water, even for a pumped system.

(iii) There seems to be not enough sites to extract uranium from sea water in the world to meet the world's uranium demand, however, the utilization of "Kuro Shio" current in the North Pacific Ocean must be considered favourably.

(iv) Most of the work done to date must be regarded as of a preliminary nature. There are so many uncertainties associated with the project that it would be unrealistic to attempt to quote even an approximate estimate of the likely cost of extraction.

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Table I. Example Projection of World Demand for Nuclear Fuel Cycle Service [1]

Fuel Cycle Service	Year					
	1975	1980	1985	1990	1995	2000
Uranium Production, (1000 tonnes/yr)	21	50	100	160	240	300
Uranium Production, cumulated from 1975 (1000 tonnes U)	21	200	600	1300	2300	3700

Table II. World Uranium Resources (1000 tonnes U) [1]

Reasonable Assured		Estimated Additional	
< 15\$/1b U ₃ O ₈	15-30\$/1b U ₃ O ₈	< 15\$/1b U ₃ O ₈	15-30\$/1b U ₃ O ₈
1080	730	1000	680

