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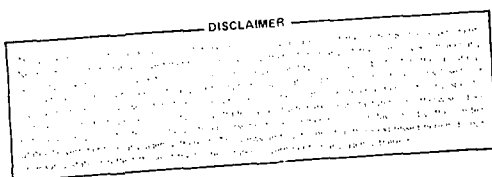
**THE RECOVERY OF URANIUM FROM SEAWATER - STATUS OF TECHNOLOGY AND
NEEDED FUTURE RESEARCH AND DEVELOPMENT***

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THE RECOVERY OF URANIUM FROM SEAWATER – STATUS OF TECHNOLOGY AND NEEDED FUTURE RESEARCH AND DEVELOPMENT*

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ABSTRACT

A survey of recent publications concerning uranium recovery from seawater shows that considerable experimental work in this area is currently under way in Japan, less in European countries. Repeated screening programs have identified hydrous titanium oxide as the most promising candidate adsorbent; however, many of its properties, such as distribution coefficient, selectivity, loading, and possibly stability, appear to fall far short of those required for a practical recovery system. In addition, various evaluations of the energy efficiency of pumped or tidal power schemes for contacting the sorbent and seawater are in serious disagreement. Needed future research and development tasks have been identified. A fundamental development program to achieve significantly improved adsorbent properties would be required to permit economical recovery of uranium from seawater. Unresolved engineering aspects of such recovery systems are also identified and discussed.

1. INTRODUCTION

The possibility of recovering uranium from seawater has received attention over the past three decades. This interest has arisen from the fact that, despite the very low concentration (3.3 ppb¹), the total volume of all the earth's oceans contains approximately 4×10^9 tons of uranium. It is obvious that the availability of a suitable extractant or sorbent would permit us, in principle, to readily recover the uranium since it is already in solution.

The published information reporting research or describing engineering studies related to uranium recovery from seawater is reviewed in Sect. 2. The literature is grouped by various countries. The first work was in the United Kingdom; then, other European countries became interested and, most recently, an extensive effort has been undertaken in Japan. A comprehensive review of the activities in several foreign countries as of the fall of 1978 is contained in Chapter 15 of ref. 2. An assessment of the current state of the technology is presented in Sect. 3, and needed future research and development is discussed in Sect. 4.

2. LITERATURE SURVEY

The literature survey was conducted primarily by searching *Chemical Abstracts*, vols. 86 (1977) through 92 (1980). A voluminous Japanese patent effort has also developed recently.

2.1 Recent Review Articles

A number of recent review articles (1977–1980) summarize the state of development of methods for recovering uranium from seawater and include references to much of the earlier work. Three articles have appeared in Japanese journals,³⁻⁵ and two in German publications.^{6,7} An extensive bibliography was published in 1979 under DOE funding.^{8,9} These sources discuss essentially all the pertinent work prior to about 1977 to 1978 and thus preclude the need for conducting another independent literature survey for the years prior to 1977.

2.2 Work in the United Kingdom

The British program, which was active from the late 1950s to about 1970, is described in a recent

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summary article.¹⁰ Screening studies investigated many possible sorbents and identified hydrous titanium oxide (titanic acid) as having the best combination of properties. An engineering analysis was performed to determine the energy requirements for both tidal basin and pumped schemes; this showed that the energy consumed in pumping seawater through an adsorbent bed can be a significant fraction of the energy available from the uranium after it has been recovered and used in nuclear power plants. Thus design emphasis was on a tidal basin concept. It was estimated that a facility to supply 10,000 tons of uranium annually would enclose 300 to 400 square miles of ocean. Work in the United Kingdom was essentially terminated in the early 1970s, when it was calculated that the combined flow of all the water through the Straits of Dover and the Irish Sea would contain less than 10,000 tons of uranium per year. These findings emphasized the need for siting a recovery plant in or adjacent to a strong ocean current where fresh seawater would be continually supplied by the current while plant effluent was removed. Only one recent British publication on the use of hydrated titanium oxide was identified.¹¹

2.3 Work in the United States

To date, only a small experimental effort has been mounted in the United States to study the recovery of uranium from seawater. This apparent lack of urgency undoubtedly stems from our relatively plentiful uranium resources, initially in the western intermountain region and more recently also from by-product recovery during phosphoric acid production.

The British technology was reviewed at ORNL in 1966, and the findings were reissued as a report in 1974.¹² This report strenuously questioned the very optimistic design parameters employed in the early British cost estimates. By using what were considered to be more realistic (but still optimistic) values for uranium recovery and titanium oxide sorbent losses, much higher estimates for uranium recovery costs were calculated.

Recently, an extensive study of the siting and design of a uranium recovery plant was funded by the DOE Grand Junction Office.^{2,8,9,13} The design work was primarily carried out by Exxon Nuclear and Vitro Engineering, while the site location and oceanographic aspects were covered by Oregon State University. The following conclusions were drawn in this study:

- Uranium is held in solution in the ocean as uranyl carbonate anions.
- It is maintained in solution for periods of time which are long, compared with the circulation and mixing times of the ocean depths.
- The uranium concentration is about 3.3 ppb, equivalent to a total of 4.5×10^9 tons. However, only the uranium present in the upper 100 m or the well-mixed surface layer of the oceans ($\sim 0.16 \times 10^9$ tons) should be considered accessible for recovery.
- Freshwater rivers and streams carry too little uranium to be practical sources; the entire flow of all the rivers in the world contain only 9000 tons year.
- The only U.S. site with a tidal range favorable to a tidal basin (nonpumped) scheme is Cook Inlet, Alaska. Unfortunately, the low water temperature of this site would adversely affect the properties of the hydrous titanium oxide sorbent, and regional circulation patterns of the water would cause considerable backmixing of plant effluent with influent.
- A coastal site in Puerto Rico adjacent to the Antilles Current was considered the most favorable site for a pumped seawater plant.
- A comparison of the known sorbents for extracting uranium from seawater has shown that hydrous titanium oxide is the most promising.
- A chemical process was selected, and flowsheet criteria were assumed for a 500-ton U_3O_8 year plant.
- Design and cost estimates were completed for a continuous fluidized-bed recovery facility. The capital costs were \$6.2 billion in 1978 dollars.
- A labor force of 700 was projected for the facility at a cost of \$12.5 million year.
- For a plant built by 1995, the cost of extracting uranium from seawater ranged from \$2100 to \$3600 per pound of U_3O_8 , depending on the criteria selected.
- Some of the key chemical process parameters, including sorbent loading capacity, kinetics, and losses due to mechanical attrition and solubility, had to be estimated due to lack of experimental data. Since the process is very capital intensive, the costs are extremely sensitive to the values selected for some of these parameters. Important factors that need further study were identified.

Another DOE-funded engineering evaluation has recently been completed at the Massachusetts Institute of Technology.¹⁴ A computer program was developed to simulate engineering performance and provide an economic analysis. A number of conceptual design systems, each of which employed a hypothetical adsorbent of hydrous titanium oxide coated on particles or on tubes, were considered. The equilibrium isotherm and the diffusion constant for the uranyl-hydrous titanium oxide system were calculated since they were not experimentally available. The costs obtained were almost an order of magnitude lower than those calculated by Exxon.² It was concluded that the minimum expected costs of uranium recovered from seawater would be no lower than \$316 lb U₃O₈ in 1979 dollars for state-of-the-art adsorber material. It was also calculated that, if the seawater were pumped higher than a 10-ft head, more energy would be consumed in pumping than would be available from the uranium. Research and development objectives to reduce the level of costs were identified.

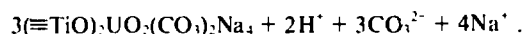
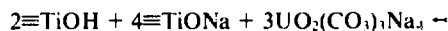
2.4 Work in European Countries

Information gathered from recent publications indicates that the most active effort in Europe is now being carried out in Germany. The present approach seems to be to consider various adsorbents in order to find or develop one with suitable properties. Three scoping studies have compared tidal and serial column methods, evaluated various organic, inorganic, and biological sorbents, and considered the design of a technical installation and the energy balance.¹⁵⁻¹⁷ Organic ion exchangers,¹⁸ silica gel,¹⁹ brown coal,²⁰ and cellulose exchangers^{21,22} are among the materials being tested. Several recent patents, which are based on German work, cover the use of these sorbents as well as magnetic adsorbents,²³ silica gel,²⁴ lignite,²⁵ peat,²⁶ microorganisms,²⁷ and special ships that would sail about the oceans and contact seawater with the adsorber in the ship.²⁸

References to only three recent Soviet Union publications were identified.²⁹⁻³¹ These consider the recovery of uranium from ²³²U-labeled seawater by sorbents such as silica, hydrated iron oxides with collectors such as steric acid, or ampholytes such as Stearox 6. In one case, the coextraction of uranium and copper was considered. In two of the studies, the pH of the seawater was changed by the addition of acid in order to increase uranium recovery.

A single recent French publication³² identifies the exchange reactions occurring when UO₂(CO₃)₃⁴⁻ is

adsorbed by titanium oxide and proposes that the uranyl moiety is retained on titanium oxide surrounded by two CO₃²⁻ and two TiO ligands. The retention equilibrium is given as



2.5 Work in Japan

In the last several years, an extensive effort has been developed in Japan, probably because of the very limited domestic uranium resources in that country. Several research groups have issued a substantial number of papers, and a large volume of patent literature has developed. Many types of sorbents are being considered, although much of the work deals with titanium oxide.

Three publications from the Hitachi Research Laboratory³³⁻³⁵ are the first to quantify some important process parameters for the recovery of uranium from seawater with hydrous titanium oxide. The kinetics of adsorption was studied and correlated with the surface properties of hydrous TiO₂ crystallites. The mechanism of sorption of the [UO₂(CO₃)₃]⁴⁻ ion was determined to be



The competitive adsorption of [UO₂(OH)₃] was also considered. The effect of other ions dissolved in seawater was measured and found to reduce the uranium uptake by a factor of 10. The deposition of CaCO₃ from seawater onto the hydrous titanium oxide was primarily responsible for depressing the uranium uptake, although magnesium also had a negative effect.

Another group of investigators at the Tohoku University, Department of Nuclear Engineering, has been studying hydrous titanium oxide.³⁶⁻³⁹ Alternative means of synthesizing the exchanger were tested, as a part of this study. Repeated aging and washing were found to be indispensable in obtaining reproducible results and high exchange capacity. Both the stoichiometry of cation exchange and the acid-base properties of the exchanger were examined. It was concluded that hydrous titanium oxide is a four-functional, weakly acidic cation exchanger. The effects of radiation and heat treatment on its properties were investigated; and a structural formula of the exchanger was suggested, based on

ion-exchange capacity, thermal decomposition curves, and x-ray diffraction and infrared spectral data. The exchanger showed an abrupt decrease in ion exchange capacity after being allowed to stand in air at room temperature for 3 to 6 months. This effect was attributed to preferential destruction of the most acidic hydroxyl groups by a dehydration-condensation type of reaction.

Two different groups have been studying composite adsorbents for use in recovering uranium from seawater, the concept being to attempt to combine the favorable properties of more than one material. The Government Industrial Research Institute at Takamatsu first studied alumina-activated carbon.⁴⁰⁻⁴³ The properties of this adsorbent were examined, and its capacity for uranium recovery from seawater was determined; Freundlich's relation was observed. Adsorption was found to be dependent on both temperature and pH. The alumina coating was shown to be bayerite when the adsorbent was prepared at low temperatures and pseudo-boehmite at higher temperatures. Heating the adsorbent to 250°C increased the uranium adsorptivity. The investigators then shifted their attention to a zinc-activated carbon composite adsorbent.^{44,45} This product, which was shown by x-ray diffraction and thermogravimetric techniques to be coated with basic zinc carbonate, $\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, displayed uranium adsorption properties similar to those of pure basic zinc carbonate. The strength of the particles was increased when the sorbent was granulated with polyvinyl alcohol. The amount of uranium accumulated was found to be directly proportional to the geometric surface area of the adsorbent granule. Most recently, this research group has been studying titanium-activated carbon.^{46,47} An evaluation of its adsorptivity of seawater constituents indicated the following order: alkali metals, halogens, sulfur < boron, alkaline earth metals < phosphorus, arsenic < transition metals, uranium. Polyvinyl alcohol was tested as a binder. Results of cyclic adsorption-desorption tests showed that the amount of adsorbed uranium decreased as the number of cycles increased.

A group at the Hitachi Research Laboratory has also been studying composite adsorbents. In their evaluation of titanium(IV)-iron(II) oxide mixtures,^{48,49} the researchers found the composite hydrous oxide to be composed mainly of relatively small particles of anatase and large particles of magnetite. Uranium adsorption capacity was related to the mean pore size and quantity of surface -OH groups. These composite adsorbents are magnetic,

and results of various tests showed that a hydrous oxide absorbent of 400-625 mesh particle size could be magnetically recovered with 99% efficiency after dispersal. The possible application of magnetic separations after contact of the adsorbent with seawater was discussed.

A group at the Okayama College of Science, Department of Chemistry and Nuclear Engineering, has been studying various other extractants. Polyacrylamide gels containing metal hydroxides were investigated,⁵⁰⁻⁵² and factors affecting their performance were examined. Of the metals tested, only titanium hydroxide was useful for the extraction of uranium from seawater. Adsorption performance was apparently not related to the degree of polyacrylamide cross-linkage; however, it was significantly affected by changes in the titanium hydroxide. In other tests, electrolysis with a platinum anode and a stainless steel cathode was tested as a method for concentrating the uranium in a $\text{Mg}(\text{OH})_2$ precipitate formed at the interface of a seawater-isobutyl alcohol mixture;⁵¹ the uranium was reported to be completely recovered.

The use of biological systems to recover uranium from seawater is being investigated by a group at the Miyazaki Medical College, Department of Chemistry.⁵⁴⁻⁵⁶ The uptake of uranium by marine microalgae was found to be in the order: *Synechococcus* > *Chlamydomonas* > *Chlorella* > *Dunaliella* > *Platymonas* > *Calothrix* > *Porphyridium*. Natural polymers such as chitin, chitosan, cellulose, and starch were also evaluated, as was a titanium(IV)-polysaccharide xanthate.

Several other recent papers were noted. In work at the Asahi Chemical Industry, it was shown that foam collected at the seashore was ten times more concentrated in uranium than normal seawater and beach sand was enriched 10 to 100 times over other sand.⁵⁷ The use of chelating resins was investigated at Kumamoto University,⁵⁸ and uranium recovery by a polymer-bound macrocyclic hexaketone was tested at Kyoto University.⁵⁹

The application of the existing technology to the recovery of uranium from seawater has been discussed in two recent articles.^{60,61}

2.6 Work in Other Countries

The results of yet another screening program to evaluate adsorbents to scavenge uranium from seawater were reported in an article from India.⁶² Hydrated titanium oxide was again identified as having the best properties—rapid pickup and good

recovery. An article from the People's Republic of China on the mechanisms of uranium adsorption on $\text{TiO}(\text{OH})_2$ was also noted.⁶³

3. ASSESSMENT OF THE CURRENT STATE OF TECHNOLOGY

Despite three decades of effort, the current state of development of technology for the recovery of uranium from seawater can only be characterized as primitive. Much of the effort has gone into empirical experimental screening studies to evaluate existing possible adsorbents or into calculated engineering cost estimates. Little work describing comprehensive development efforts that would establish firm process parameters has been reported.

Several engineering design and cost estimate studies of uranium recovery from seawater utilizing hydrous titanium oxide have been completed in the last two decades. Since the results of comprehensive process development efforts have not been published (if carried out) and values have not been established for many of the key process parameters, these engineering studies can be no more accurate than the assumed values for the process parameters. Also, a complete process flowsheet has never been reported based on actual tests. Thus, it is not surprising that estimates for the cost of uranium production vary by more than an order of magnitude. Further, estimates of the energy efficiency of uranium recovery vary similarly. The most recent energy analysis¹⁴ stated that, if the seawater is pumped to a height greater than 10 ft, more energy would be consumed in pumping than could be generated by the uranium in a typical LWR, assuming no other energy requirements in the recovery process and 100% uranium recovery. Thus all the published values of costs and energy efficiency should probably be viewed with healthy skepticism.

The concentration of uranium in seawater is at least three orders of magnitude more dilute than that in any commercial process for the economic recovery of a metal. This fact, in turn, places stringent requirements on the properties of the adsorbent selected for uranium recovery from seawater. The properties of a successful extractant for economic recovery of uranium from seawater are characterized in general terms in the following paragraphs, and the needed properties are qualitatively compared with the state of development of hydrous titanium oxide. Hydrous titanium oxide was selected for this comparison since screening tests conducted over three decades in several different countries have

repeatedly identified it as the most effective of those tested. A successful extractant must have the following characteristics:

- Very high distribution coefficient, since the uranium is so dilute in seawater. To obtain reasonable adsorbent loading levels, distribution coefficients of 10^6 to 10^8 would be needed. No known extractants for any metal from any solution have distribution coefficients (DCs) in this range. The best practical liquid extractants have demonstrated DCs of about 10^5 , while the DCs for solid ion exchangers are more typically 10^3 to 10^4 . The value for hydrous titanium oxide for uranium from seawater was given in ref. 35 as 2×10^4 .
- A very high selectivity, since the seawater contains many other ions at much higher concentrations. The adsorption of uranium on hydrous titanium oxide is reported to be reduced by an order of magnitude from seawater due to calcium carbonate extraction, as compared with synthetic uranium solutions.³⁵ Thus loaded hydrous titanium oxide may contain 200 times as much calcium and magnesium as uranium.⁴
- A high loading. The reported concentration of uranium on loaded hydrous titanium oxide is only in the range of 100 to 1000 ppm due to the combination of the distribution coefficient and selectivity characteristics. This concentration is lower than that for some conventional uranium ores. Thus additional concentration and purification steps must be employed after the uranium has been adsorbed onto the hydrous titanium oxide. These steps have never been clearly defined experimentally, and the preparation of significant numbers of samples of purified uranium from seawater has not been reported.
- Rapid loading kinetics, in order to minimize contact times. This is very important in a seawater scheme because of the very large volumes of water involved. Recent kinetic data³² show contact times of 1 to 2 h for hydrous titanium oxide with seawater in order to attain equilibrium. Such long contact times are highly unfavorable and would greatly increase the size of any proposed installation; conversely, shortened times would decrease the overall recovery efficiency.
- Rapid elution kinetics; also ideally the eluent should be different from the extraction medium. Unfortunately, only concentrated carbonate or bicarbonate solutions have proven effective for

stripping uranium from hydrous titanium oxide without destroying the adsorbent. Thus the uranium in the eluate is still very dilute (ppm range) in a concentrated carbonate solution, and a difficult second purification step must be undertaken. This second step has never been defined experimentally. Elution kinetics are also reported to be very slow, and extended contact times are required.^{3,4}

- Very low losses of the extractant, to ensure favorable process economics and to avoid contamination of the ocean. Data on the physical stability of hydrous titanium oxide and the losses sustained during contact due to attrition or solubility are fragmentary but suggest that losses may be very significant economically.¹² Further, since the uranium is sorbed only on the surface of the particles, any surface loss as dispersed fines would also represent a preferential uranium loss.
- Low in cost, since very large volumes would be required in any recovery scheme to contact the large volumes of seawater. The losses must also be extremely low to minimize costs. In addition, the surface should not be fouled by the growth of marine organisms. Few reported values exist for these aspects of hydrous titanium oxide.

Most hydrous metal oxide precipitates have an indefinite or gel-like structure and are composed of a variety of bonds and cross-linkages. They may contain several types of surface oxide and hydroxide groups. Thus chemical properties, such as ion adsorption, can vary dramatically depending on the preparation and the history of the sample. Hydrous titanium oxide is apparently no exception. Research groups have reported widely varying exchange properties and stabilities for hydrous titanium oxide as well as different equations for the exchange reaction. This lack of agreement, which undoubtedly results from differences in the preparation and treatment of the samples, complicates attempts to make quantitative comparisons.

4. NEEDED FUTURE RESEARCH AND DEVELOPMENT

4.1 Chemical Development

Every technological assessment or engineering analysis concerning the use of adsorbents to recover uranium from seawater has confirmed that inadequate characteristics of the available materials limit the application of the concept. Although hydrous

titanium oxide has been repeatedly identified as the best adsorbent material tested, its properties still fall short of those required for a practical recovery system. In particular, the uranium distribution coefficient, loading level, and loading and elution kinetics need to be improved by several orders of magnitude.

Significant future progress in developing dramatically better adsorbents can likely be achieved only through a long-term fundamental chemistry research program. Development of a viable experimental approach could require a multiyear several-person effort. Essentially, significant breakthroughs to new levels of understanding of adsorption and/or ion exchange technology will be required in what is a relatively mature technological area.

The research program should be comprised of the following elements:

- Information exchange. The literature review revealed that at least six to ten laboratories, primarily in Japan but also in Germany, maintain ongoing research efforts to develop and apply adsorbents for uranium recovery from seawater. It would be highly desirable to establish an information exchange mechanism with these laboratories.
- Soluble species identification. Additional information is needed to actually identify the uranium species in seawater; based on known stability constants, $\text{UO}_2(\text{CO}_3)_3^{4-}$ has been assumed to be the major form.
- Fundamental sorption studies. The factors controlling metal carbonate anionic adsorption or ion exchange should be identified and quantified so as to maximize the distribution coefficient, rejection of other carbonates, and sorption-desorption kinetics. Few metals form soluble carbonate anionic complexes, and only limited existing extraction technology is available to guide this work. Most uranium recovery systems involve acidic systems where uranyl cations or uranyl sulfate or nitrate cationic complexes are extracted or absorbed; thus that experience is not applicable to seawater recovery systems.
- New sorbent development. Using the fundamental information acquired, sorbents for uranium from seawater should be prepared in developmental quantities and evaluated in experiments at an ocean-side facility so that practical aspects such as the fouling due to marine growth or mineral deposition can be evaluated as well as sorption properties.

4.2 Engineering Studies

A critical analysis should be performed to determine the energy efficiency of uranium recovery from seawater. Previous estimates have varied widely. Since most of the energy is involved in handling the enormous volume of seawater associated with any practical-sized recovery plant, such an analysis could probably be made by using a generically defined sorbent. Some previously published analyses have apparently precluded pumped schemes because of the pumping power required, while others have precluded tidal basin schemes due to factors such as lack of suitable sites, ecological disturbances, and size of the civil works involved. The results of the analysis could be used in establishing minimum absorbent criteria for the developmental work.

Obviously, unless the recovery plant can deliver a substantial energy gain, the entire concept of uranium recovery from seawater is invalid. A 1000-MW(e) LWR reactor requires an initial charge of ~500 tons of uranium and an annual replacement of ~150 tons of uranium, or has a 30-year lifetime demand of ~5000 tons of uranium. Thus a 10,000-ton/year uranium from seawater plant could refuel 66 existing LWRs or start up 20 new LWRs. At 100% uranium recovery efficiency, an ocean stream equivalent to 25 times the annual Mississippi River flow would have to be processed to recover 10,000 tons/year. This scale of operation raises fundamental engineering questions such as: Can a flow of this magnitude be pumped through adsorbent beds and returned to the sea in such a manner that no backmixing with plant influent occurs and still achieve an attractive overall positive energy balance? Can any sort of nonpumped (tidal flow, etc.) scheme offer a more attractive energy balance after consideration of the civil engineering works necessary to confine this nonpumped flow? A generic engineering examination of these and related questions could offer guidance to considering the practical aspects of uranium recovery from seawater.

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