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Proceedings of a Topical Meeting
On
The Recovery of Uranium from Seawater

by

F. R. Best and M. J. Driscoll (Eds.)

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PROCEEDINGS OF A TOPICAL MEETING ON THE RECOVERY OF URANIUM FROM SEAWATER

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F. R. Best and M J. Driscoll

(Eds.)

December 1-2, 1980

Sponsored by:

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Hosted by:

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and

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Massachusetts Institute of Technology

Cambridge, MA 02139

ABSTRACT

This report is the proceedings of a topical meeting on the recovery of uranium from seawater, held at the Massachusetts Institute of Technology on December 1-2, 1980. The meeting was sponsored by the United States Department of Energy and hosted by the MIT Energy Laboratory and Nuclear Engineering Department.

Workers from six different countries presented a total of sixteen papers in three major categories: the state-of-the art resulting from past efforts; detailed results from sorber preparation and performance experiments; and overall system design aspects.

Sorbers discussed include hydrous titanium oxide, ion exchange resins, chitosan, humic acids and activated carbon. Systems for contacting seawater with the sorber include actively pumped, current and wave-powered concepts. Filter configurations include thin multilayer stacks, fluidized beds and free falling particles.

Several of the researchers estimated eventual production costs in the 200-400 \$/lb U_3O_8 range, although values as high as 2000 \$/lb were also quoted.

The bulk of the proceedings is comprised of the unedited papers, as provided by the authors. The proceedings also include edited transcripts of the discussions on all papers and the panel and concluding discussions.

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Chapter 1

Introduction

1.1 Foreword

This report constitutes the proceedings of a topical meeting on the recovery of uranium from seawater held at the Massachusetts Institute of Technology on December 1 and 2, 1980.

The meeting was sponsored by the United States Department of Energy through a research contract with the MIT Energy Laboratory/Nuclear Engineering Department.

The purpose of the meeting was to convene a representative group of research scientists and engineers working on this problem at various laboratories around the world, and thereby to provide a coordinated review of the state-of-the-art in this field, to assess progress toward the goal of commercial practicality, and to identify R&D initiatives needed to advance these endeavors.

1.2 Background

In August 1980, as part of the review and negotiation process involved with a research proposal submitted to DOE by MIT dealing with the extraction of uranium from seawater, it was concluded that an important phase of this work should include holding a meeting of the type reported here. The concept paralleled in many respects a similar successful conference on the extraction of uranium from shale, sponsored earlier by DOE.

Invitations were distributed in early September, and the list expanded to accomodate additional suggested invitees based on feedback from the first mailing. Persons who elected to attend and present a paper were asked to make available a ready-to-reproduce copy of the paper to the sponsors at the meeting. These submissions form the backbone of the present report. Because of the tight schedule, which imposed many other burdens on those attending, it was decided not to have papers submitted in advance of the meeting or to attempt to reproduce copies for distribution at the meeting. Instead the editors of this report committed themselves to as rapid a publication schedule as practicable. For that reason we have not retyped the papers to conform to a uniform editorial policy. All papers are reproduced as provided by the authors.

1.3 Format of This Report

The hosts for the conference/editors of this report felt that slightly different formats were most appropriate for these entities. Thus the body of the report is made up of three major chapters in which the papers are sorted by topic, and ordered in the way which appeared to be most logical. Thus we have:

Chapter 2	State of the Art Reviews
Chapter 3	Sorber Preparation and Performance
Chapter 4	Recovery System Studies

The actual order in which the papers were delivered is recorded in the agenda reproduced as Appendix A. Note that in several instances more than one paper was given pertaining to different aspects of the same research program at a given institution. We have separated those companion papers according to their subject matter.

Chapter 5 contains a synopsis of the panel and concluding discussions which we have transcribed from tape recordings. These summaries are not verbatim and have been heavily edited. Thus the editors accept the responsibility for any misinterpretations. We have also in most instances attempted to identify the questioner, but this was not always possible; again we apologize for any errors in this regard. A similar comment applies to the discussions following each paper, which we have summarized and appended to the papers as they appear in each chapter.

A complete list of persons who officially registered as conference attendees is enclosed as Appendix B: this list includes all speakers and their business addresses.

Finally, at the end of this chapter we include the introductory remarks of John Patterson, of the USDOE, whose initiative caused the conference to be held. His remarks are followed by those of Dr. Fujii of the IAEA, who addressed the conference at its close.

1.4 Acknowledgements

We wish first of all to acknowledge the cooperation of the Department of Energy through its Division of Resource Assessment Operations and its Grand Junction Operations Office in facilitating this endeavor.

Particular thanks are due to all of the speakers, authors and attendees who responded at such short notice, and who were undoubtedly inconvenienced in this regard. Our apologies to all, and especially to those who were either invited and could not attend, or who were inadvertently overlooked in the rush.

We also wish to thank the following MIT students who acted as co-hosts at the conference, operated audio-visual equipment, and who also contributed to the technical input for the MIT papers: Raymond Coxe, Charles Graves, David Medek, Cynthia Nitta, Lance Riniker, David Surber, and Jeffrey Whaley.

Finally our thanks to Ms. Barbara Duffney and Ms. Christal Whelan, whose secretarial skills before and after the conferences contributed so much to its success and the timely issuance of this report.

Remarks by John A. Patterson
Director, Division of Resource Assessment Operations
U.S. Department of Energy

at the
Conference on the Recovery of Uranium
from Seawater

Massachusetts Institute of Technology
Boston, Massachusetts
December 1 and 2, 1980

On behalf of the U.S. Department of Energy, I would like to welcome you to this Conference on Recovery of Uranium from Seawater. The potential extraction of materials from seawater has been a challenge to science and industry for a long time. However, there have been very few commercial successes.

The large quantity of uranium that exists in the sea at a low concentration has intrigued researchers in many countries. The extensive information on uranium chemistry and on techniques for processing low grade materials has provided an excellent technological base from which to proceed. Substantial progress has been made toward the defining of means by which uranium might be recovered from seawater and the costs that might be involved. A variety of problems remain to be resolved before sound judgments can be made regarding the practicality of commercial uranium recovery. Nonetheless, the progress in recent years suggests there are possibilities to develop workable processes that would involve costs that are in the range of interest to those planning for future energy systems and for the conduct of research and development, particularly in the nuclear reactor and fuel cycle area.

This meeting is designed to bring together active workers - and thinkers - in this field to clarify the state-of-technology and the key problem areas, and to focus on critical problems ahead, so that better research programs can be carried out in all the involved organizations.

Seawater is a truely international resource, so it is gratifying - and promising - that workers from most of the active countries are here. I hope we can have a free exchange of ideas so the meeting can provide improved concepts of the potential long range role of uranium from the sea and what we need to do to better understand and perhaps utilize this resource.

We extend our thanks to Professor Driscoll and Dr. Best and to the Massachusetts Institute of Technology for their efforts in organizing and hosting this conference.

Comments by Dr. Fujii of the IAEA

At the conclusion of the conference Dr. Fujii of the International Atomic Energy Agency addressed the attendees. His remarks, as summarized by the editors from a tape recording, are as follows.

Dr. Fujii expressed his appreciation at being allowed to address this first international meeting on the extraction of uranium from seawater. He noted that the technical information collected and reported here would be of considerable use to IAEA staff members in their program planning activities.

He called attention to several pertinent IAEA activities. One of the five major departments of the IAEA has as one of its divisions the Nuclear Fuel Cycle Section, of which he is a member. One of their areas of cognizance is that of uranium production. While most of their work to date has been on conventional processes they are currently planning their new program in which non-conventional sources are under consideration. The cognizant technical committee will be convening in 1982. The meeting may include discussion of uranium from seawater. Final plans will be formulated next year.

The IAEA has had some past interest in uranium from seawater: several papers on this topic were included in the Advisory Group Meeting on Uranium Ore Processing in 1975. The agency supported research by a Korean scientist to evaluate these papers during the past year.

Another related activity has been that of the Working Group on Uranium Extraction jointly organized by the IAEA and the ENEA who have discussed the topic of uranium recovery from seawater in their last meeting this past May. No conclusions regarding international cooperation in this area were reached at that time, but this topic will be discussed again at their next meeting in February 1981 in the U.S.

In view of the above, the present conference should provide some timely technical input in this area. Dr. Fujii also expressed the hope that the participants would comment as to the possibility of international cooperation and the role of the IAEA in this field. In particular he recommended that the participants contact their own respective national representatives to the Working Group.

Dr. Fujii concluded by requesting comments on other areas of potential applicability for the technology developed for uranium recovery from seawater. He noted that the IAEA Fuel Cycle Section was also concerned with other separation processes, such as uranium recovery in mine and mill effluents, and similar processes in other facilities.

At the conclusion of Dr. Fujii's remarks Prof. Driscoll indicated that it would appear appropriate to ask that the attendees respond to Dr. Fujii's concerns in the concluding discussion, which was scheduled to take place as the next and final step of business.

Chapter 2

State-of-the-Art Reviews

In this chapter we have concentrated papers which deal mainly with the task of providing comprehensive overviews of the field of uranium extraction from seawater. These include:

A.D. Kelmers

"The Recovery of Uranium From Seawater -- Status of Technology and Needed Future Research and Development"

M.H. Campbell and S.E. Binney

"Feasibility Study on Uranium Extraction from Seawater"

E.W. Hooper, N.J. Keen and G.I.W. Llewelyn

"The Recovery of Uranium from Seawater"

As previously noted, these papers are reproduced here directly as submitted by the authors. Appended to each paper, however, are edited transcriptions of the brief discussion sessions which followed each paper.

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

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To be presented at a topical meeting: The Recovery of Uranium from Seawater, December 1–2, 1980. Massachusetts Institute of Technology, Cambridge, Massachusetts.

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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 ppb[1]), 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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*Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

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 deeps.
- 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 U_3O_8 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 ^{232}U-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 publication[32] identifies the exchange reactions occurring when $UO_2(CO_3)_3^{4-}$ is adsorbed by titanium oxide and proposes that the uranyl moiety is retained on titanium oxide surrounded by two CO_3^{2-} and two TiO^- ligands. The retention equilibrium is given as

$$2{\equiv}TiOH + 4{\equiv}TiONa + 3UO_2(CO_3)_3Na_4 \rightarrow$$
$$3({\equiv}TiO)_2UO_2(CO_3)_2Na_4 + 2H^+ + 3CO_3^{2-} + 4Na^+ .$$

2.5 Work in Japan

In the last several years, an extensive effort has 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 Laboratory[33-35] 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 TiO_2 crystallites. The mechanism of sorption of the $[UO_2(CO_3)_3]^{4-}$ ion was determined to be

$$TiO(OH)_2 + [UO_2(CO_3)_3]^{4-} =$$
$$TiO_3{\cdot}UO_2 + 2HCO_3^- + CO_3^{2-} .$$

The competitive adsorption of $[UO_2(OH)_3]^-$ 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 $CaCO_3$ 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 indispensible 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, $ZnCO_3 \cdot 3Zn(OH)_2 \cdot 2H_2O$, 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 $Mg(OH)_2$ precipitate formed at the interface of a seawater–isobutyl alcohol mixture;[53] 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 Kumanoto 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 $TiO(OH)_2$ 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 analysis[14] 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 data[32] 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, $UO_2(CO_3)_3^{4-}$ 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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Discussion of Dr. Kelmer's Paper

The existence of a wide range of performance data regarding hydrous titanium oxide was brought out. Distribution coefficients substantially better than those most commonly quoted were occasionally reported. It was suggested that this might apply to very finely divided powders, as opposed to the larger particles which would be suitable for practical applications.

Mr. Campbell remarked that it was often difficult to determine from the literature whether measurements were made in seawater and/or whether additional uranium was added to the seawater to facilitate analysis.

FEASIBILITY STUDY ON URANIUM EXTRACTION FROM SEAWATER

A SUMMARY

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FEASIBILITY STUDY ON URANIUM EXTRACTION FROM SEAWATER
A SUMMARY

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1. Introduction

The overall objective for this study(1,2) was to determine the resource base and the technical, economic, and environmental feasibility of large scale recovery of uranium, as a co-product and a single product, from the territorial coastal waters of the United States. A typical site was chosen and a 500 tonne per year plant was conceptually designed. Extensive bibliographies on this subject were also produced[3,4].

A multidisciplinary work group was assembled under the project management of Exxon Nuclear Company, Inc., to fulfill this broad objective. Oregon State University provided technical expertise primarily from its Department of Nuclear Engineering and School of Oceanography. Vitro Engineering Corporation developed engineering flowsheets and provided architectural engineering design.

In that much of the prior work on recovering uranium from seawater was reported by European and Japanese scientists and engineers, trips were taken to these locations to learn of the state-of-the-art. These visits were most helpful in providing a more substantial basis for the many decisions needed in arriving at acceptable data and facility designs.

During the course of this study, several key assumptions had to be made in the absence of concrete experimental evidence (e.g., loading capacity, kinetics, loss due to mechanical attrition and solubility, etc.).

2. Uranium Resource Evaluation

The general approach to this work was to consider a number of interrelated parametric studies.

Examination of the marine and physical chemical literature revealed nothing to weaken the conception currently held by marine chemists that approximately 98% of the uranium in seawater occurs in the dissolved state as negatively charged uranyl carbonate complex ions. Somewhat less than 2% occurs as negatively charged uranyl hydroxide complex ions. Other forms, such as overall neutrally charged chemical forms, may exist but probably in relative amounts much less than 1%.

Uranium behaves as a conservative constituent of the oceans, i.e., it remains dissolved in the oceans on the average for periods of time which are very long compared to the circulation and mixing times of the deep waters of the oceans. This results from the annual supply and removal rates of uranium to and from the sea being very small fractions of the total amount contained therein. As a result, uranium is distributed much like sea salt in the oceans. Hence, to maximize the local uranium resource, a location where the salinity is high should be sought.

Although the concentration of uranium is quite low, about 3.3 parts per billion in seawater of average oceanic salinity, the amount present in the total volume of the oceans is very great, some 4.5 billion tonnes. Of this, perhaps only that uranium contained in the upper 100 meters or so of the surface well-mixed layer should be considered accessible for recovery, namely, some 160 million tonnes. Practically speaking, the amount contained in the ocean surface layers is unlimited with respect to large scale extraction in the foreseeable future. This results from the replenishment by continental weathering and river runoff being much larger than anticipated extraction rates.

This study indicated that open ocean seawater would be a more favorable resource for the purpose of uranium extraction than would rivers entering the sea, the cooling water of present or planned power plants (either fossil fuel or nuclear), or the feed or effluent streams of existing plants producing other products such as magnesium, bromine, or potable and/or agricultural water from seawater. This is evidenced by the fact that production on the scale of a thousand tonnes of uranium per year would require total extraction of the uranium from a major fraction of even the largest river in the United States, the Mississippi. Furthermore, the sediment load carried by any large river would incapacitate any known process for the extraction. In the case of existing power or material production plants utilizing seawater as coolant or feed, the scales are simply too small for large scale uranium extraction. Hence, only seawater pumped or otherwise accessed for the purpose of uranium extraction constitutes a viable resource.

3. Extraction Plant Site Selection

Process and plant specific criteria for site selection of an extraction plant include relatively high temperature of the local seawater, topography, geological and geophysical suitability of the potential site, availability of sufficient fresh water and other process needs, and accessibility to logistic and labor bases for plant construction and operation. Resource specific considerations include ready access to a steady supply of relatively saline seawater with minimal biological or other fouling potential, and assurance that the uranium-stripped plant outflow stream will not mix back into the plant intake.

Process selection and plant design are intimately connected with certain aspects of resource evaluation concerning regional oceanographic conditions. Three basic plant configurations were considered: 1) an open ocean platform, either bottom supported, free floating with dynamic position control, or more or less loosely moored to the bottom, 2) a tidally driven seawater feed stream, and 3) a coastal plant with a pumped seawater feed stream.

Offshore plants, either bottom mounted or floating, would offer several advantages in principle. These include accessibility to more steady surface currents than available close inshore, typically lower sediment loads and biological fouling, and potentially better separation of feed and outflow streams. Current flow delivery was discussed with Japanese and German investigators. Within current documentation, the configuration of adsorbent beds or films was still in the developmental stages and not yet sufficiently well defined for conceptual design and cost estimation; hence this delivery scheme was not considered further, particularly due to the limited time frame of this study.

Such considerations led to the selection of a site for a pumped seawater coastal plant at a coastal location. A location in southeastern Puerto Rico, Puerto Yubucoa and the Guayanes River Valley, was selected as the reference design plant site. This coastal site has a narrow (less than two kilometers) continental shelf which allows the Antilles Current to bring a relatively constant supply of warm (25°C to 30°C), saline seawater with low water clarification requirements fairly close to the potential plant site and to assist in carrying away the plant outflow. More than six square kilometers of nearly level terrain less than three meters above sea level, suitable for a plant site, abut the shoreline. An ample fresh water supply (over 100,000 cubic meters per day) is available or could be economically developed. The present land use is of relatively low intensity, as is human habitation.

4. Chemical Extraction Process

The various known methods of extracting uranium from seawater (adsorption, flotation, solvent extraction, co-precipitation, electrolysis, and biological) were evaluated in light of a set of criteria to determine the optimal extraction process. Adsorption appeared to be the most reasonable chemical process on the basis of specific uranium yield, required seawater treatment, recyclability of raw materials, and developed engineering technology. Of the many adsorbent materials which have been investigated, hydrous titanium oxide was chosen as the most promising adsorbent at the present time.

The hydrous titanium oxide adsorption process for separating uranium from seawater requires four operational steps: 1) loading the hydrous titanium oxide adsorbent with uranium by direct contact with seawater; 2) eluting the uranium from the hydrous titanium oxide with ammonium carbonate; 3) steam stripping the eluate to remove and recover the ammonium carbonate; and 4) preparing a solid uranium product.

5. Reference Extraction Plant Design

In the process design, four possible configurations for the adsorption beds were considered, namely, a static downflow bed, a static upflow bed, a continuous slurry bed, and a continuous fluidized bed. The continuous fluidized bed was selected for design and cost estimating because it had several advantages over the static beds. These include nearly continuous operation; washing and elution in a separate continuous operation; reduced sizes for pumps, piping and storage; and elimination of three piping systems and reduction in water requirements. Flowsheet criteria were developed for process design purposes which included:

- Uranium concentration in seawater is 3.35 parts per billion
- Plant capacity is 500 tonnes U_3O_8 per year
- On-stream load factor is 90% for a continuous fluidized bed
- Adsorbent is hydrous titanium oxide
- Adsorbent bed adsorption efficiency is 80%
- Adsorbent capacity is 210 mg U/kg Ti
- Elution efficiency is 97%
- Product concentration and recovery efficiency is 91%
- Mean flow through the adsorbent bed is 0.4 cm/s
- Ammonium carbonate is used to elute uranyl ions from the hydrous titanium oxide
- Pumped flow is used to pass seawater through the hydrous titanium oxide

One hundred sixty vertical turbine pumps were needed for meeting the peak flow and spare equipment requirements for a 500 tonne per year reference plant. The seawater pumps were used to maintain a constant head differential between a forebay and adsorbent bed influent canal system.

A 4 m head above sea level was required. Since the seawater of the Caribbean Sea is nearly void of nutrients and the fluidized bed can pass up to 50 micron sand particles, the design included seawater pretreatment by drawing it through a 278 mesh fabric screen.

The fresh water pumping system was planned to meet a peak flow of 200,000 cubic meters per day with one pump out of service. The system was designed to pump from a stream-fed, wet well to a pressure balancing and storage reservoir. The system included major water pipes, mechanical filtration equipment, chlorination equipment for potable fraction, and pressure regulation equipment.

The total geographical area requirements were 8,000 hectares for the basic plant area, 200 hectares for pipelines and roadway rights-of-way, 200 hectares for port and storage facilities, 900 hectares for a fresh water reservoir, and 1,000 hectares of sea floor for the forebay and miscellaneous area.

6. Economic Considerations

A labor force of 700 was projected for this facility with an annual labor cost of $12.5 million.

Extensive material takeoff sheets for the reference design were prepared for pricing and extension to a complete construction estimate. The approximate capital cost for the reference design of the continuous fluidized bed uranium recovery facility, using the criteria previously referenced, was estimated to be $6.2 billion in 1978 U.S. dollars.

On the basis of capital and operating cost breakdowns, sensitivity studies were made using a computer model to vary a number of process, construction, and financing parameters. These sensitivity studies indicated that increasing the flow rate of seawater through the adsorbent beds would reduce the overall cost of product uranium. Practically, this can be accomplished by increasing the particle size. At this point, adjusted takeoffs were made and a new lower capital cost estimate of $4.9 billion (1978 dollars) was projected.

It was concluded that if a plant such as the reference plant were built by 1995 the cost of extracting uranium from seawater would range from $2100 to $2600 per pound of U_3O_8. The production cost is extremely capital intensive and, as such, the projected costs are sensitive to the method of financing the project. A private venture, without government support, could not produce uranium for under $2700/lb, and the most probable commercial cost would be about $3600/lb.

7. Environmental Effects

Uranium can be removed from seawater by a process that can generally be made to be compatible with the environment within which it is located. The environment of the site would have to be evaluated prior to the start of detailed design so that the environmental inputs could be used to the final design. Although there would be a major environmental impact due to the removal of uranium from seawater, these impacts appeared to be amenable to mitigation by current technology.

8. Summary

Feasibility of uranium recovery has four readily definable sub-divisions: (1) technical feasibility; (2) engineering feasibility; (3) economic feasibility; and (4) social feasibility. It was found in this study that it would be technically feasible to recover uranium from seawater, although there are a number of site-specific studies that should be conducted prior to site selection. It is not feasible from an engineering viewpoint to go beyond the preliminary conceptual design for a pumped flow system without conducting further studies. It would be socially feasible to recover uranium from the seawater as long as the plant site were in a low population area. Without several major technical breakthroughs leading to significantly lower production costs and/or federal subsidy, a pumped seawater plant to extract uranium from seawater is not economically feasible at the present time.

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Discussion on Mr. Campbell's Paper

Professor Kanno remarked that state-of-the-art adsorber technology for hydrous titanium dioxide now provides capacities approximately four times greater than that used in the EXXON study.

Mr. Campbell responded to another question by remarking that time constraints did not permit any extensive sensitivity studies or iterations to optimize the overall design.

Dr. Llewelyn's questions brought out some points with regard to the site section: that only U.S. sites had been examined; that the engineering staff involved felt that the final site had roughly five times the production potential; that deep water was available close offshore, including the proximity of an OTEC test facility; and that the availability of fresh water was a key limitation -- one which mitigated against use of a site on Key Largo.

Professor Kanno and Dr. Llewelyn raised the question as to the effect of interest rate and long construction times on the cost of product. During a subsequent break Professor Driscoll attempted clarification of some of the points involved by noting: that the annual carrying charge (ϕ in his paper, to be presented later) was approximately given by $\phi \simeq x/(1-x)$, where x is the discount rate, sometimes known as the tax-sheltered cost of composite capital ($x = (1-\tau) \cdot f_b r_b + f_s r_s$; with f_b and f_s being the bond and stock fractions, r_b and r_s being the bond and stock rates, and τ the tax fraction: $\sim 1/2$ in the U.S. for commercial ventures, 0 for government ownership). In the U.S. $x \simeq 0.09\ \mathrm{yr}^{-1}$, hence $\phi \simeq 0.18\ \mathrm{yr}^{-1}$ for investor owned utilities, twice this for speculative industries, and half this for government activities. Thus large differences in projected costs can be explained by the financial environment assumed.

THE RECOVERY OF URANIUM FROM SEA WATER

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Background

Early work in the UKAEA on the extraction of uranium from sea water has been reported by Davies et al.(1) A large number of possible solid absorbers were tested(2) and a hydrous titanium oxide was selected as the most promising for further development.

Later work(3) at AERE, Harwell, and at an outstation at Portland Harbour, was concentrated on the preparation of a titania absorber with better properties than hitherto and the testing of this absorber in flowing sea water to examine its performance in service. The elution of uranium from the loaded absorber was also studied.

In a subsequent programme of work, solutions to many of the problems were identified and although the work was far from complete and some major issues remained unresolved, the work was stopped in 1970 after a very rough assessment of cost indicated that the process would not be economic for many years.

By the time work on the project ceased the following information had been obtained:

(a) Hydrous titanium oxide can be prepared in granular form on the multi-kilogramme scale with a good capacity for absorbing uranium from sea water. It has a low solubility in water.

(b) Packed beds of granular absorber (100-300 μm diameter) can extract uranium with high efficiency on a laboratory scale given appropriate bed geometry and flow rates. The performance of the absorber does not deteriorate in service.

(c) Absorber losses arising from dissolution and from breakdown of particles amounts to about 10% per annum.

(d) Loss of eluting reagent during absorber regeneration is large and this will be one of the major costs in uranium extraction from sea water. The losses arise from (i) precipitation of absorbed calcium and magnesium as carbonates, (ii) entrainment, and (iii) during reconcentration to remove water picked up during the elution process.

(e) Ammonium carbonate was the best eluant but sodium hydrogen carbonate is likely to be good enough and would probably be cheaper to produce on site. The concentration of uranium in the eluant can be increased by passage from bed to bed. Recovery of uranium from the eluant can be achieved through conventional uranium mill technology using anion exchange.

Sea Water Trials of the Cycle

During the three phases of the work outlined in Section 1, the scale of operation of sea water test rigs increased.

In the early work 2.5 cm diameter glass tubes were used to contact 20 cm^3 portions of different absorber preparations with flowing sea water. The absorber was fluidised by an upward flow of sea water at 10 litres/hr and the absorber was sampled periodically to determine the uptake of uranium with time. Figure 1 shows a typical uptake curve obtained in these experiments.

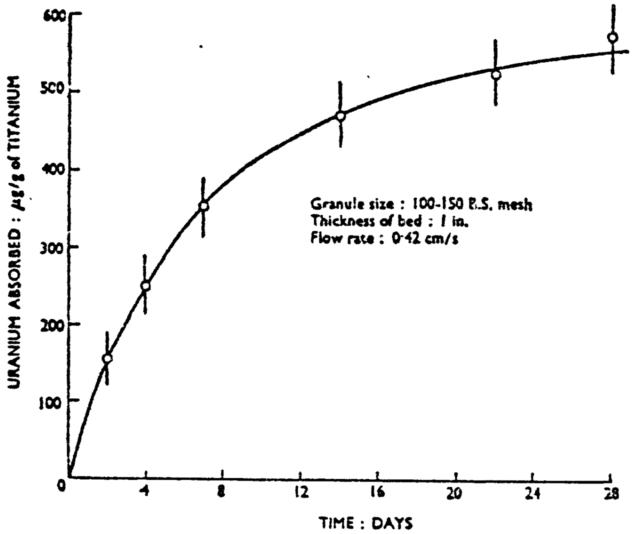

Fig 1 Uranium absorbed from flowing sea water by hydrous titanium oxide gel granules

When the preparation route for a suitable absorber had been established, kilogramme quantities were prepared and used in 30 cm diameter columns. The main aim in this series of experiments was to study the ability of the absorber to retain its uranium absorbing power over a long period in service by subjecting it to many complete load/elute cycles, using conditions similar to those expected in a production plant. The object was to maintain a batch of absorber in service for at least a year.

Figure 2 shows the uranium content before and after elution in each of 26 cycles carried out over 14 months of operation. In cycles 4-21 the sea water flow was downward through the bed at ~ 0.14 cm.sec^{-1} for 8-12 days in each cycle; the average absorption efficiency in these cycles was 59%. When the flow rate was increased to 0.25 cm sec^{-1} and the duration to 16 days as in cycles 22-26, the average efficiency fell to 26; this is the behaviour to be expected when uranium is being supplied faster than it can be absorbed and when loading is continued to the point where the rate of absorption is beginning to decrease (see Fig. 1).

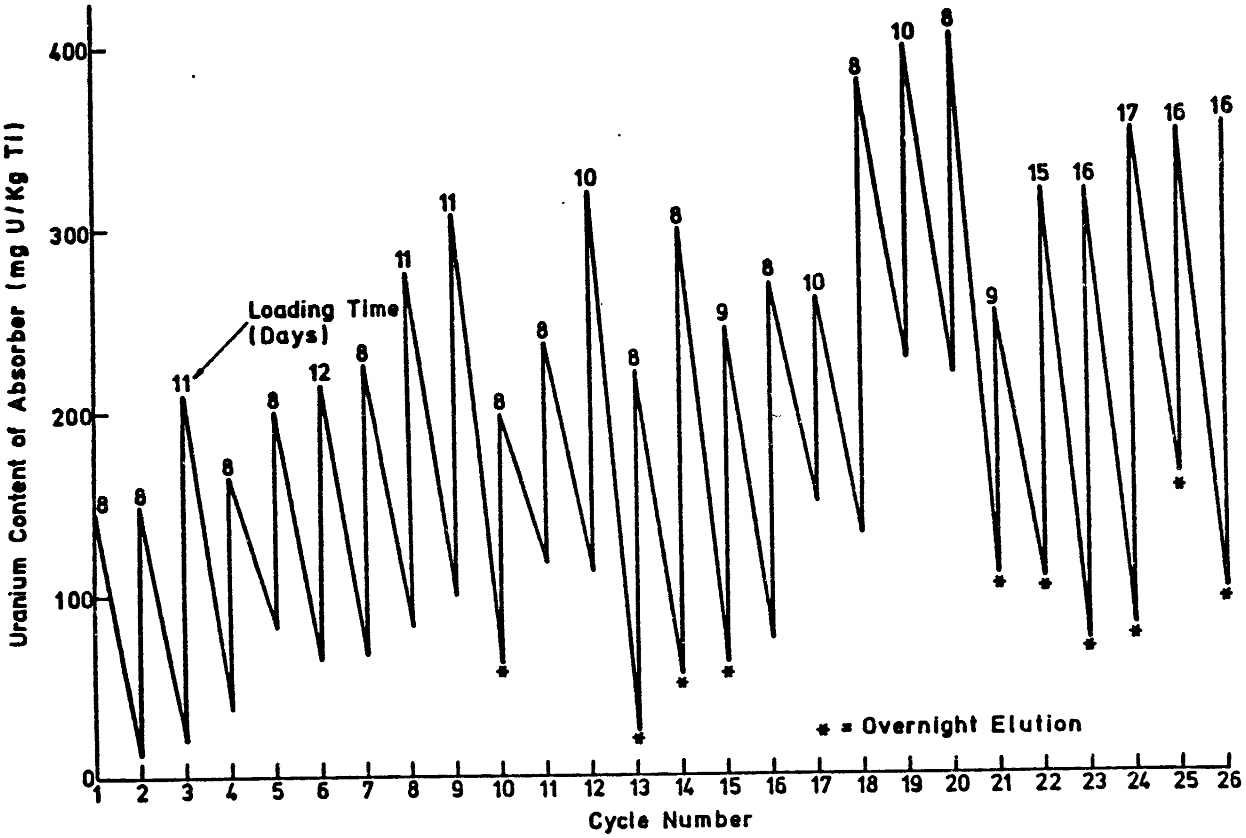

FIG.2.URANIUM CONTENT OF ABSORBER BEFORE AND AFTER ELUTION

It should be noted that the actual efficiency of uranium absorption varies with the sea water temperature.

The average elution efficiency in this experiment was 98% for the 25 elution cycles and so a gradual build up of uranium on the absorber occurred.

The uranium concentration in eluants was progressively increased when ammonium carbonate solution was re-used in several successive cycles. Thus in cycles 5-9 the uranium concentration in eluants was as follows:

Cycle No.	Concentration of U in eluant (after making up volume for next cycle)
5	17.7 mg/l
6	27.0
7	25.1
8	42.7
9	58.6

There is no evidence that the concentration could not be taken higher but this was not pursued; concentrations up to 84 mg/l were recorded in small portions of the eluant taken at the peak in the elution curve.

Operation of Pilot Plant Module

Towards the end of the UKAEA work a pilot unit was operated at the Portland Harbour Laboratory with the objective of testing the practicability of a module of the bed that might be employed in a conceptual plant, i.e. to test the principle of self-cleaning beds for operating in unfiltered sea water.

Figure 3 is a diagram of the pilot module; the unit contained two beds, each of 1.2 metres diameter and 10 cm deep. The absorber was contained between sheets of porous plastic which acted as filters to remove solids suspended in the sea water. Provision was made for automatic reversal of the direction of flow of sea water when the pressure drop across the bed reached a pre-set level. Eight cycles were completed in each of which 4,500 cubic metres of sea water were passed in 8 days, followed by treatment to remove the absorbed uranium.

The results obtained with the pilot module were disappointing; the calcium and magnesium carbonates precipitated in the bed during the elution process caused blinding of the bed which led to channelling and the consequent reduction in extraction efficiencies. It was concluded that the design of bed used was unlikely to be practicable and that a radical change in bed concept would be necessary.

When the absorber in the beds was replaced with sand of the same particle size, the self-cleaning performance of the bed was found to be satisfactory over a 30-day period of operation with unfiltered sea water.

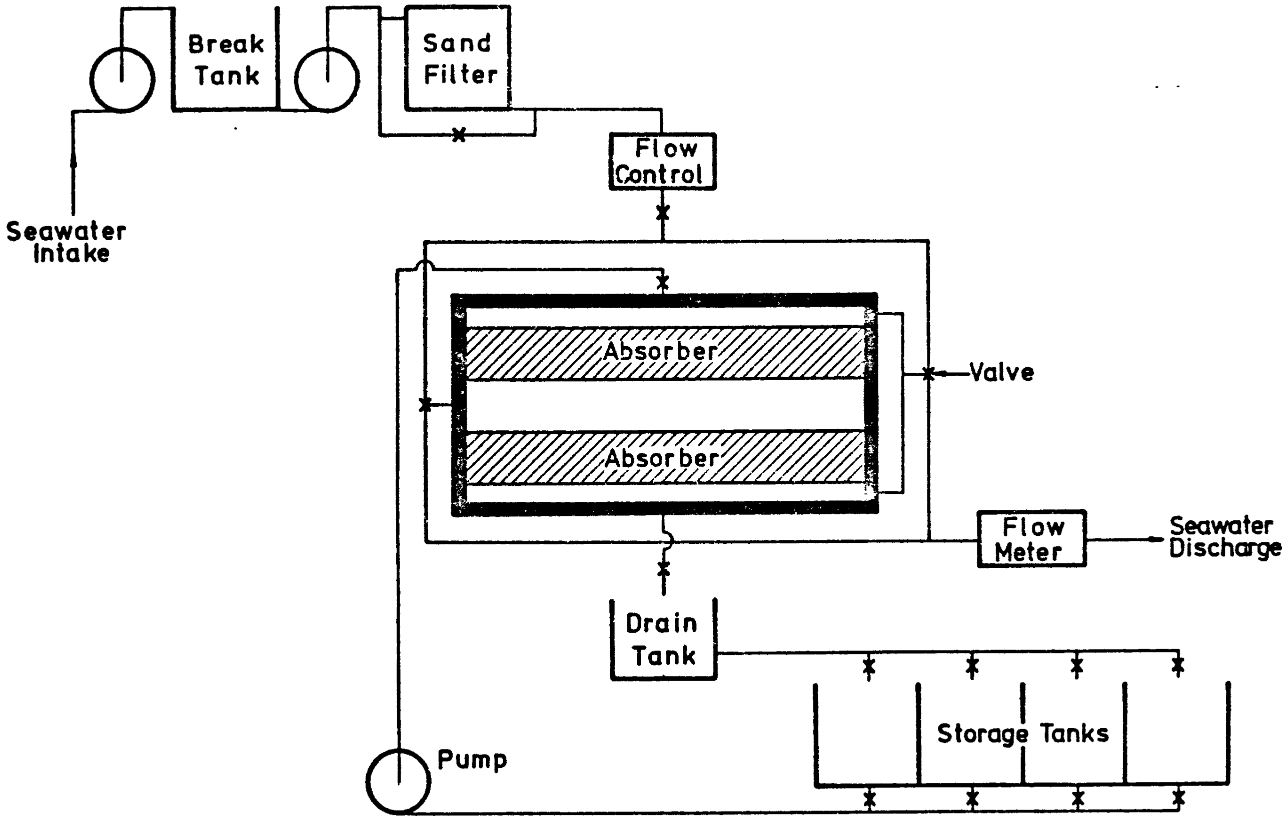

FIG. 3. DIAGRAM OF PILOT MODULE

As a possible alternative to shallow packed beds, a 30 cm diameter fluidised bed of absorber granules was operated successfully for several weeks in a stream of unfiltered sea water; the head of water required was less than that for an equivalent packed bed and the precipitated calcium and magnesium carbonates were flushed out of the bed. However, loss of absorber due to attrition occurs and a stronger absorber would be required for this type of operation. The method of preparation used can produce a stronger absorber but our observations indicate that this would involve a loss in absorption capacity.

Status Review

A review of the status of the study of the extraction of uranium from sea water was made in the UK in 1974/75. The aspects considered and conclusions made were published(4,5) and reported.(6,7) It is felt that the conclusions made at that time are probably still valid to a great extent. These conclusions were as follows:

(i) Whilst process techniques developed on a small scale demonstrate the possibility of extraction and subsequent recovery of uranium from sea water under the right conditions, there are a number of uncertainties associated with the process. Extensive further research work would be necessary to reduce appreciably the level of these uncertainties.

(ii) Uranium extraction combined with other proposed schemes which handle large volumes of sea water (desalination plants, coastal power stations, barrages) would only have a marginal effect on expected demand to feed thermal reactors.

(iii) The most promising extraction system is that based on pumped flow of sea water.

(iv) On the assumptions made, a rough energy accounting exercise indicates that a considerable energy gain might be achieved through extraction of uranium from sea water, even for a pumped system.

(v) It seems unlikely that there are sites around the UK coast where uranium extraction could meet UK demands.

(vi) Some sites probably exist, around the world, where conditions are reasonably favourable to the extraction of uranium from sea water on a scale significant in relation to large thermal reactor programmes. However, insufficient work has been done to be confident that this is so, particularly in relation to the need to avoid the recycling of depleted sea water.

(vii) A large-scale uranium extraction plant could involve a major biological management effort both within the process and in its environmental consequences. The extent of the measures required could only be assessed in relation to a specific site but there is no present reason to believe that there would be any biological problems that could not be overcome.

(viii) 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.

(ix) It would be unwise to expect uranium from sea water to contribute significant amounts to the world's uranium demand

> for thermal reactors on an acceptable timescale. New deposits must be found elsewhere, including low grade ore bodies which will be a more certain source of supply in the foreseeable future than sea water uranium.

We are not aware that new data have emerged during the last five years that could affect the general validity of these conclusions, but some comment can be made to update the position.

Little has been publicly released by those laboratories working experimentally on the subject and we appreciate that a reassessment may be necessary if it becomes evident that significant progress has been achieved. Other methods for contacting the absorber with fresh sea water might be better than pumped flow provided the mechanical properties of the absorber are taken into account.

The effect of sea water temperature on the rate of absorption would significantly reduce the production capacity of a plant in UK waters in winter but the operating temperature ranges would be adequate for some of the world's warmer seas.

Nuclear programmes world-wide have been appreciably delayed, and forecasts significantly reduced, since 1975. Based on uranium requirements, the acceptable timescale for the development and introduction of uranium extraction from sea water on a strategically important scale is today almost certainly longer than was thought to be the case five years ago.

The conclusion that there would be an energy gain in the pumped scheme has been questioned in an independent energy accounting exercise in the UK.(8) This conclusion is very sensitive to the assumed pumping power requirement.

We are often asked to give a 'guesstimate' of the possible cost of extracting uranium from sea water. Whilst still entirely concurring with the above conclusion that there are too many uncertainties to quote even an approximate estimated cost, we have examined the possible cost figures sufficiently to hazard the opinion that production costs would be at least several hundred dollars per lb. of uranium.

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UKAEA
Harwell.

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Discussion on Mr. Hooper's Paper

In response to a question on uniformity of flow by Dr. Best, Mr. Hooper indicated that representative bed samples were insured by homogenization via fluidization before sampling, and also that in other cases beds had been studied by taking core samples. He also said that stainless steel was used as the structural material to a considerable extent but that epoxy coated mild steel had performed well; in general there were no major corrosion problems.

Dr. Fremery pointed out that fluidized beds were advantageous in avoiding the detrimental buildup of calcium and magnesium carbonate scale on the sorber particles observed in the UK experiments. He felt that attrition problems can be overcome by using the right gel preparation conditions. A glassy surface can be obtained, but at the expense of a high effective surface area, hence there is a compromise to be struck.

Best noted that early (UK/ORNL/EXXON) system design studies were predicated on the use of active coatings on an inert substrate. Hooper replied that such particles had never been fabricated in practice. Some early work was done using floc deposited on muslin, but losses were high. He noted that uranium pickup was a surface phenomenon. Capacities of 700μg U/g Ti overall correspond very nearly to a monomolecular layer. Diffusion into the granules is clearly an extremely slow process.

Chapter 3

Sorber Preparation and Performance

This chapter contains papers whose main theme was the physical-chemical properties of sorber materials, in particular:

M. Kanno

"Adsorption and Elution of Uranium in Seawater"

K. Schwochau, L. Astheimer, H.-J. Schenk and E.G. Witte

"Studies on Complexing Resins Accumulating Uranium from Seawater"

I. Tabushi and Y. Kobuke

"Specific Uranyl Binding By Macrocyclic Ligands Attached to Resins"

S. Maroldo and G. Beasley

"A Convenient Laboratory Screening Test for Potential Sorbers of Uranium from Seawater"

H. Denzinger, Ch. Schnell, D. Heitkamp and K. Wagener

"The Advantage of Fast Reacting Asorbers Like Humic Acids for the Recovery of Uranium from Seawater"

R.A.A. Muzzarelli, F. Tanfani and S. Mariotti

"The Recovery of Uranium from Sea Water by Chelation on Chitosan"

B.L. Averbach

"Mechanism of Chelation of Heavy Metals by Chitosan"

Adsorption and Elution of Uranium in Seawater

by Masayoshi Kanno

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Faculty of Engineering, University of Tokyo

ABSTRACT

In Japan, the essenciality of the development of nuclear power generation has become enhanced, and it needs to ensure uranium resources mainly from foreign countiries. Though several policys have been taken, extraction of uranium from seawater has been interested and some investigations have been carried out mainly by the Metal Mining Agency of Japan since 1975. In this programme, selections of chemical processes, adsorption tests mainly with hydrous titanium oxide, elution processes, washing processes, the recovery of eluate by steam stripping or electrodialysis, secondary concentrations of uranium in the eluate by ion exchange or ion flotation etc., and some tentative cost estimations have been carried out. Some results of the experiments for each unit process will be described.

INTRODUCTION

As shown in the previous paper (1), the adsorption process by inorganic adsorbents has been considered to be the most promising process to extract uranium from seawater at present. In the initial stage, some coagulation and co-precipitation processes were investigated by Ogata (2). H_4TiO_4, $MnO_2 \cdot nH_2O$, $Fe(OH)_3$, $Pb(OH)_2$, ZnO, $Zn(OH)_2$, $Cr(OH)_3$, $Mn(OH)_2$ etc. were found to have considerable uranium extractabilities among about fifty insoluble compounds of Ti, Al, Mn, Ca, Si, Zn, Cr, Pb and Sn. However, the heighest uptake capacity was obtained for titanium hydroxide. Several investigations on the adsorption by hydrous titanium oxide (titanium hydroxide, titanic acid) including composit metal oxides have been carried out (3)(4)(5)(6).

Though several preliminary experiments for looking for new adsorbents are being performed, mainly our investigations of adsorption have been concentrated on the hydrous titanium oxide. Various kinds of preparations of hydrous titanium oxide have been investigated and it was found that the hydrous titanium oxide prepared by the urea method gave the highest uranium uptake capacity. To improve the mechanical strength and avoid the blockage of the adsorbent bed, some granulation tests including pressing and crushing, screw extrusion and agitating granulation were carried out.

To accomplish the total process, some elution experiments, prewash and postwash experiments and the secondary concentration experiments have been performed. Finally, several kinds of seawater contacting structures have been investigated conceptionally and some cost analyses mainly based on the pumping and fixed-bed system have been carried out. Some results of these experiments will be described.

DEVELOPMENT OF ADSORBENT

The general requirements of the extractants of uranium from seawater are as follows:

(1) The final selection must take into consideration the results obtained with natural seawater. The results obtained with artificial seawater, uranium enriched seawater, and with seawater by changing pH and the concentration of HCO_3^- etc. cannot be applied to natural water in many cases.
(2) A comprehensive judgement must be made as to the adsorption capacity, adsorption rate, fabricability, solubility in seawater, durability with acids and alkalines, long term stability and biological toxicity etc.
(3) Supplies of the adsorbent material must be stable and the price must be reasonable.

Hydrous titanium oxide appears to be the best adsorbent which satisfies the above conditions at the present time. As for this adsorbent, the improvement of the quality and the development of industrial preparation of hydrous titanium oxide are being performed. Various kinds of preparations of hydrous titanium oxide have been reported, but they can be roughly classified into the following three types.

a) Neutralization method: A titanium solution is neutralized by alkali.
b) Urea method: Urea is added to a titanium solution and then heated.
c) Thermal decomposition method: A titanium solution is heated and hydrolyzed.

All these methods were tested and the urea method gave the best adsorption capacities and stabilities. In initial stage, the uptake capacity of 268 μg U/gTi was reported in England for the hydrous titanium oxide prepared by the reaction of titanium tetrachloride and sodium hydroxide(5). Later, the uptake capacity of about 550 μg U/gTi was reported for the hydrous titanium oxide prepared by the reaction of titanium tetrachloride and ammonia (7). According to the urea method with the reaction of titanium sulfate and urea, the maximum uptake capacity of 660 μg U/g dry adsorber has been obtained at 25 °C for fine powder materials. This value is equivalent to about 1600 μg U/gTi. To improve the mechamical strength and avoid the blockage of the adsorbent filled bed, some granulation tests including pressing and crushing, screw extrusion and agitating granulation were carried out.

The adsorption capacity decreases markedly with increasing the granulating pressure, but appropriate pressure is necessary to maintain some mechanical properties. Several kinds of inorganic and organic binder have been tested, however, the addition of binder usually decreases the adsorption capacity. The uranium adsorption curves by fixed-bed columns, the effect of the temperature and of the particle size on the adsorption of uranium were reported in the previous paper (1). The flow sheet for the preparation of granulated hydrous titanium oxide adsorbent is shown in Fig. 1, and the equipment of the adsorption experiments for relatively long-term experiments is illustrated in Fig. 2.

Some experimental results of the uranium adsorption equilibrium are shown in Fig. 3. As shown in Fig. 3, the adsorption equilibrium of powder form hydrous titanium oxide is generally conformed to Freundlich's isothermal equation $C = KC_0^n$ where C is the concentration of uranium in the adsorbent, Co is the concentration in seawater and K is a constant. Experimental values of n were 0.568,0.621 and 0.733, and an average value of 0.64 was obtained. The equilibrium data were taken by adding fine powder adsorbent to the natural seawater contained in a vessel and by keeping it for 48 hrs with stirring. The constant K varies considerably due to the difference of adsorbnets, however, the slopes of the lines in Fig. 3 were not much different.

ELLUTION PROCESSES

Such acids as hydrochloric acid and sulfuric acid and solution of such carbonates as ammonium carbonate, sodium cabonate and sodium bicarbonate can be used for the elution of the uranium adsorbed on the hydrous titanium oxide. However, the elution of uranium on granulated hydrous titanium oxide adsorbents with relatively concentrated acids causes granule breakage due to gas evolution and dissolution of adsorbent. In addition, the elution rate by using relatively low concentration acid, for example, hydrochloric acid of less than 0.2 N, was slower than that by using carbonate solutions. Accordingly, ammonium carbonate was chosen as an eluant in the initial stage.

For estimating the elution rate, some experiments with column were carried out. One example is shown in Fig. 4. 1.0 N ammonium carbonate, and the granulated adsorbent with average particle size of 0.6 mmϕ were used. The initial uranium content of the adsorbent was 72.8 μg U/g ad. It shows almost no effect of eluate flow rate on the elution rate, and it needed more than 48 hrs for eluting more than 90 % of the adsorbed uranium at room temperature. If we raise the temperature, the elution rate becomes much faster.

WASHING PROCESSES

Prewash process appears to be necessary to remove the salts in the loaded adsorbent and to avoid the accumulation of salts. Postwash process is also needed for improving the uranium and carbonate recovery and preventing the deposite of calcium and magnesium carbonates produced by the reaction of seawater with the carbonate eluant. Fig. 5 shows changes of the chlorine concentration of the effluent of prewash water and the carbon dioxide concentration in the effluent of postwash water. The experiments were carried out with 30 cm ϕ column, 1.9 cm of adsorbent bed depth and a flow rate of 4 cm/min after eluting by ammonium carbonate. It shows that at least 5 BV of fresh water is necessary for prewash and 8 BV for postwash processes.

RECOVERY OF ELUANT

The relatively expensive carbonate in the eluate must be recovered for the recycle use and for reducing the pH of the eluate for the following uranium recovery processes. For this purpose, some experiments of steam stripping were carried out. The equipment of the experiment is illustrated in Fig. 6. A 1.1 mole ammonium carbonate solution was decomposed with internal pressure below atmospheric pressure. Fig. 7 shows a typical data obtained at 80 °C. The heat balance made it possible to derive a sensible heat of 365 kcal (5 l solution), steam evaporation latent heat of 750 kcal, ammonium carbonate decomposition heat of 113 kcal, outlet ammonium carbonate concentration of 0.1 mole/l, and heat efficiency of 82.3 %. From these results, it was shown that 0.387 tons/m^3 (in terms of 7 kg/cm^2 G steam) of steam was required to reduce the concentration of 1.0 mole/l to 0.1 mole /l in the case of 82.3 % heat efficiency. The recovery ratio of carbonate has not been confirmed. The ammonium carbonate solution obtained was estimated to have a concentration of 2.42 mole/l which was sufficient for recycle use.

Later, by the viewpoint of the reduction of the necessity of waste effluent treatment of the ammonium carbonate process, sodium carbonate and sodium bicarbonate solutions have been chosen as eluant. In these cases, the electrodialysis by using ion-exchange membranes has been studied. The schematic diagram of the experimental apparatus is shown in Fig. 8. The experiment was carried out usually for 9 hrs using 10 monovalent-ion-selective ion-exchange membranes with a effective area of 1 dm^2, employing a 1 mole/l sodium bicarbonate solution and circulating a 0.2 mole/l sodium bicarbonate solution in the concentration chamber, with an applied voltage of 35 V.

A typical result is plotted in Fig. 9 which shows changes in uranium concentration and carbonate concentration with operation time. Apparent current efficiencies were 86.3 % in the mother solution chamber and 73.2 % in the concentration chamber. In the case of the elution by ammonium carbonate, the steam stripping process will be used, and in the case of elution by sodium carbonate the electrodialysis process will be used. Some quantitative comparisons of the two processes have been carried out as follows.

a) Ammonium carbonate elution-steam stripping
   1) The simple equipment structure leads to low construction cost and easy maintenance and control.
   2) In the case of the pumping scheme, it seems to be necessary to build a self-operated power generation plant for the pumping power. In that case, the waste steam from the power plant can

be used for the steam stripping.
   3) If the effluent from the extraction plant contains some ammonium salt, it may be more harmful to the environment than the case of sodium carbonate, therfore, it will require large facilities for waste water treatment.
- b) Sodium carbonate elution-electrodialysis
   1) High membrane prices and the complicated equipment structure including instrumentations, make the construction cost high, and it will require higher technologies and personnel for maintenance and control.
   2) If it is not the case of the pumping scheme, it is easy to use other commercial electric power.
   3) Sodium carbonate does not contaminate seawater, it will reduce the amount of washing water and waste water treatment facilities.

Considering above conditions, the sodium carbonate elution-electrodialysis process appears to be more advantageous at present.

TENTATIVE COST ANALYSES

The cost of the extraction of uranium from seawater is much dependent on the systems and there are much uncertainties. If we fix the system to be the pumping and fixed-bed system, some uncertianties on such adequate conditions like the seawater flow rate, uranium recovery by the adsorbent, adsorption capacity of the adsorbent, recoveries of the secondary concentration and separation processes etc. remain unfixed. The possibility of the use of multi-layer fixed beds and the necessity of such pretreatment as filtration must be investigated. However, some tentative cost analyses have been carried out for the "pumping and fixed-bed system" and the "sea current direct utilization system". The artist drawings of these systems are illustrated in the previous paper (1). A cost classification based on the above conceptual design for the "pumping and fixed-bed system" is shown in Fig. 10. The capital cost forms about 75 % of the total cost. This fact appeared to be in good agreement with the Exxon Company's results (8).

CONCLUSION

Hydrous titanium oxide has still shown the best adsorption capacity of uranium and small scale operations have been carried out successfully. However, a lot of engineering problems remains unsolved. Extensive further research would be necessary. In parallel with these, some exploitations of new types of adsrobents are also desirable.

As for the contacting system of adsorbents with seawater, the pumping and fixed-bed system appears to be most promising at present, however, many experimental and modeling studies including such other systems as slurry type, magnetic separation type, fluidized bed type, moving bed type, transimission type, sea-bed marine structure type, off shore floating structure type etc. must be investigated.

For these studies, the cooperation among not only chemists, mechanical engineers, civil engineers but also oceanographers, topographers, biologists, meteorologists, ecologists and other researchers and engineers in the wide field might be necessary.

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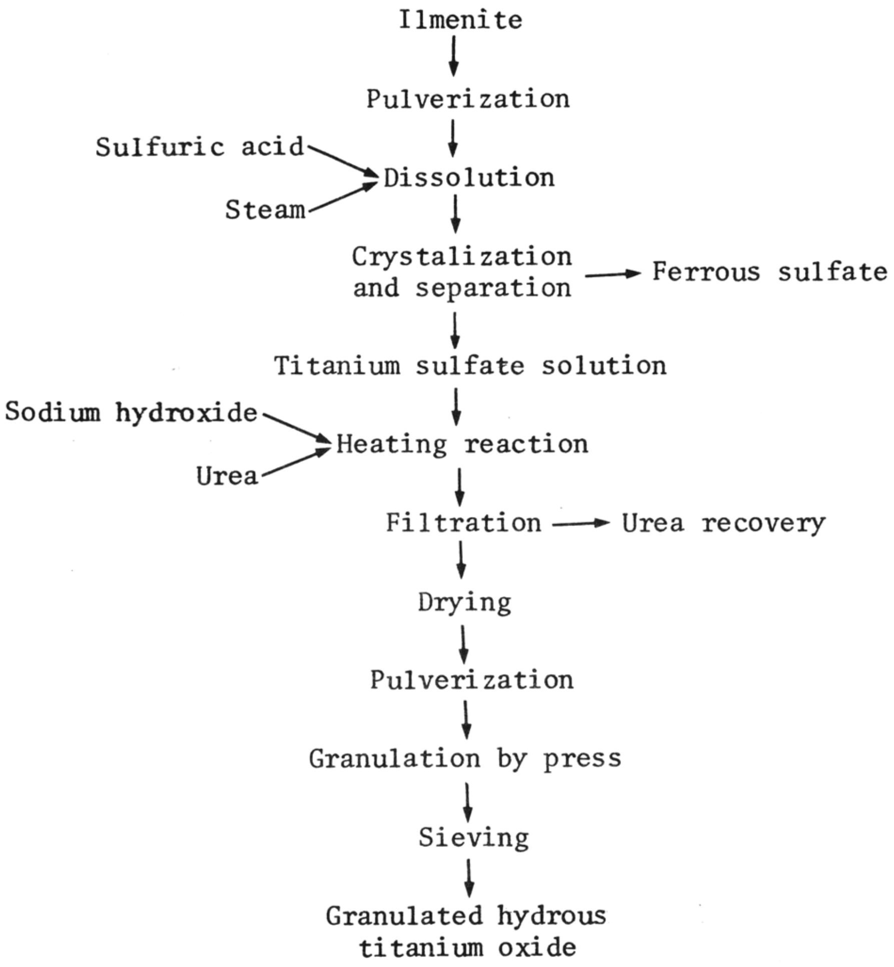


Fig.1 Flow Sheet for Granulated Hydrous Titanium oxide Preparation

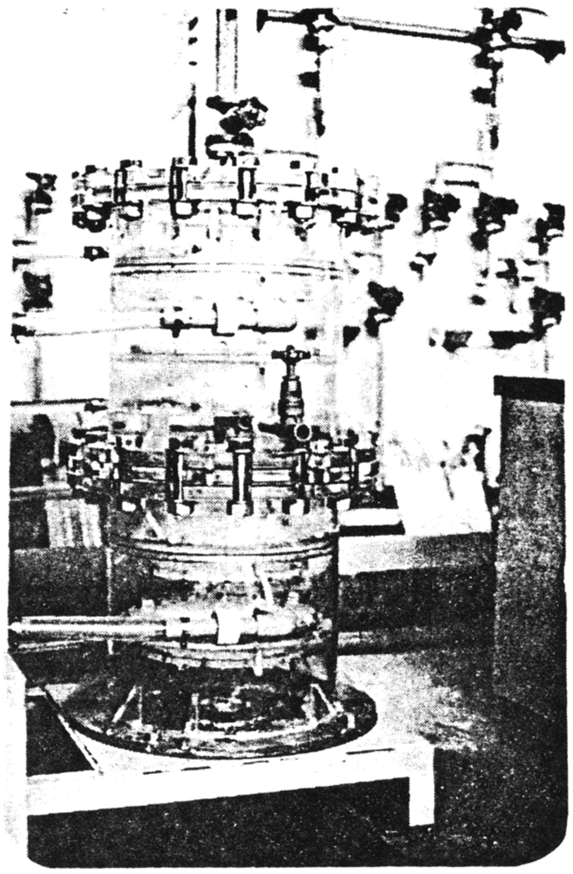


Fig.2 Equipment of Adsorption Experiment

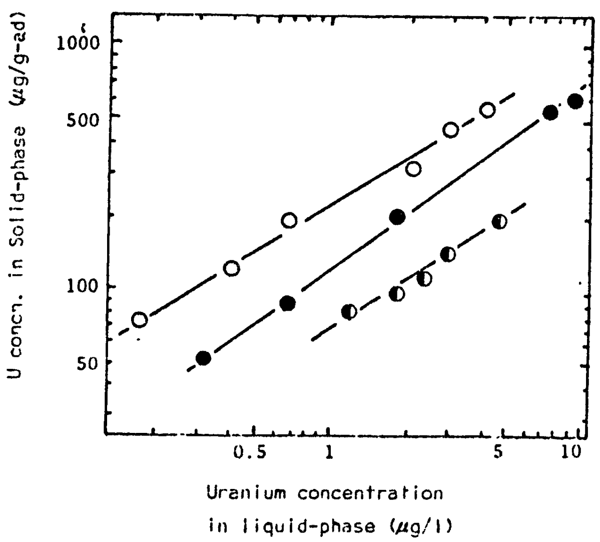
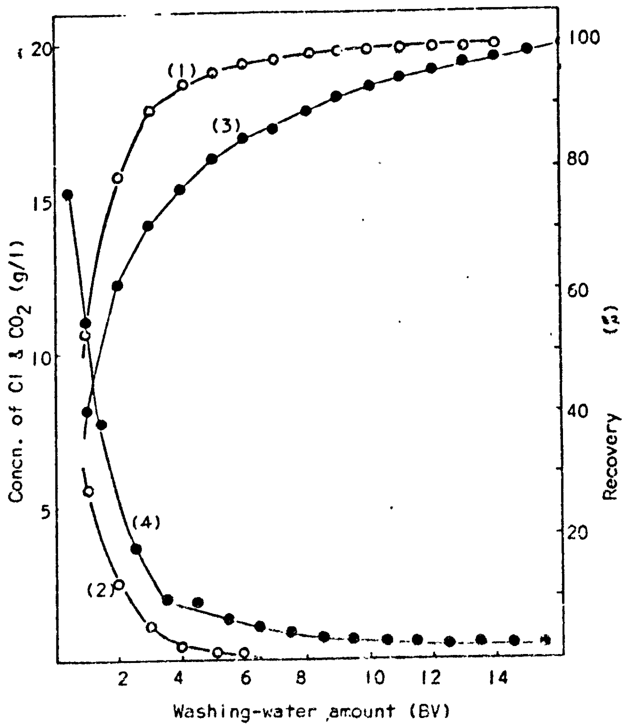


Fig.3 Adsorption Equilibrium on Hydrous Titanium Oxide



(1) Recovery of chlorine in prewash water

(2) Concentration of chlorine in prewash water

(3) Recovery of carbon dioxide in postwash water

(4) Concentration of carbon dioxide in postwash water

Fig.5 Changes in Chlorine and Carbon Dioxide Concentration in Washing

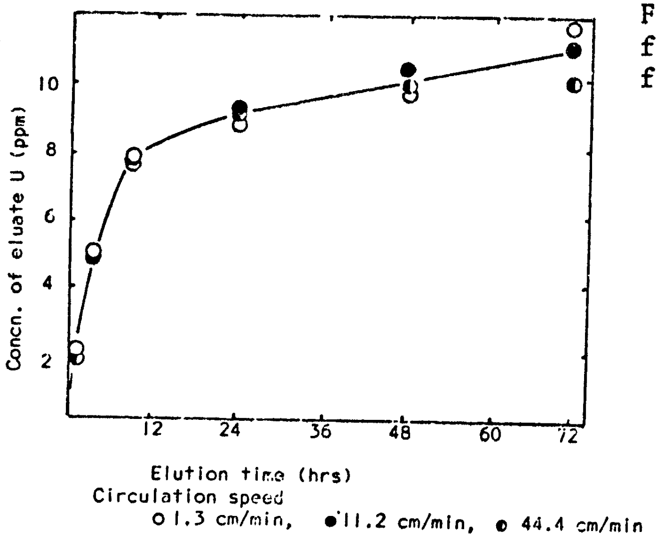
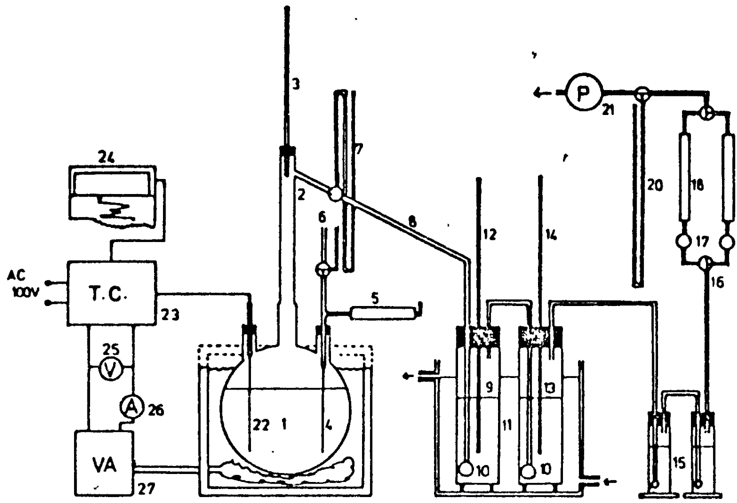


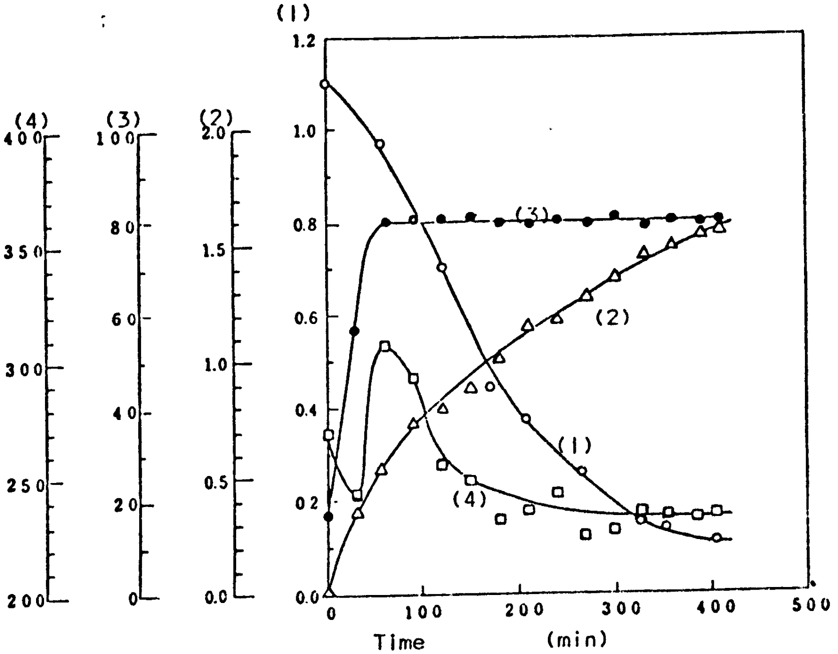
Fig.4 Elution Curves for different eluant flow rate

54U



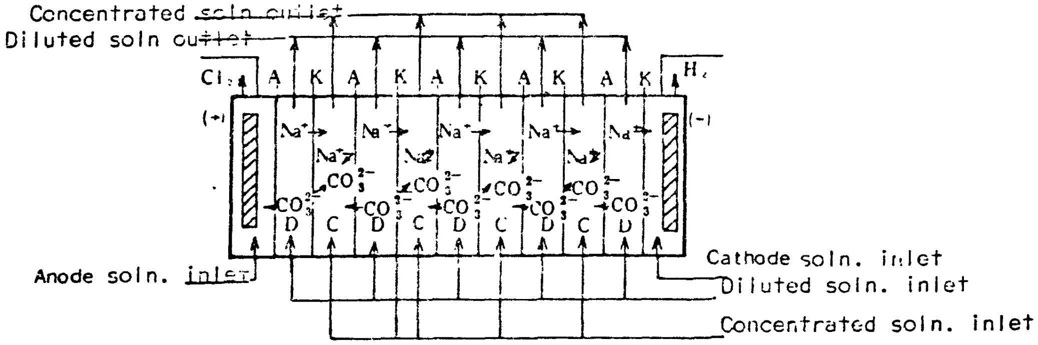
1.Distillation flask (51)
2.Gas outlet
3.12.14.Thermometer
4.Capillary tube
5.Calcium chloride tube
6.Safety cock
7.20.Mercury manometer
8.Transporting tube
9.13 Recovery vessel
10.Ball filter
11.Cooling bath
15.Moisture adsorption trap
16.Switching cock
17.Flow-rate control cock
18.19.Gas flow meter
21.Suction pump
22.Thermister
23 Power control unit
24.Recorder
25.Voltmeter
26.Ammeter
27.Watt-hour meter

Fig.6 Equipment for Steam-Stripping Experiment



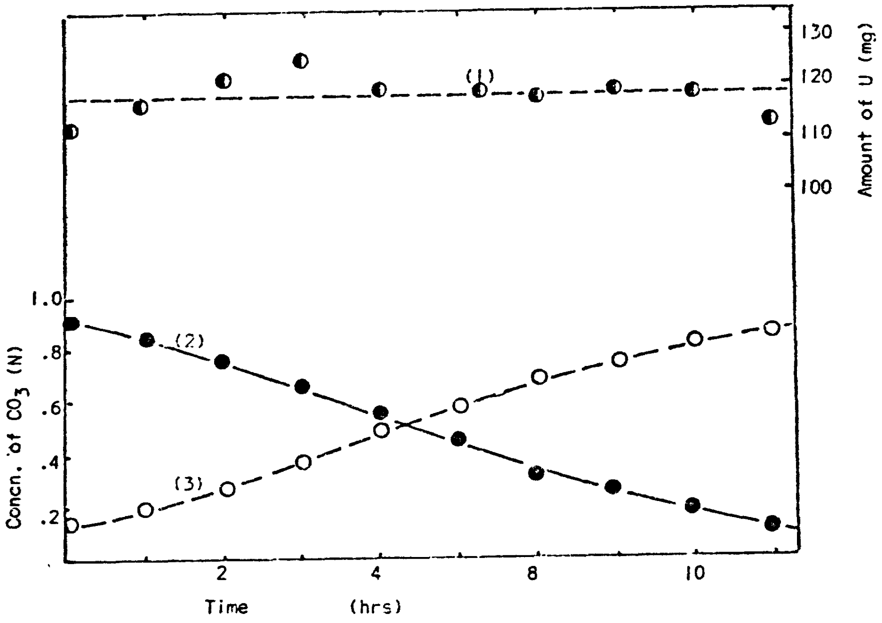
(1)Concentration of ammonium carbonate (M)
(2)Power consumption (KWH)
(3)Liquid temperature inside the distillation flask (°C)
(4)Gas-emission system pressure (mmHg)

Fig.7 Results of Steam-Stripping Experiment



K: Cation exchange membrane
A: Anion exchange membrane
D: Dilution chamber
C: concentration chamber

Fig.8 Schematic Diagram of the Equipment for Electrodialysis



(1) Uranium in D-chamber
(2) Concentration of carbonate in D-chamber
(3) Concentration of carbonate in C-chamber

Fig.9 Results of the Electrodialysis

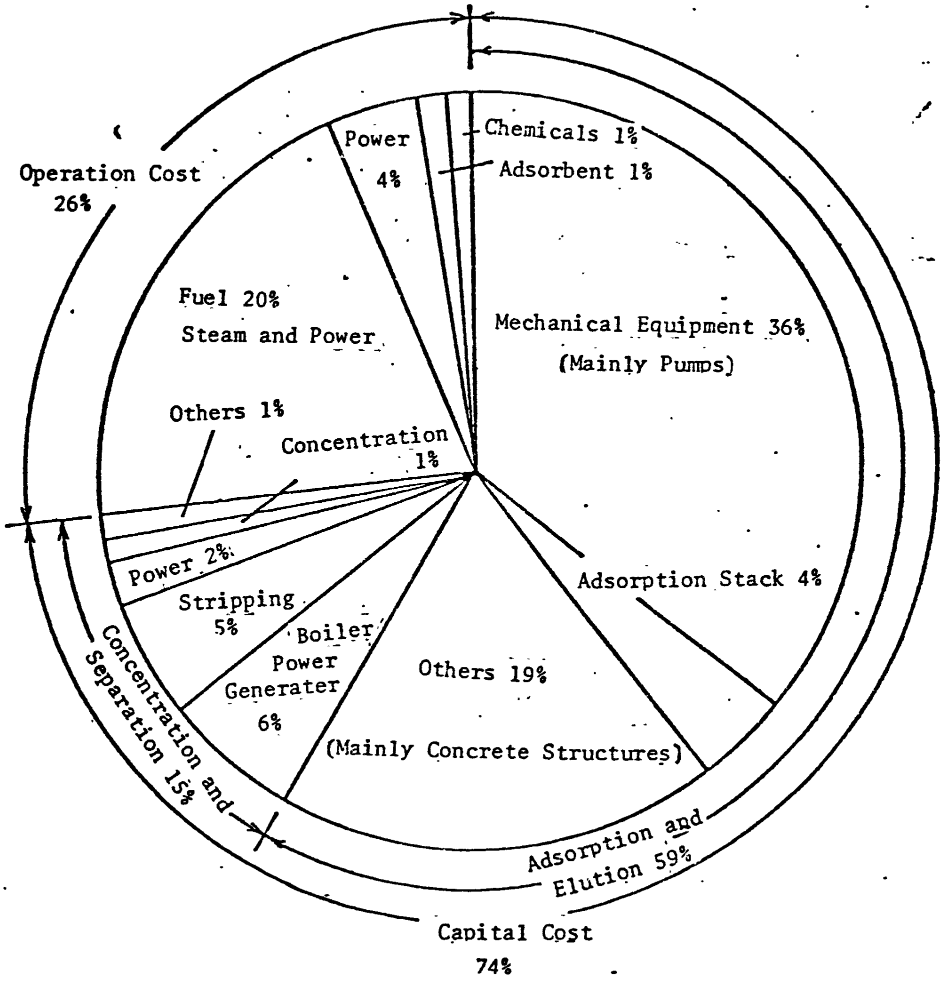


Fig.10 Cost Classification
(Pumping and Fixed Bed Scheme)

Discussion on Prof. Kanno's Paper

In response to a question Prof. Kanno indicated that hydrous titanium sorber costs on the order of 1 $/lb titanium.

In a discussion as to why the elution process was being changed to use sodium carbonate rather than ammonium carbonate, Prof. Kanno agreed that ecological reasons were a major factor. A comment from the floor cited the additional consideration that the solubility of hydrous titanium oxide is an order of magnitude higher in an ammonium carbonate solution than it is in sodium carbonate solution. Prof. Kanno also noted that while the initial cost of the sodium carbonate system is higher, its operating cost is lower.

Dr. Wang asked why one observed a difference in hydrous titanium oxide properties when changing from sodium hydroxide to ammonium hydroxide to urea. Prof. Kanno indicated that the reason a more active material was obtained with urea may have something to do with temperature: the urea was added at room temperature and the temperature gradually raised to 95°C. In response to a second question by Wang, Prof. Kanno indicated that a 48 hour elution was needed to obtain 90-95% recovery in a 1 molar solution, and that below a certain carbonate concentration elution efficiency becomes very low. Higher temperature also favor faster elution.

STUDIES ON COMPLEXING RESINS ACCUMULATING URANIUM FROM SEAWATER

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In view of the anticipated exhaustion of terrestrial uranium reserves of the western world in the near future [1], the recovery of uranium from sea water is increasingly taken into consideration [2-91]. The oceans contain more than 4 billion tons of dissolved uranium, about the thousandfold of reasonably assured and estimated terrestrial resources. The concentration of uranium in the oceans seems to be nearly constant at about 3.3 $\mu g/l$ [1o-12]. Certainly, sea water is a very low grade uranium source, however the advantage of the dissolved state and the almost exhaustless quantities of uranium should be kept in mind [8].

In consequence of the relatively high carbonate concentration in sea water uranium predominantly should occur as the tricarbonato uranyl complex, the structure of which is shown in Fig. 1.

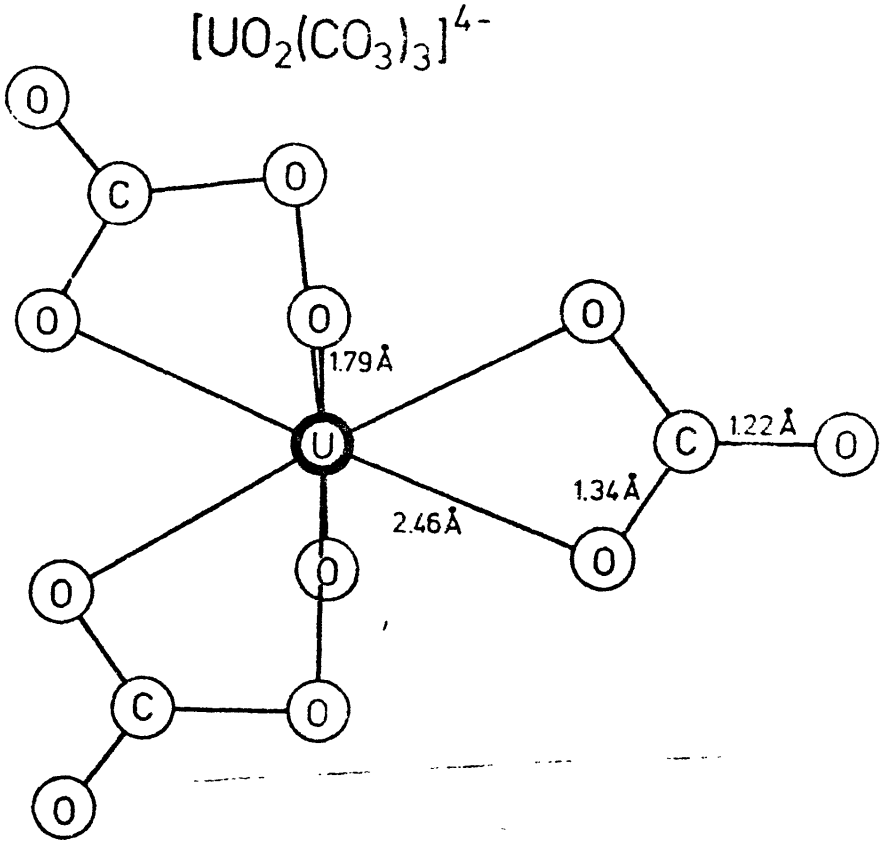


Fig. 1 The structure of the complex anion $[UO_2(CO_3)_3]^{4-}$ [13]

The uranium atom is eight-coordinate. The linear uranyl group is equatorially surrounded by six oxygen atoms of the three bidentate carbonate groups. In the equatorial plane the radius of the complex ion amounts to 4.85 Å, thus this ion is one of the largest occuring in sea water.

The molar concentration of uranium is by nearly 8 magnitudes lower than the total concentration of the major ions in sea water. But it should be mentioned too, that the uranium concentration is higher than that of more common metals like copper, manganese or chromium [14]. Uranyltricarbonate is an extremely stable complex with the overall formation constant of log β_3= 22.6 and the stepwise formation constant of log k_3 = 5.41. Finally, it should be mentioned that the tricarbonato complex is easily decomposed when the pH is lowered beneath 8.

Several methods of uranium accumulation such as solvent extraction, ion flotation or coprecipitation have been considered, but only the sorptive concentration using a suitable solid sorber seems to be feasible. Hydrous titanium oxide which was developed in England, has a uranium loading capacity of some hundred ppm; it is used at present in Japan, China, France, and also in the Federal Republic of Germany.

Due to the low concentration of uranium in sea water vast volumes of sea water have to be contacted with the sorber. Nearly $1o^9 m^3$ or 1 km^3 are necessary for the extraction of 1 ton of uranium. Therefore a high mechanical and chemical stability of the sorber against sea water and eluents and a very low solubility are stringent requirements.

It can be understood from Fig. 2 that already a small solubility will lead to a considerable loss of sorber, which is calculated for the extraction of 1 ton of uranium in dependence on the extraction efficiency. Even in the case of the slightly soluble hydrous titanium oxide - its solubility was found to be o.1 mg/l [15] - the loss amounts to 1oo tons taking into account for example an extraction efficiency of 3o %. Moreover hydrous titanium oxide lacks in more selectivity, mainly calcium and magnesium seriously interfere with the adsorption and elution of uranium.

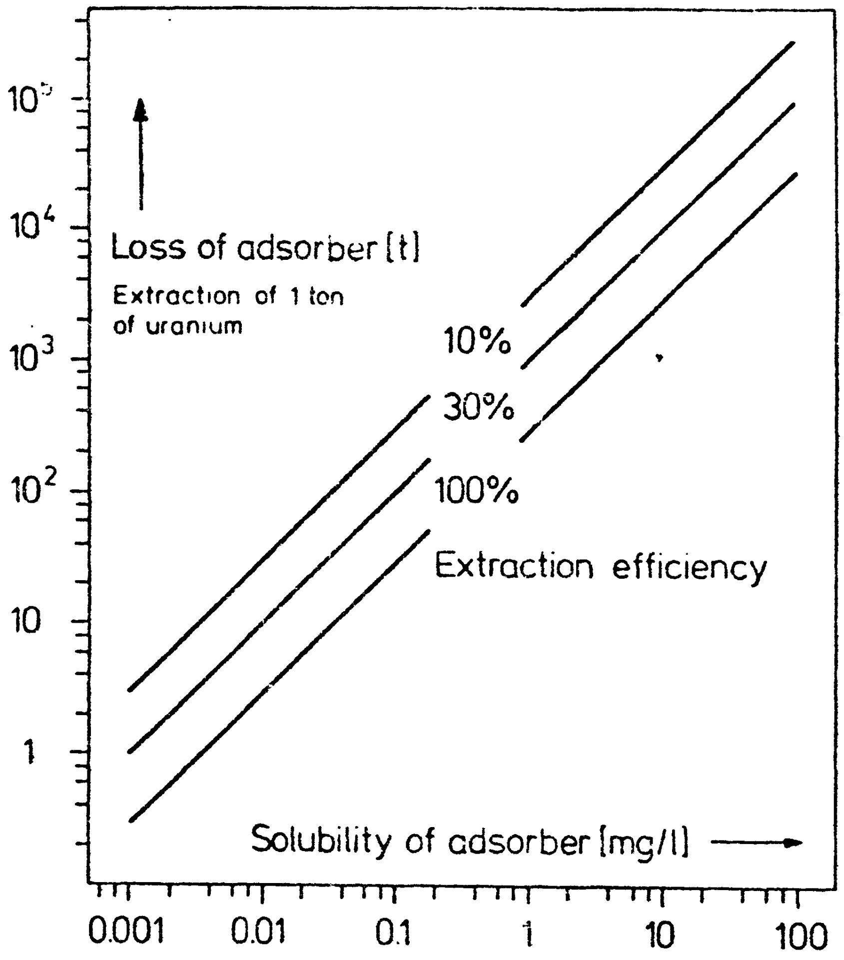


Fig. 2 Loss of adsorber for the extraction of 1 t of uranium in dependence on solubility and extraction efficiency.

We have determined the uranium uptake of a large number of inorganic, organic, and biological materials in natural sea water, but none of them satisfied all the requirements. Recently we have turned our attention to ion exchange resins, because it should be expected that they are almost insoluble; in particular suitable functional groups can be bound to the polymer framework.

Table 1 Uranium uptake of some representative ion exchange resins

Ion exchange resin	Functional group	Concentration factor	pH maximum	f_{U-O} [mdyn·Å^{-1}]
Ag 11 A 8 weakly acidic strongly basic	$-COOH$ $-N^+(CH_3)_3Cl^-$	$2.1 \cdot 10^2$	6.3	7.24
IRC 75 weakly acidic	$-COOH$	$8.8 \cdot 10^3$	7.2	6.82
Chelex 100 chelating	$-N\begin{smallmatrix} \nearrow CH_2COOH \\ \searrow CH_2COOH \end{smallmatrix}$	$2.8 \cdot 10^2$	8.0	6.64
Srafion chelating	$-C\begin{smallmatrix} \nearrow NH \\ \searrow \overset{+}{N}H_3Cl^- \end{smallmatrix}$	$9.7 \cdot 10^2$	8.0	6.38

Table 1 collects some representative resins of the numerous commercial resins which we have tested in natural sea water. In spite of the fact that uranium occurs in sea water as an anionic complex, anion exchange resins appeared to be ineffective. The uranium uptake of amphoteric resins represented by Bio-Rad Ag 11A8 is found to be low, the concentration factor is only about 2oo. Better results could be achieved by weakly acidic resins containing carboxylic groups. For example Amberlite IRC 75 yields a concentration factor of nearly 9ooo. The uranium uptake of the chelating resins Chelex 1oo and Srafion is lower by one magnitude of more. It should be emphasized that nearly all uranium binding resins only can accumulate uranium from sea water at pH values lower than the pH of natural sea water. In the last column of the table the uranyl valence force constants of the uranium-resin adducts are given, which were derived from the symmetric and asymmetric vibrations in the luminescence and infrared spectra. By approximation the force constant of the uranium-oxygen bond of the uranyl ion decreases with increasing coordination number and strength of bonding in the equatorial plane. All constants in the column are higher than in the case of the tricarbonato complex, pointing to a weaker bonding of uranium by the functional groups.

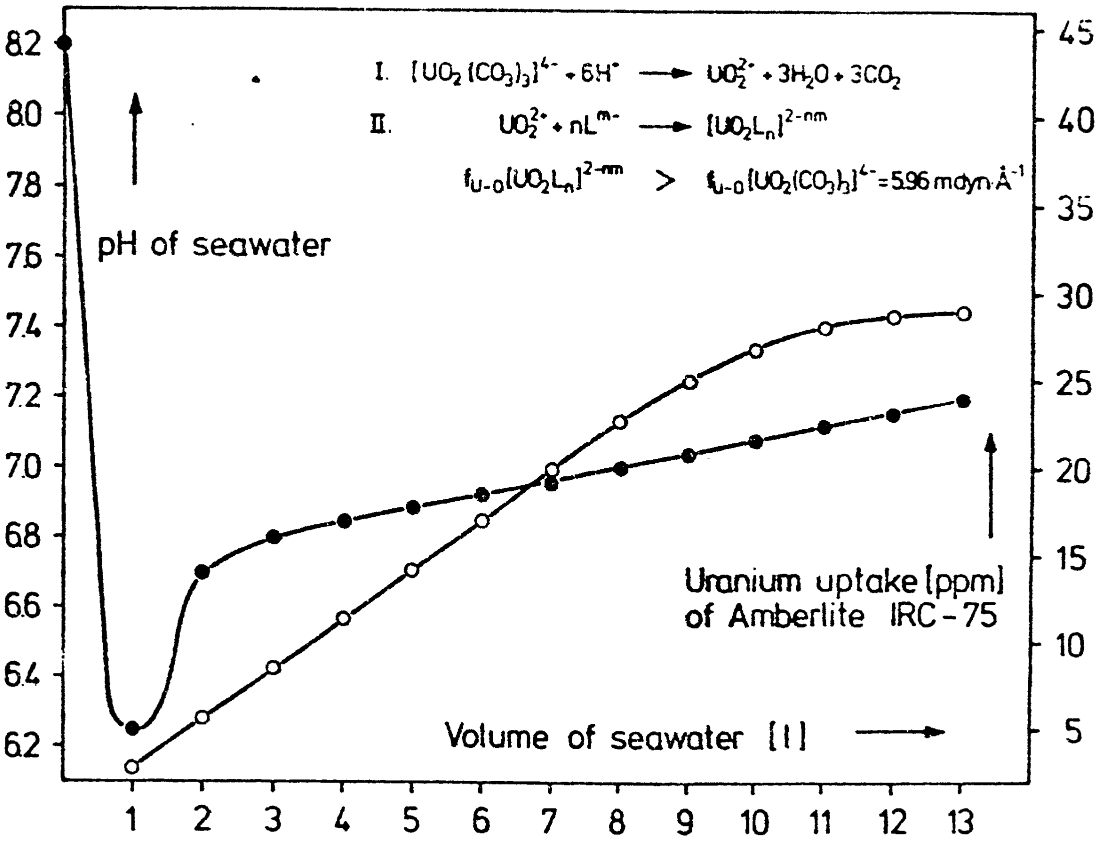


Fig. 3 Uranium uptake of Amberlite IRC-75 and the acidification of seawater

According to Fig. 3 the uranium uptake of the before mentioned Amberlite IRC-75 is clearly restricted by the pH. On the left side the pH of sea water, on the right side the uranium uptake is plotted against the cumulative volume of sea water which has been contacted with 1 g of the resin. At the beginning the pH of natural sea water, given by the black dotts, is decreased by the resin up to about 6.2. Then the pH increases slowly, but the original pH of 8.2 is not yet reached after 13 litres. The curve of uranium uptake given by the white dotts shows a saturation already after 1o litres. Thus we suggest the reaction steps of the uranium uptake written in the upper part of the figure. The first step leads to the decomposition of the uranyltricarbonate complex by protons released from the resin. Thereafter the complexation of the free uranyl ion can take place. From our experience the uranyl force constants of such uranium-resin adducts are higher than in the case of the tricarbonato complex. Such resins are unsuitable for extracting uranium from sea water, since an acidification of sea water cannot be accepted.

In order to select functional groups capable of competing with carbonate ligands at the pH of natural sea water we have tested the influence of a large number of organic substances on the solution spectrum (Fig. 4) of the tricarbonato uranyl complex. This spectrum is represented by the solid line. The dotted line shows the spectrum of the solution after adding a ligand containing suitable functional groups.

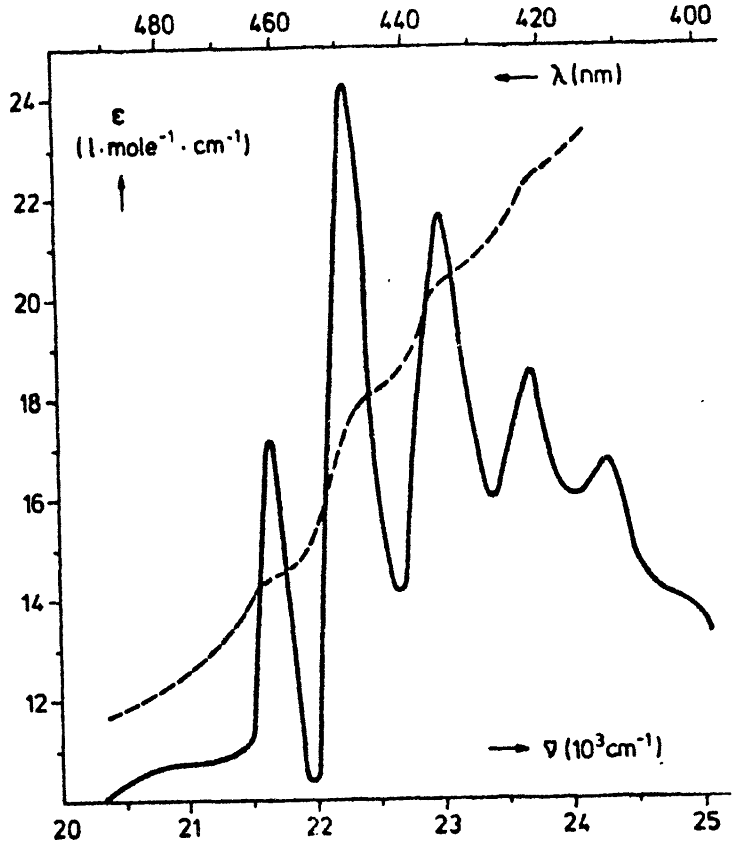
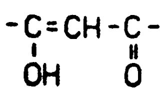
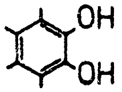
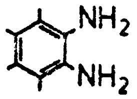
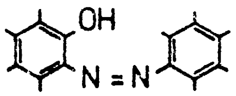


Fig. 4 Solution spectrum of $[UO_2(CO_3)_3]^{4-}$ before (——) and after (----) adding an organic compound with an effective functional group.

In this way we could select some effective classes of compounds such as 1.3 diketones, hydroxylamines, o-dihydroxyaromatics, o-diaminoaromatics, and o-hydroxyazoaromatics which are summarized in Table 2.

Table 2 Effective classes of organic compounds

1,3-Diketones	Hydroxyl-amines	o-Dihydroxy-aromatics	o-Diamino-aromatics	o-Hydroxyazo-aromatics
 $-\underset{OH}{C}=CH-\underset{\parallel \atop O}{C}-$	>N-OH			

Using the just mentioned results on suitable functional groups we could find a complexing resin, the behaviour of which is described in Fig. 5.

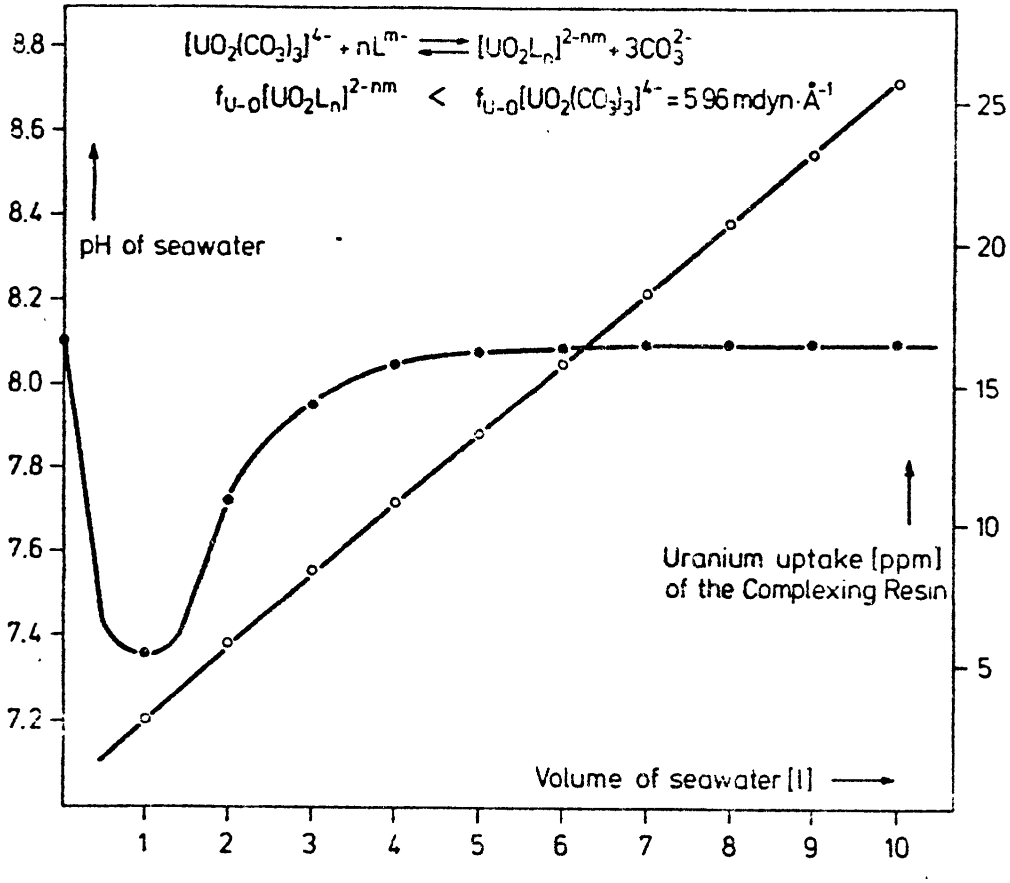


Fig. 5 Uranium uptake of the complexing resin.

At the beginning the pH decreases, but after some litres the original pH of natural sea water is reached. The curve of uranium uptake is an almost straight line not depending on the pH. Thus we suggest the given ligand exchange reaction between carbonate and the functional group proceeding without previous decomposition of the uranyl carbonate complex by hydrogen ions. From our studies such exchange reactions can be expected, if the bonding of the functional group is stronger than the bonding of carbonate. The smaller uranyl force constant of this complex points to such a stronger bonding.

In Table 3 some experimental values concerning hydrous titanium oxide and the just mentioned complexing resin are compared.

<u>Table 3</u> Uranium uptake and selectivity of hydrous titanium oxide and the complexing resin

Adsorbent	Functional Group	Uranium Uptake [ppm]	Concentration Factor U	Ca	Mg	Na
Hydrous Titanium Oxide	$>\mathrm{Ti(OH)_2}$	230	$7.2 \cdot 10^4$	70	6.5	0.69
Complexing Resin		2400	$7.5 \cdot 10^5$	28.9	11.6	2.14

For hydrous titanium oxide we have found a uranium loading of 23o ppm, for the complexing resin a loading of 24oo ppm. Moreover a higher selectivity of the resin can be derived from the concentration factors. In spite of the 1o times higher uranium loading the resin accumulates less calcium than hydrous titanium oxide, and the concentration factors for magnesium and sodium are only 2, respectively 3 times higher than those of hydrous titanium oxide.

It should be emphasized that the effectiveness of any uranium sorber does not only depend on the uranium loading, but at least as much on the rate of the uranium uptake.

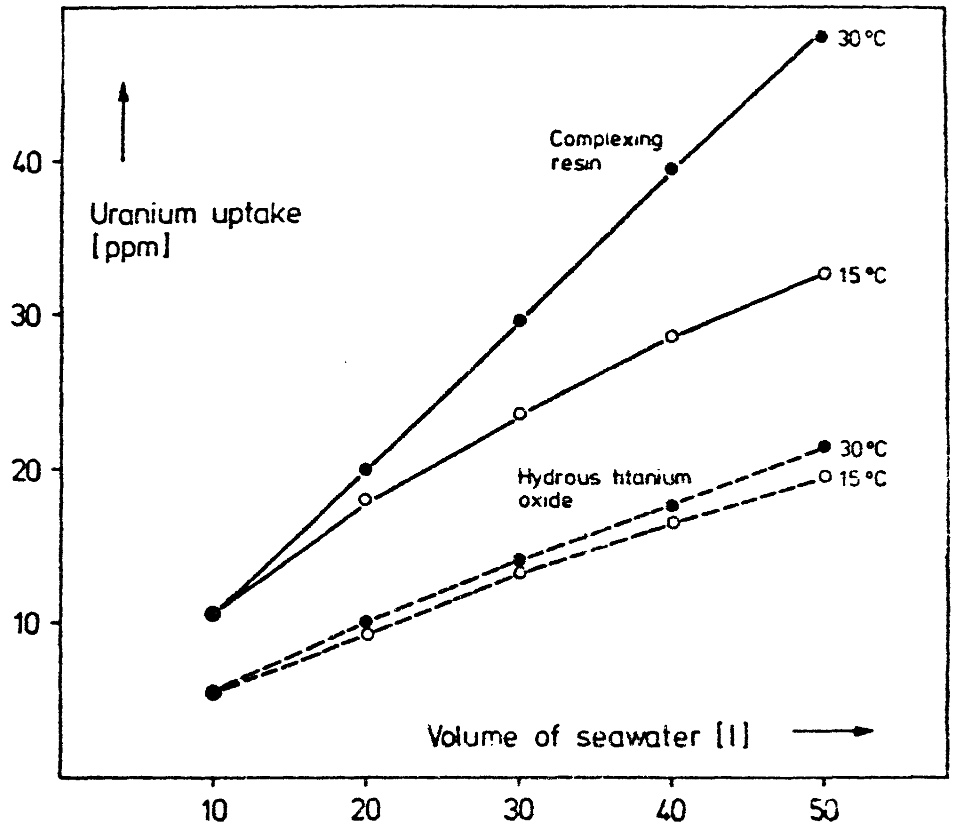


Fig. 6 Rate of the uranium uptake of hydrous titanium oxide and the complexing resin at 15°C and 3o°C.

In Fig. 6 the uranium uptake of both the complexing resin and hydrous titanium oxide are compared at 15 and 3o°C. Under the same conditions the uranium uptake of the complexing resin is much faster. For example at 3o°C the uptake was found to be more than twice as high than for hydrous titanium oxide.

Finally a photograph of the complexing resin beads, which have been in a fluidized bed in natural seawater for several months, demonstrates the nearly unchanged surface of the beads. A cross section photograph of a bead shows a narrow coloured zone indicating that only a surface layer is loaded with uranium.

Summarizing we would like to point out that resins containing suitable functional groups are capable of concentrating uranium from sea water. In comparison with hydrous titanium oxide resins can present some advantages such as higher uranium loading, more selectivity, and higher stability against sea water.

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Discussion on Dr. Schwochau's Paper

Dr. Schwochau indicated that capacity had been expressed on a whole-bead basis, that the resin beads were 0.5 mm dia, but that the uranium was concentrated in a thin layer on the surface, less than around 0.1 mm thick. The brown color of this layer was due to transition elements, copper and manganese in particular. The color disappears during elution. Not enough copper or other metals are recovered to be of economic interest. Hydrous titanium oxide also turns brown during loading.

The complexing resin they now use loses on the order of 20% of its capacity in 10 cycles due to the loss of functional groups, whose hydrolysis products are observed. This is too high, and Dr. Schwochau indicated that they hope to stabilize the material by use of another matrix or by other means.

In response to Prof. Kanno, Schwochau noted that shrinkage and swelling due to water uptake were insignificant. In response to other inquiries he indicated there was no serious mechanical attrition problem, that resin specific gravity was in the range 1.1-1.2, and that the price (in a large scale operation) could be comparable to that of hydrous titanium oxide.

Specific Uranyl Binding By Macrocyclic Ligands Attached To Resins

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The authors are currently interested in extraction of uranium from sea water by some specifically designed organic compounds. Although uranyl concentration in sea water is extremely low (ca. 3.3 ppb), the total amount is huge, estimated at 4—4.5 x 10^9 tons and the extraction of uranium from sea water deserves to be examined more extensively.

Hydrous titania sorber is an excellent adsorbing material known up to date but it still shows some poor characteristics to be improved, for the practical uranium extraction from sea water. The most weak points are:

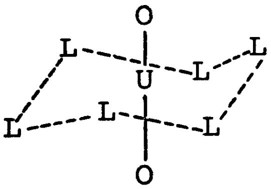
1. A considerable amount of hydrous titania sorber is lost during adsorbing and desorbing processes, mostly due to its low but appreciable solubility in water and/or somewhat lower mechanical strength.
2. The equilibrated amount of uranium adsorbed by hydrous titania sorber is not too small but the velocity of uranium adsorption is slow.
3. Discriminating adsorption of uranium by hydrous titania sorber is really observed but this specificity (degree of discrimation)

is not satisfactorily high.

The authors have been interested in the designing and the preparation of new chemical adsorbing reagents by which the above poor characteristics of hydrous titania sorber may be greatly improved.

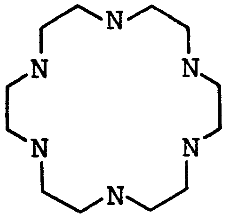
Macrocyclic polydentates have attracted enormous attention from chemists because of their unique and significant characteristics of the strong and selective binding of a variety of metal ions.[1,2] The metal binding is governed mostly by the size of the macroring and the nature of heteroatoms involved. The most important role of the macrocyclic structure is, in general, the so-called "macrocyclic effect"[3] —— to increase (making less negative) a large negative entropy change involved in the polydentate chelation.

Basic strategy of uranium binding, then, is to design a ligand of very strong metal binding to take advantage of this macrocyclic effect, where number of chelating heteroatoms and their spatial arrangement is designed to be most appropriate for uranyl (UO_2^{++}) binding, since in natural sea water uranium is dissolved mostly in a form of uranyl carbonate. The most appropriate arrangement of heteroatoms for uranyl binding should be taken from the X-ray crystallographic studies of stable uranyl complexes and several complexes studied crystallographically up to date clearly indicate that the pseudo-planar hexagon arrangement (1) should be the best for the discriminating uranyl binding.



1

First chemical model thus chosen was the macrocyclic hexamine (**2**). As expected, this hexamine chemically bound to an insoluble polystyrene resin can extract uranyl satisfactorily from the aqueous solution, leaving less than 2 ppb of uranyl uncomplexed in the aqueous solution. Liberation of uranyl was also very simple and on treatment of the resin-uranyl complex with dilute mineral acid (such as HCl), the uranyl adsorbed on the polymer immediately started to be liberated and within one hour the liberation of uranyl was practically quantitative.



2

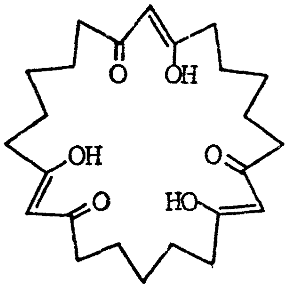
However, unfortunately, this potent adsorbing material could not extract uranyl appreciably from natural sea water. In order to clarify the major factors contributing to this poor extractability only observed for natural sea water, some model systems have been investigated. The conclusion drawn from such experiments is the following.

Carbonate and/or bicarbonate anion dissolving in sea water in a high concentration (HCO_3^- 2.38 ppm, $CO_3^=$ 0.27 ppm) competes with the present hexamine and competition is somewhat more favorable for carbonate binding ($K(UO_2^{++}-CO_3^{=}) \approx 10^{22}$).

$$UO_2^{++}\cdot 2 \rightleftarrows UO_2^{++} \rightleftarrows UO_2^{++}(CO_3^{=})_x \quad 3$$

etc.

This strongly indicates that macrocyclic effect (favorable entropy effect) alone is not enough to compete with electrostatic effect (enthalpy effect) between positively charged uranyl and negatively charged ligands. Based on this concept, the second adsorbing ligand was designed by taking this enthalpic effect associated with the chelation under consideration, and as a macrocyclic hexadentate ligand negatively charged at the pH of natural sea water ($\approx$ 8.1), macrocyclic hexaketone, **4**, was chosen and it was successfully prepared according to equation **5**.



4

$$CH\equiv C(CH_2)_5COCl + CH\equiv C(CH_2)_5C\equiv CH \xrightarrow[CH_2Cl_2]{SnCl_4}$$

$$CH\equiv C(CH_2)_5COCH{=}CCl(CH_2)_5C\equiv CH + CH\equiv C(CH_2)_5COC\equiv C(CH_2)_5C\equiv CH$$

$$+ CH\equiv C(CH_2)_5COCH{=}C{=}CH(CH_2)_4C\equiv CH$$

$$\xrightarrow[AlCl_3/CH_2Cl_2]{ClCO(CH_2)_5COCl} \quad \xrightarrow[H_2O]{H^+} \mathbf{4} \qquad (5)$$

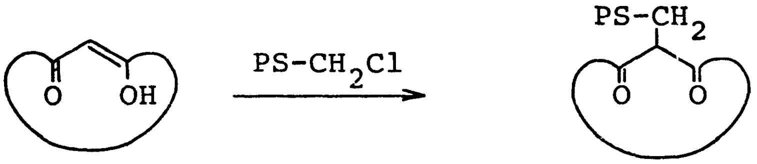
Its noteworthy characteristics are followings:

1. Six oxygen atoms can be directed towards the inside of the

ring, if necessary, to form hexadentate coordination in near coplanarity which corresponds to the crystalline structure of various uranyl salts.

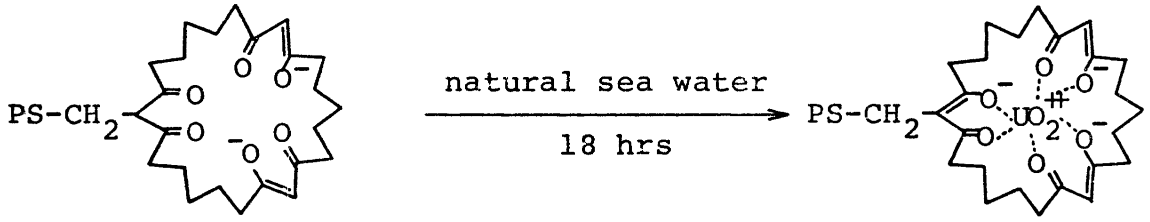
2. β-Diketone can easily be dissociated in a water to a some reasonable extent (pKa is 8.95 for acetylacetone) to form a much stronger ligand, ketoenolate anion.
3. The bound uranyl ion is readily liberated by the treatment with dilute aqueous acid (relatively high pKa helps).

The hexaketone (170 mg, 0.4 mmol) was treated with partially chloromethylated polystyrene (chloromethyl content 18.8 %, 82 mg, 0.14 mmol equiv. for CH_2Cl unit) in dimethylformamide (1 ml) in the presence of anhydrous potassium carbonate (138 mg, 1.0 mmol). An IR spectrum of resulting polymer, after usual purification, showed that CH_2Cl absorption band had almost disappeared (note where CH_2Cl is high, the complete conversion becomes more difficult) and new absorptions at 1,720 and 1,600 cm^{-1} had appeared which correspond to keto and enol forms of hexaketone unit.



and other tautomeric states

Polymer-bound hexaketone (98 mg) dissolved in chloroform (30 ml) was stirred magnetically with 3.5 l of sea water sampled at 20 m off the coast of Ohara, Chiba Prefecture. After 18 hr, a chloroform solution (chloroform was added during the extraction, if necessary) was separated and sea water was further extracted with chloroform (5 ml x 2) to recover any dissolved polymer and/or polymer-uranyl complexes. From the combined chloroform solution, uranyl was liberated by the treatment with 1 N HCl solution (5 ml). The resulting acid solution was analyzed by the aresenazo III method,[5] showing that 0.84 ppm of uranyl ion is present which corresponds to 36 % of the UO_2^{2+} present in the original natural sea water. An independent analysis of UO_2^{2+} by atomic absorption spectrometry was also made to demonstrate the presence of approximately the same amount of uranyl ion. Repeated (three times) extraction and liberation of uranyl ion using the recovered hexaketone-resin accumulated 1.5 ppm of UO_2^{2+} in 9.2 ml of acid solution (13.8 µg) for total sea water of 3 x 5 l.



UO_2^{++}, 36 %

After these cycles, the same procedure using the hexaketone-resin recovered, was repeated to extract 11 µg of UO_2^{++} from further 3 x 5 l of sea water. This demonstrated that the recovery and and regeneration of the hexaketone-resin was satisfactory. The extraction time was then reduced to 1 hr and gave practically the similar same efficiency.[6]

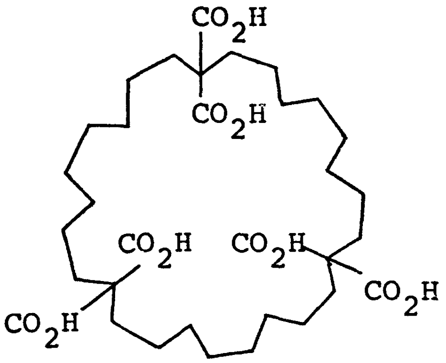
This new adsorbing agent seems to be quite satisfactory except following two points.

1. Hexaketone still competes whth carbonate, not seriously but appreciably based on the model system studies for the high

carbonate concentration.

2. Preparation of hexaketone seems to be too elaborative to be applied to the practical extraction.

In order to overcome these weak points of a very potent ligand **4**, two macrocyclic ligands negatively charged at the pH of natural sea water **6** and **7**, were newly designed and prepared.



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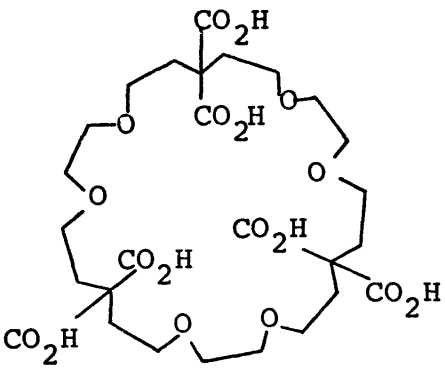

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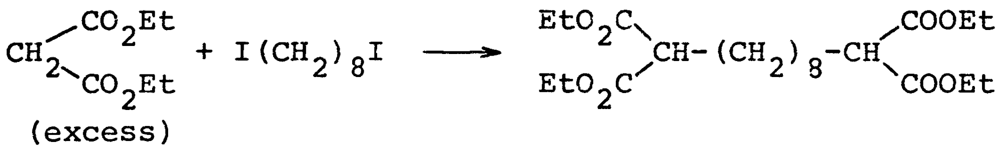
These ligands were prepared by symmetrically arranging six carboxylates on a macrocyclic skelton in which the ring size was adjusted to give a cavity to accomodate uranyl ion comfortably. Three of six carboxylates seem to compose a binding site. One of three additional carboxylic acid units in either **6** or **7** is amenable to attachment to a suitable polymer support. The other two probably act to make the microscopic environment around the metal binding site more hydrophilic as well as to decrease the entropy loss involved in the complexation. Compared with the previous hexaketone, the new macrocyclic hexacarboxylic acids are capable of much more facile preparation in reasonable overall yields and are more effective and selective for the binding of the uranyl ion.

Preparation is straightforward and is described by eq. **8**.



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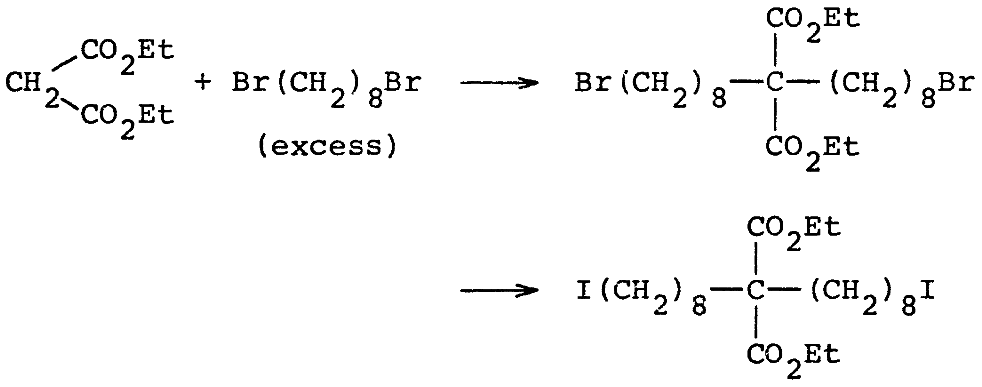

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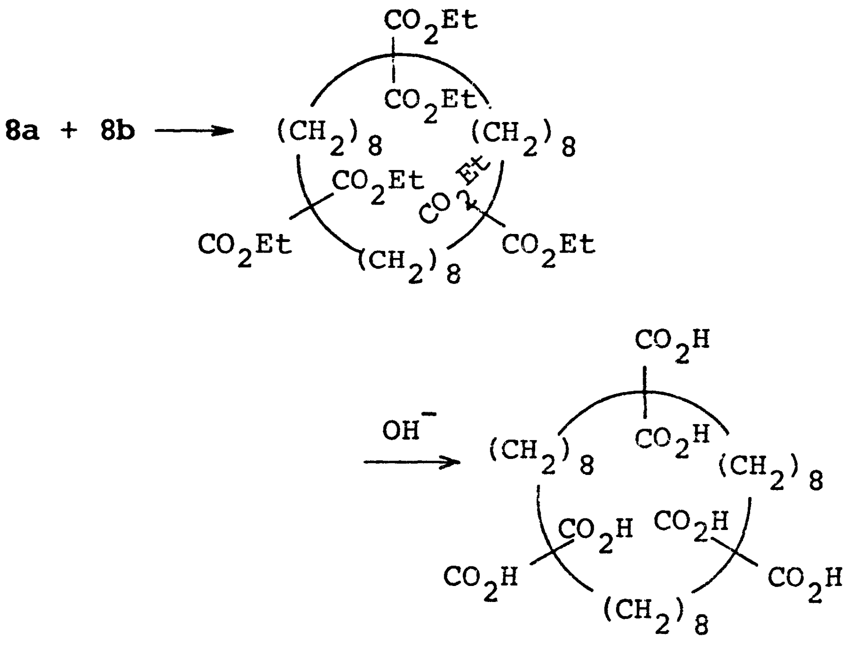

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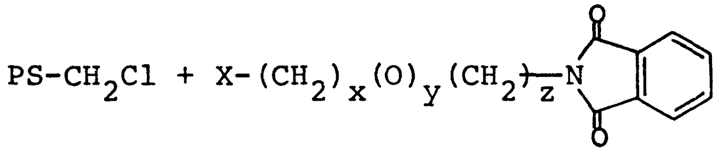
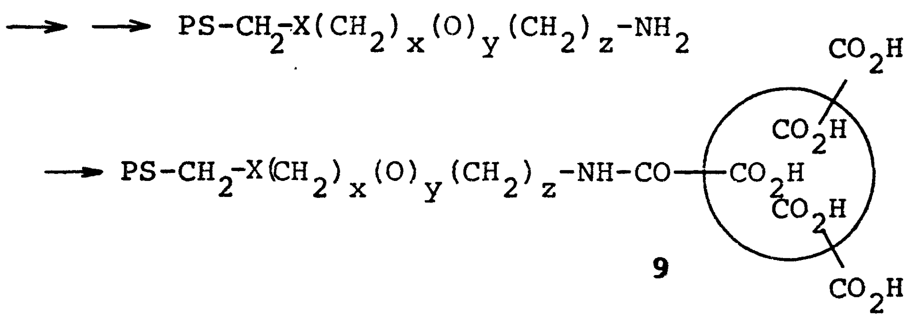
Uranyl ion is known to form a stable complex with carbonate ($CO_3^{=}$). The stability constant ($\log K_f$) ranges from 20.7 to 23.0, depending on the conditions. The addition of hexacarboxylic acid **6** (1.0×10^{-3}M) to a uranyl tricarbonate solution (5.0×10^{-4}M of UO_2^{2+} in 1.0×10^{-2}M Na_2CO_3, pH 10.4) gave a change of visible absorptions due to the competitive formation of the $\mathbf{6}\cdot UO_2^{2+}$ complex. From this competitive binding, a relative formation constant, $K_{rel} = K_{\mathbf{6}\cdot UO_2^{2+}} / K_{CO_3^{=}-UO_2^{2+}}$, was estimated to be 10^{-5},[1] giving a log K_f value of 16.4 at 25°C for $\mathbf{6}\cdot UO_2^{2+}$ complex. The value is the largest among the hosts ever reported to bind uranyl ion. The large stability constant observed for the present macrocyclic hosts seem to be due to appropriate ligand arrangement as well as to the strong ligation of carboxylate anion.

High selectivity of the present host to uranyl was ascertained also by competition with other metal cations. An ethereal solution of **6** (4.2×10^{-4}M, 1 ml) was stirred with a dilute solution of uranyl acetate (3.2×10^{-5}M, 5 ml) in the presence of a large excess of a competing cation such as Na^+ (0.469 M), Mg^{2+} (7.82×10^{-2}M), pH 8; Ni^{2+} (1.70×10^{-4}M) or Zn^{2+} (3.06×10^{-4}M), pH 6. Selectivity factors, $K_{M^{m+}}/K_{UO_2^{2+}}$ for these metal ions were;

$Na^+ < 1/180{,}000$, $Mg^{2+} < 1/31{,}000$, $Ni^{2+} = 1/210$, $Zn^{2+} = 1/80$.

The macrocyclic hexacarboxylic acid was also bound to polystyrene, through a so-called spacer group. A typical example is shown in equation **9**.





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Thus, 100 mg of cross-linked insoluble polystyrene-bound hexacarboxylic acid (capacity 630 μg of uranium/100 mg of polymer) was stirred with 5 l of natural sea water (from Pacific Ocean) for 4 days. The polymer beads were separated, and uranyl ion was liberated by treatment with 15 % ammonium bicarbonate solution (10 x 6 ml). The amount of uranium liberated was determined to be 6.85 μg, which corresponds to 41.5 % of the total uranium present in the sea water treated.[7]

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Discussion on Dr. Tabushi's Paper

In response to a question by Dr. Schwochau, Dr. Tabushi indicated that their best ion exchange material had capacities approaching one milligram uranium per gram of sorber. In response to Dr. Wang he indicated that tests were conducted in real seawater, both with and without uranium additions.

Questions by Fremery and Campbell with respect to susceptibility to attack of the organic ion exchange media by micro-organisms elucidated the observation that the periodic elution using dilute acids (pH$\sim$3) should be sufficient to kill any biological organisms.

Dr. Tabushi noted the advantages that should accrue because of the low solubility of the resin, the ability to adjust strength via crosslinkage, and the flexibility as to choice of shape. In response to further questions along these lines he noted that while they had not yet fabricated fibers of such material, this was now being investigated.

Mr. Hooper commented that organic materials had fared poorly in early work at Harwell due to chemical attack, but Dr. Tabushi noted that the IX resin had demonstrated stability in both strongly acidic and basic solutions. He also noted that tests had been conducted for as many as twenty regeneration cycles, but that up to 1000 cycle runs were being contemplated.

A Convenient Laboratory Screening Test for Potential Sorbers of Uranium from Seawater

Stephen G. Maroldo and Glenn H. Beasley

Abstract

Progress on a convenient method for measuring the sorption pseudoisotherm of uranium from natural or synthetic seawater with experimental sorbers is described. This permits comparisons of the performances of different experimental sorbents. Solutions were analyzed using laser induced fluorescence.

I. Introduction

The possibility of extracting uranium from seawater was first proposed in the late 1940's.[1] Since that time, several excellent reviews[2-7] have appeared in the literature summarizing the many attempts to achieve the economically feasible extraction of uranium from seawater. Sorbers used have ranged from orange peels[8] and inorganic sorbers (i.e. hydrous titanium oxide)[2,3] to organic polymers containing exotic crown ethers.[9] It is interesting to note that between 1977 and 1980, there were 23 publications (18 papers and 5 patents) pertaining to the application of organic ion exchange resins to the extraction of uranium from seawater. However, one must bear in mind that in most cases, these results were conducted in laboratories on a small scale. Therefore, the results of these studies are only suggestive of economically feasible commercial processes.

Most of the work that has been published to date has used hydrous titanium oxide (HTO) as a sorber. HTO has moderate capacity for the extraction of uranium from seawater ranging from 100-1000 μg U_3O_8/g sorber, depending on particle size and the method of preparation of the sorber. The rate of sorption of uranium on HTO is slow, requiring several hours to reach equilibrium. Finally, HTO shows appreciable losses through mechanical attrition and solubility in seawater which decreases the overall efficiency of sorption.

Organic polymeric sorbers, permit variation of performance by varying surface area, pore size, functionality and degree of crosslinking. These parameters will presumably alter the kinetics and capacity of uranium sorption. Crosslinking changes the strength of ion exchange resins making them more resistant to mechanical attrition. However, the effects of these variables on the performance of an ion exchange resin towards the sorption of uranium from seawater has not been reported in the open literature.

In order to effectively evaluate ion exchange resins and to compare them to existing sorbers, the development of a practical screening test was required. This paper describes our efforts to develop such a test. The results presented here are not complete, but can best be regarded as a progress report.

II. Methods of Analysis

There are numerous methods for the analysis of uranium with varying levels of sensitivity. The standard[10] uranium analysis used is a colorimetric method using Arsenazo III.[11] The sensitivity of this analytical technique is low, being on the order of 0.5 ppm U_3O_8. Application of this method of analysis to the extraction of uranium from seawater therefore requires either concentration of the sample or using U_3O_8 spiked samples and extrapolating the results to a thousandfold more dilute solution. Concentration is usually achieved by solvent extraction followed by evaporation, ion exchange sorption, adsorbing colloid flotation, or coprecipitation. Each procedure assumes that 100% of the uranium in the sample is being concentrated which is suspect at the ppb level. Extrapolation to more dilute solutions is risky due to the possibility of competing processes (i.e. the sorption of other ions from seawater) altering the kinetics and the capacity of sorption of the resin.

More sensitive techniques are delayed neutron counting (<0.1 ppb U_3O_8)[12], neutron activation analysis (0.1 ppb U_3O_8),[13] and the most sensitive method available, nuclear (fission) track analysis (<0.01 ppb U_3O_8).[14] However, each of these methods requires a neutron source which limits their availability. In addition, neutron activation requires and assumes quantitative sorption of the uranium on a solid support such as an ion exchange resin.

Presently, the most popular method is optical fluorimetric analysis[15,16] which has a sensitivity of 0.1 ppb U_3O_8. This technique uses a high carbonate flux fused salt which requires moderately high temperatures to prepare.

The method of analysis we chose to use was that of laser induced fluorescence,[17] a technique which is commercially available (Scintrex. Inc.), provides high sensitivity (0.05 ppb U_3O_8) and relatively simple sample preparation. The instrument for the technique was developed for analysis of uranium in ground water and is primarily used by geologists for searching for uranium ore bodies. The primary advantage of this technique is its high sensitivity.

III. Laser Induced Fluorescence

The process of laser induced fluorescence[17] consists of irradiating a sample with an ultraviolet laser (wavelength of 337 nm) and observing the resulting fluorescence, which is shown in Figure 1. The fluorescence of the sample consists of contributions due to "organics" and to uranium and is monitored perpendicular to the excitation beam by a photomultiplyer tube. The radiation emitted from the organic matter is centered at about 400 nm and is filtered out with the use of a green filter.

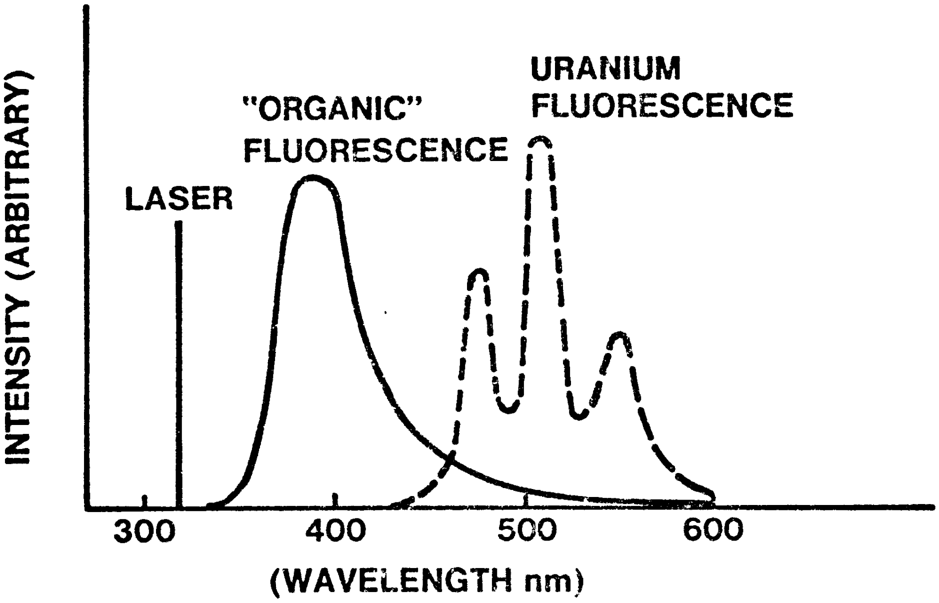

FIGURE 1: LASER INDUCED FLUORESCENCE OF WATER SAMPLES

The tailing of the organic fluorescence which can not be filtered out is eliminated by taking advantage of the lifetime of the emission processes. The organic emission is complete after approximately 4-10 nanoseconds whereas, the uranyl emission requires several microseconds to reach completion. By irradiating the sample with 4-10 nanosecond laser pulses and delaying the fluorescence reading by a microsecond, the reading is taken after the organic emission is complete and only the uranyl fluorescence remains.

The uranium fluorescence occurs as a triplet at 494 nm, 516 nm, and 540 nm. The addition of a phosphate based complexing agent (trade name "Fluran") causes an 80% enhancement of the intensity of the uranium emission, allowing the very high sensitivity of 0.05 ppb U_3O_8 achieved by this instrument.

Interferences to the analytical procedure consist of inner filters and lifetime quenchers. Inner filters are those substances which significantly adsorb at the excitation wavelength such as Fe^{3+} and humic acids. These species, when present at a concentration of 20 ppm, decrease the apparent uranium sensitivity by 50 and 60% respectively.

Lifetime quenchers interfere by shortening the lifetime of the uranyl fluorescence. Ions such as Ca^{2+}, Mg^{2+}, and Cl^- in concentrations of 45 ppm, 60 ppm, and 5,000 ppm respectively cause a 50% reduction in sensitivity for uranium.[18] As mentioned previously, the chloride present in natural seawater is oxidized to chlorine which is then driven off, eliminating this interference. The presence of Ca^{2+} and Mg^{2+} is corrected for by spiking the sample with a known amount of uranium which provides an internal standard.

IV. Screening Test

In order to compare the performance of new sorbers, a screening test was devised which consisted of measuring the capacity of a resin as a function of final uranium concentration. The length of time that the sorber was in contact with the natural or spiked seawater was determined by the kinetics of sorption. These curves were measured by placing a weighed amount of resin in one liter of solution, shaking, withdrawing aliquats as a function of time, and determining the uranium concentration in each sample.

An example of our screening test was carried out using an experimental styrene based ion exchange resin containing sodium iminodiacetate functionality as shown in Figure 2. Preliminary screening tests indicated that this resin sorbs uranium from uranium enriched (10 ppm) seawater. The resin is a highly porous macroreticular resin which has not been optimized for performance for extracting uranium from seawater.

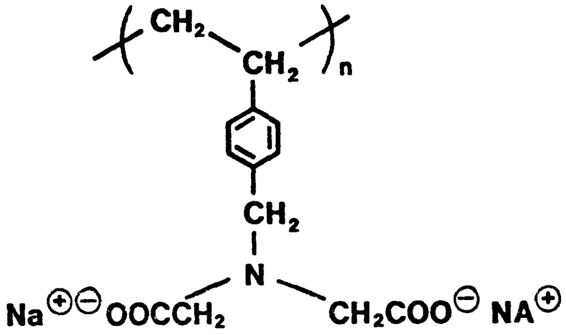

FIGURE 2: CHEMICAL STRUCTURE OF THE EXPERIMENTAL RESIN USED IN OUR TRIALS

Figure 3 shows the concentration of U_3O_8 in solution as a function of time when 0.5g of resin (dry weight) was placed in a 4000 ppb U_3O_8 synthetic seawater solution and in a 4000 ppb U_3O_8 deionized water solution. At this concentration of uranium, the kinetics of sorption is independent of the solution background. Approximately 62% of the uranium is sorbed by the resin in the first hour of contact. After 5 hours, the uranium concentration in synthetic seawater is 180 ppb U_3O_8 (95% sorption) and is close to the value of 100 ppb U_3O_8 obtained after 20 days. These results indicate that the system is close to equilibrium after five hours.

The rate of sorption of uranium by 0.1g of resin from one liter of a 4 ppb (deionized water background) is shown in Figure 4. After one hour, 50% of the uranium in the solution is sorbed. After twenty days, the U_3O_8 concentration was down to 0.07 ppb U_3O_8, indicating 98% of the uranium was sorbed onto the resin.

The analogous experiment using natural seawater has not been completed as yet. However, when 0.1g of the sodium iminodiacetate resin was placed in one liter of natural seawater, approximately 60% of the uranium was picked up by the resin in 16 hours and >95% was sorbed within four days.

The kinetic results indicate that after sixteen hours, the resin-seawater system was reasonably close to equilibrium. The capacity of the resin was measured by placing varying amounts of resin in one liter samples of natural or synthetic seawater[19] that had been spiked with uranium, and measuring the final uranium concentration after sixteen hours. By knowing the weight of the resin added and the initial and final uranium concentrations ($[U_3O_8]_2$ and $[U_3O_8]_f$ respectively), the capacity of the resin at the determined final concentration could be calculated. By plotting $[U_3O_8]_f$ vs. resin capacity, the capacity at 1.6 ppb U_3O_8, an arbitrary point corresponding to 50% efficiency of pickup, can be read directly from the graph.

Figure 5 shows the capacity pseudoisotherm for our sodium iminodiacetate resin. The capacity for this resin is about 250 μg U_3O_8/g resin at 50% sorption efficiency. This value is within the range of capacities attributed to HTO but is not necessarily the optimum performance that can be expected for an iminodiacetate resin.

V. Resin Performance

In order to provide the most efficient organic sorber, parameters such as surface area, particle size, degree of porosity, pore size, functionality, and degree of crosslinking can be varied. The number of permutations possible are enormous and permit a great deal of flexibility in designing a sorber of maximum performance. Little research has been done in this area to date.

Functionality is important in determining the capacity and kinetics of sorption of uranium on the resin. Functional groups on varying polymer supports such as hydroxamic acid,[20,21] amidoxime,[22] iminodiacetate,[23] and β-diketone[24] have been used to concentrate uranium from seawater. Theoretically, any functionality capable of complexing uranyl cation has potential to extract uranium

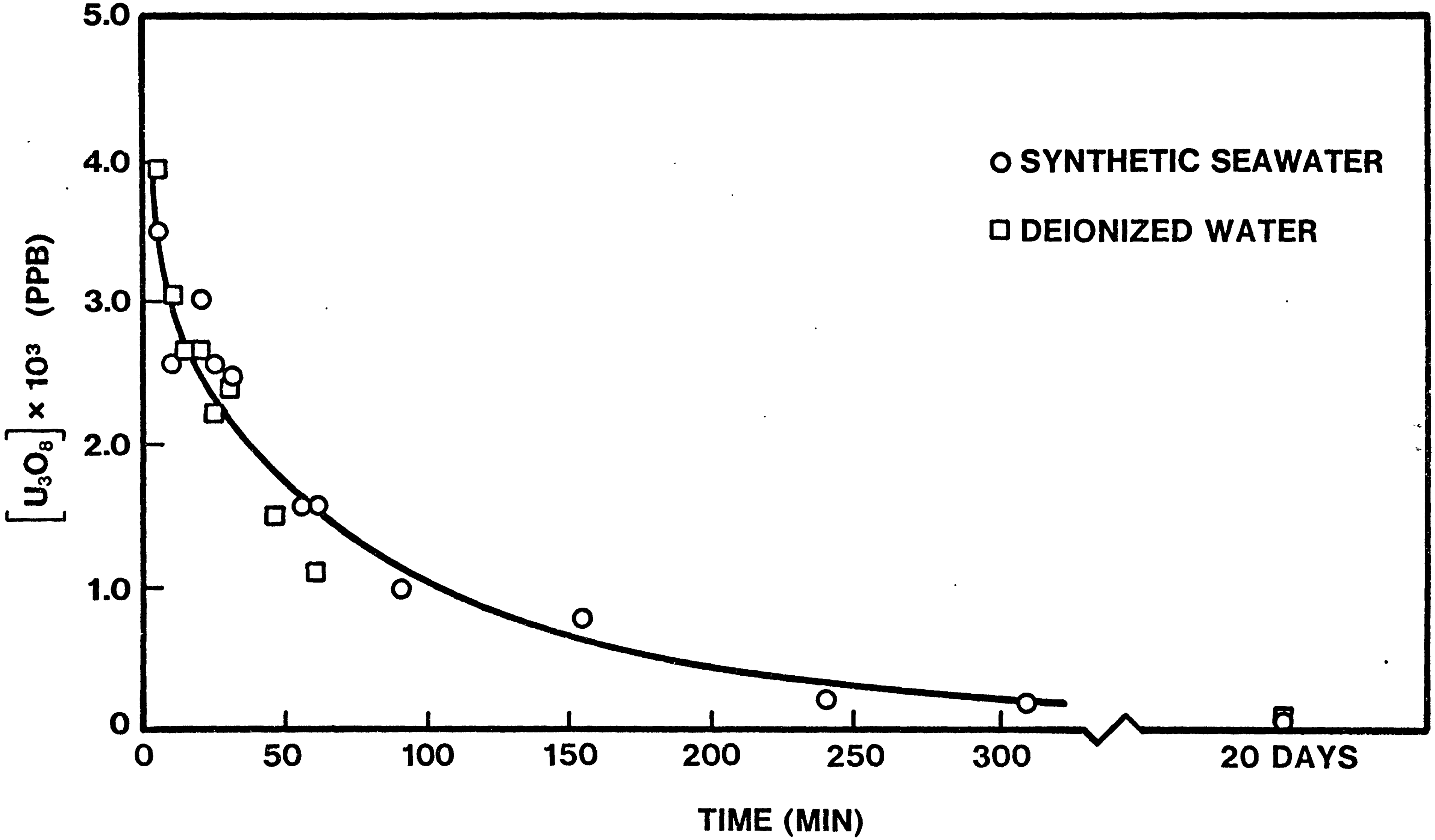

FIGURE 3: KINETICS OF SORPTION OF U_3O_8 FROM 4000 PPB SOLUTIONS

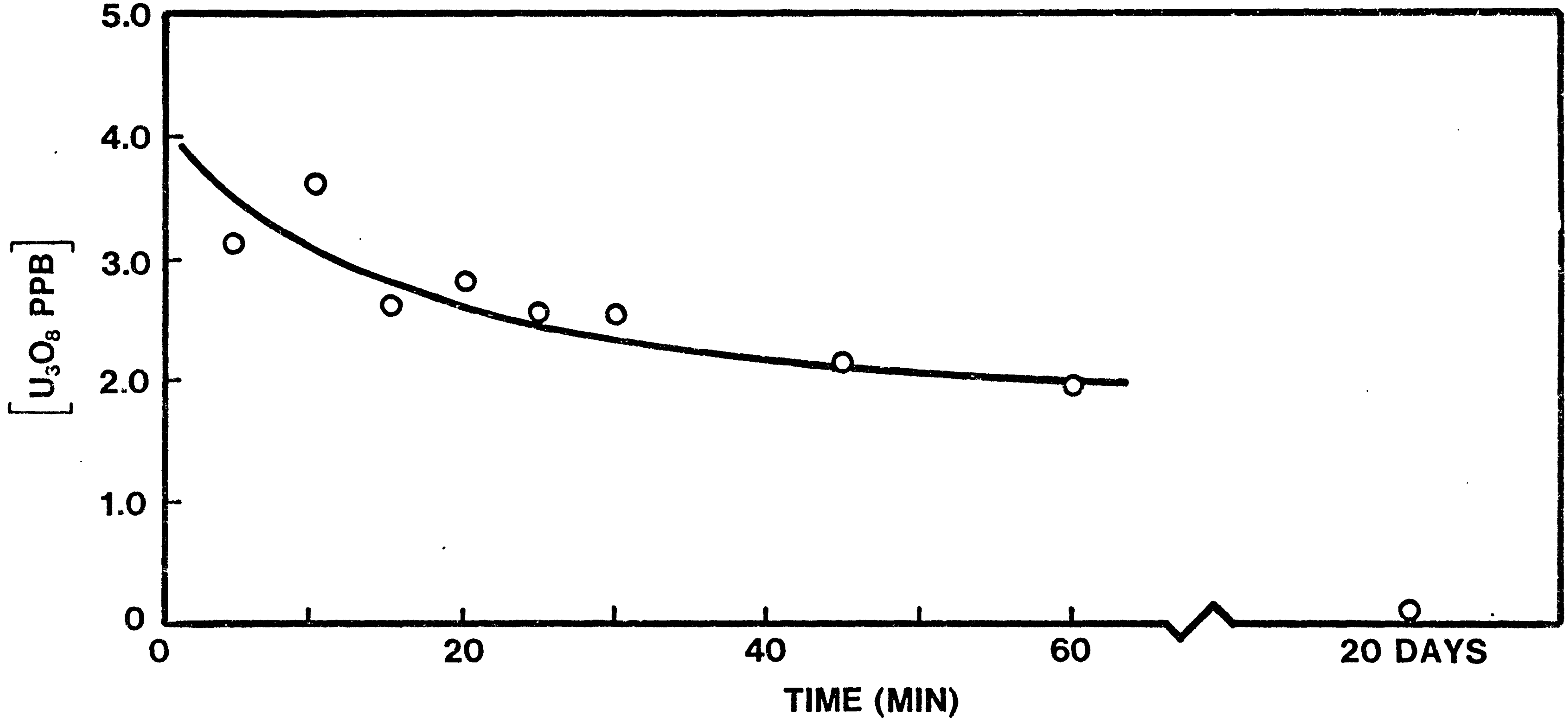

FIGURE 4: KINETICS OF SORPTION OF U_3O_8 FROM 4 PPB U_3O_8 (D.I. WATER)

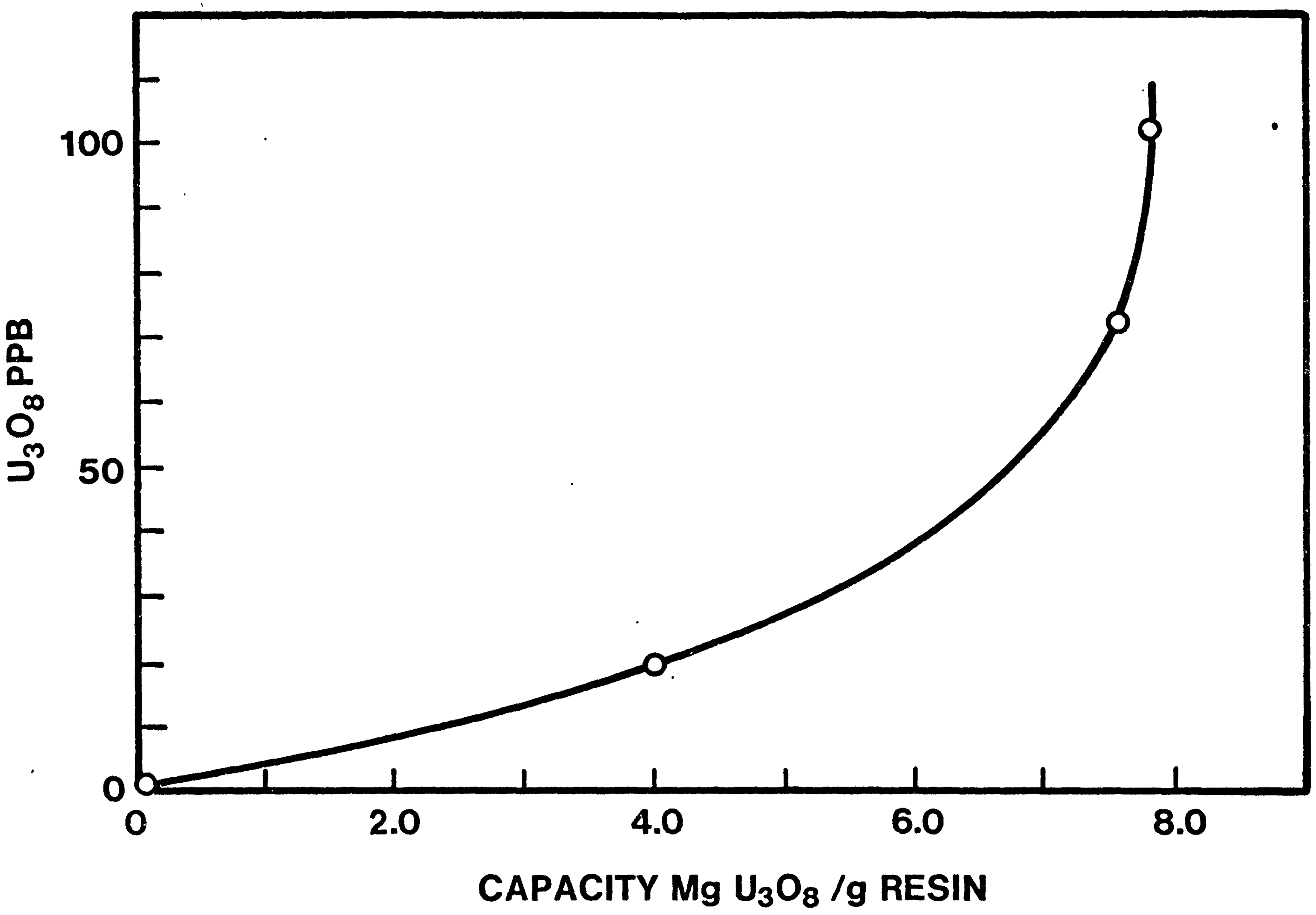

FIGURE 5: CAPACITY SCREENING TEST

from seawater when bonded to an inert polymer support. For a given functionality, performance optimization can then be determined by varying other parameters.

In the case of sorption only occurring on the surface, surface area and particle size are important factors to the overall capacity of the resin. If sorption occurs throughout the particle, then porosity becomes important. These parameters also partially determine the kinetics of sorption.

In order to maintain a high capacity, losses due to attrition must be minimized. A higher degree of crosslinking may provide greater mechanical strength and reduce attrition losses. Crosslinking however, decreases pore size and therefore, reduces the kinetics of the sorption in the interior of the resin bead. The maximization of performance is therefore a tradeoff between strength, rate of sorption, and capacity.

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Discussion on Dr. Maroldo's Paper

Dr. Maroldo indicated in response to questions that capacities of 50 ppm had been reached in the preliminary tests in natural seawater to date; that only acetate groups had been tested so far; that the functional group was similar to Kelex-100, but that his resin was of the highly porus macroreticular form. Dr. Beasley responded to another questioner in regard to whether the resin could be fabricated in a fiber form by saying that this may well be possible, but had not been looked into in any detail.

In response to Dr. Muzzarelli's questions it was explained that sample preparation time for the anayzer was on the order of 1/2 hour, and while the persulfate treatment should do away with organic contaminants, the analyzer and the procedure were originally developed for determining uranium in groundwater as a geological prospecting tool, and not specifically for the current application.

It was noted that 10% sulfuric acid was used as the elutant, yielding essentially 100% recovery. No change in pH is observed after 12 hours in seawater.

Dr. Maroldo noted several times that the resin tested so far had not been optimized. Tests, for example, will be conducted in seawater under field conditions at Woods Hole, and resin strength and durability can be tailored to fit the observed requirements.

A member of the audience commented in regard to resin durability that their resin had successfully undergone seven months of exposure to seawater in a fluidized bed. Rohm and Haas experience with resin in even more severe environments over many years was also noted.

Dr. Maroldo indicated that the uranium analyzer was available commercially at a price of just over $20,000, or on a monthly rental basis.

He indicated in response to a questioner who was concerned over the chelation of other ions, that he was concerned about copper, which is present in seawater at about the same concentration, and had sent samples out for atomic absorption analysis, but that results were not yet available.

The advantage of fast reacting adsorbers like humic acids for the recovery of uranium from seawater

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THE ADVANTAGE OF FAST REACTING ADSORBENTS LIKE HUMIC ACIDS FOR THE RECOVERY OF URANIUM FROM SEAWATER

This report is divided into two sections (A, B). The first part comprises experimental data of humic acid adsorbers whereas the second concerns design parameter and costs of a recovery plant using fast reacting adsorbents.

Part A:

I. Introduction

There is no doubt that developing a suitable sorber for uranium in seawater is one of the crucial points in designing an economically acceptable large-scale process for uranium recovery from seawater.

However, still different assessments exist on the significance and priority of criteria to be met by uranium sorber to become the basis of a technical recovery process.

Besides a sufficiently high uranium adsorption capacity, essential sorber criteria are the availability in large quantities at moderate costs, the chemical, biological and mechanical resistivity against decomposition and abrasion as well as a simple elution process which is also effective in regenerating the sorber for the next loading cycle.

One of the prime objectives of this paper is to draw attention to a further criterium, the adsorption kinetics, and to its importance as one of the major cost-determining factors in a technical recovery process /1/. This results from the fact that, independent of the design of such a process, the total amount of the sorber needed for a given uranium production is roughly inversely proportional to the accumulation rate. Hence, by increasing this rate, the size of the sorber beds and of associated plant constructions may be reduced.

This point of view led us to focus our interest on two points, investigation of

(1) humic acids as an adsorbent with an exceptionally fast uranium fixation kinetics in seawater and

(2) concepts of recovery processes taking advantage of such fast reacting adsorbents.

II. Uranium Adsorption of Humic Acids in Seawater

Independent of the nature of the adsorption process, the accumulation of uranium at the adsorbent may be characterized by the accumulation factor, A, the equilibrium value, A_∞, and the relaxation time, τ,

$$A = \frac{\text{g uranium/g adsorbent}}{\text{g uranium/g seawater}} = A_\infty \ (1-e^{-t/\tau}) \qquad (1)$$

(t denotes the time)
or, alternatively, by the initial accumulation rate

$$\left(\frac{dA}{dt}\right)_{t=0} = \frac{A_\infty}{\tau} \qquad (2)$$

Besides the chemical adsorption reaction, other processes may be involved in the accumulation. Processes of this kind are the uranium transport to the sorber surface, through the hydrodynamical surface layer and, if effective, into the sorbent material. The thickness, δ, of the hydrodynamical film increases with the sorber size (for instance grain diameter, d,) and the water viscosity, η, but decreases with the density, ρ, and flow velocity, v, of the seawater. For a laminar flow

$$\delta \sim \sqrt{\eta d / v\rho} \qquad (3)$$

The slowest kinetic step becomes rate-determining.

For the adsorption studies, humic acids (HA) were extracted from peat, fractionated, fixed on anion exchange resins as carriers and eluted with hydrochloric acid.

From previous results obtained in batch-experiments /1/ we know that (1) the equilibrium accumulation of such prepared HA in natural seawater amounts to $8 \cdot 10^4$ (related to the dry HA-weight) and (2) under standardized experimental conditions, the accumulation rate of HA is up to two orders of magnitude higher compared to other adsorbents with good or even excellent loading capacity including hydrous titanium oxide (fig. 1).

Under the given conditions of the batch-experiments (small grain size and vigorous stirring of the suspended sorber particles), the uranium diffusion through the hydrodynamic film is not rate-determining. The observed accumulation rates, therefore, reflect the kinetics of the chemical fixation reactions. The outstanding kinetics of humic acids is probably due to the fact that hydrogen-loaded HA with $pK_{diss} \sim 5$ behave like a sponge the pores of which have a lower pH than the outside. In this interstitial space, the tricarbonato uranyl complex $[UO_2(CO_3)_3]^{4-}$ which is dominant at the pH of seawater decomposes to uranyl ions thus accelerating their reaction with the functional groups of HA /2/.

To maintain this fast binding kinetics also in a technical recovery process, this technique must be chosen in a way that slow kinetic steps preceding the uranium fixation at the sorber are avoided as far as possible.

Under this aspect, the uranium performance of humic acids fixed on Dowex 1x2 anion exchange resins in fluidized beds was investigated as a function of the flow velocity, v, the degree of initial uranium depletion, $\Delta|U|_0$, and temperature, T, of the seawater and the grain diameter, d, of the sorber particles. In these experiments, only one of these parameters was varied each time keeping all others konstant (fig. 2-5).

In the logarithmic presentation of the uranium accumulation curves, we always observe two intervals demonstrating that there is a change in the rate-determining kinetic process. This behaviour may be interpreted as due to a change in the local pH of the humic acids arising after some time of contact with seawater or, alternatively, by uranium diffusion into the sorber particles which may come into effect after completion of the surface loading. Further experiments are necessary to clarify this question. Both intervals, however, can be consistently described by the exponential law (1) with different relaxation times.

In Fig. 2 we note that a stronger uranium depletion of the seawater, as a result of an increases bed depth, is kinetically less favourable.

The accelerating effect of a smaller grain size and larger sorber surface on the accumulation kinetics is, at least qualitatively, anticipated (fig. 3).

There is, if any, only a minor influence of temperature. The small differences indicated in fig. 4 are not clearly beyond experimental error of measuring the uranium concentrations of both the sorber and the seawater.

In fig. 5, showing the effect of the flow velocity, the relaxation times of both kinetic intervals turn out to be inversely proportional to the squares of the thicknesses of the hydrodynamic surface layers. This indicates that uranium diffusion through this layer is a rate-controlling factor. Minimizing the hydrodynamical films by increasing the flow velocity of the seawater (according to Eq. 3) should, therefore, lead to an increase of the accumulation rate, eventually approximating the rate observed in the batch-experiments (fig. 1). To accomplish this in a fluidized bed concept, the density of the carrier material must be increased since, for a given density, the grain size of the fluidized sorber and the flow velocity of the seawater passing through the sorber bed cannot be varied independently.

In connection with their adsorption performance, some short remarks should be made on other properties of humic acid. Elution and regeneration can be done fast and efficiently with acid of pH 0,6 or acidified seawater. Fixed on peat, HA show no significant loss of loading capacity after 40 cycles of consecutive adsorption and elution. Humic acids are easily available in large quantities and there is no objection from an ecological standpoint to use them in seawater.

Summarizing the experimental results, we have seen that hydrogen-loaded humic acids on carriers show an exceptionally fast kinetics of uranium fixation in seawater which is practically temperature independent. This fast adsorption performance may be maintained in a technical recovery process if care is taken to minimize slow diffusion controlled steps preceding the uranium fixation reaction. The resulting advantages with regard to the cost structure of a pumped seawater concept to recover uranium will be discussed in the next section.

Acknowledgements

The authors wish to thank G. Putral, F. Ringelmann and E. Borchardt for carrying out the experiments.

References

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Industrial & Engineering Chemistry, Process Design and Development, submitted for publication

/2/ K. Wagener, D. Heitkamp
Thalassia Jugoslavica, in press

Legends

Fig. 1: Comparison of the initial uranium accumulation rate of different sorbers (grain diameter 0,1 - 0,2 mm) in standardized batch experiments /1/: humic acids (extracted from peat fixed on Dowex 1 x 2 anion exchange resin); hydrous titanium oxide (Harwell); Duolite ES 346 cation exchange resin (amidoxime groups) and Hyphan cellulose (2,2'dihydroxyazo-groups)

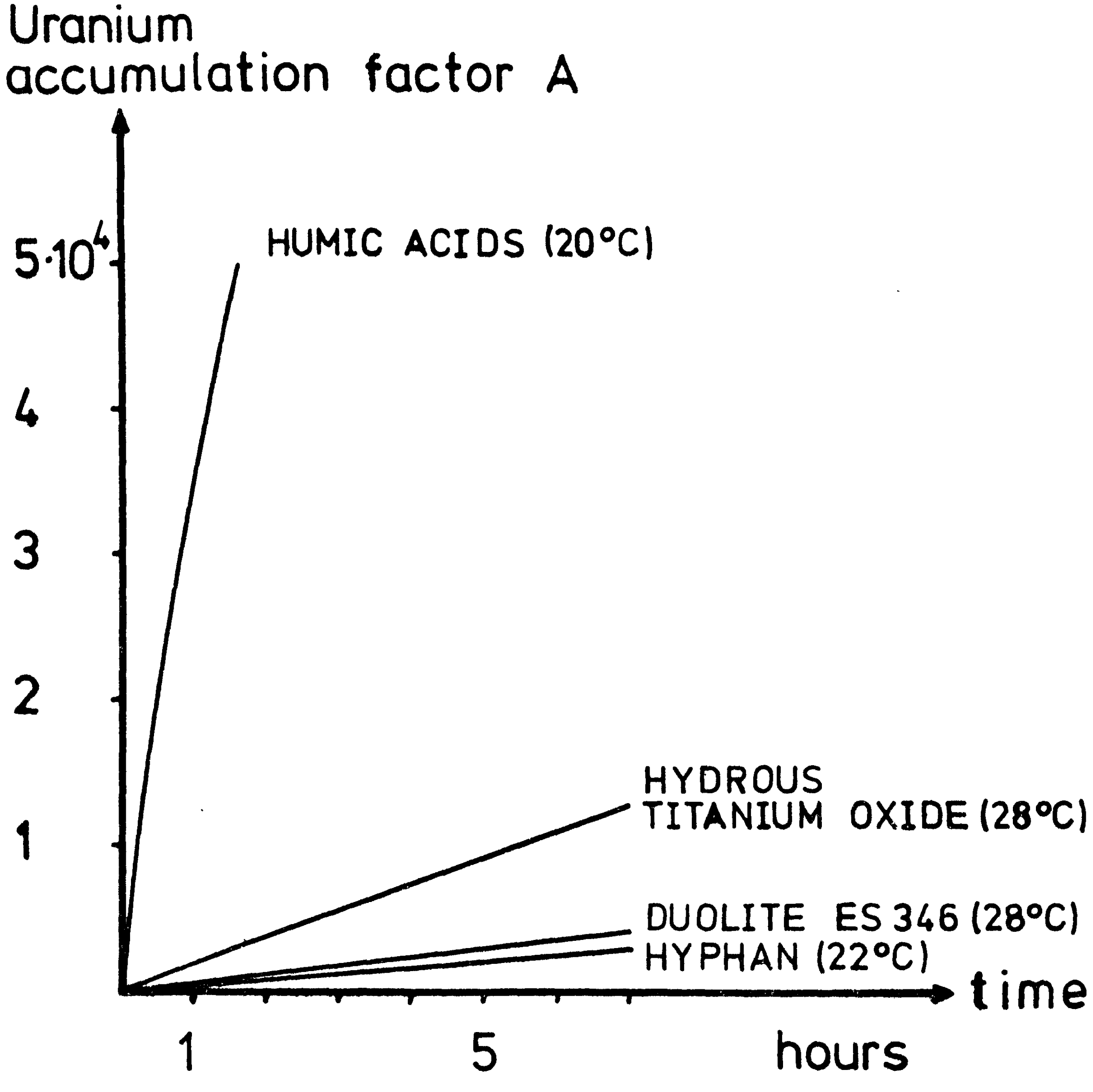
Fig. 2: Effect of uranium depletion in the seawater on the uranium accumulation kinetics of humic acids (fixed on Dowex resin),
$d = 0{,}4 - 0{,}5$ mm, $v = 0{,}33$ cm/sec, $T = 18^{\circ}C$,
$\Delta|U|_o$ (H2) = 19%, $\Delta|U|_o$ (H3) = 53%

Fig. 3: Effect of grain size on the uranium accumulation kinetics of humic acids (fixed on Dowex resin),
$v = 0{,}16$ cm/sec, $T = 18^{\circ}C$, $\Delta|U|_o = 34\%$, d (H4) = 0,3 - 0,4 mm, d (H5) = 0,1 - 0,3 mm

Fig. 4: Effect of temperature on the uranium accumulation kinetics of humic acids (fixed on Dowex resin),
$d = 0{,}3 - 0{,}4$ mm, $v = 0{,}16$ cm/sec, $\Delta|U|_o = 34\%$,
T(H4) = 18°C, T(H7) = 27°C

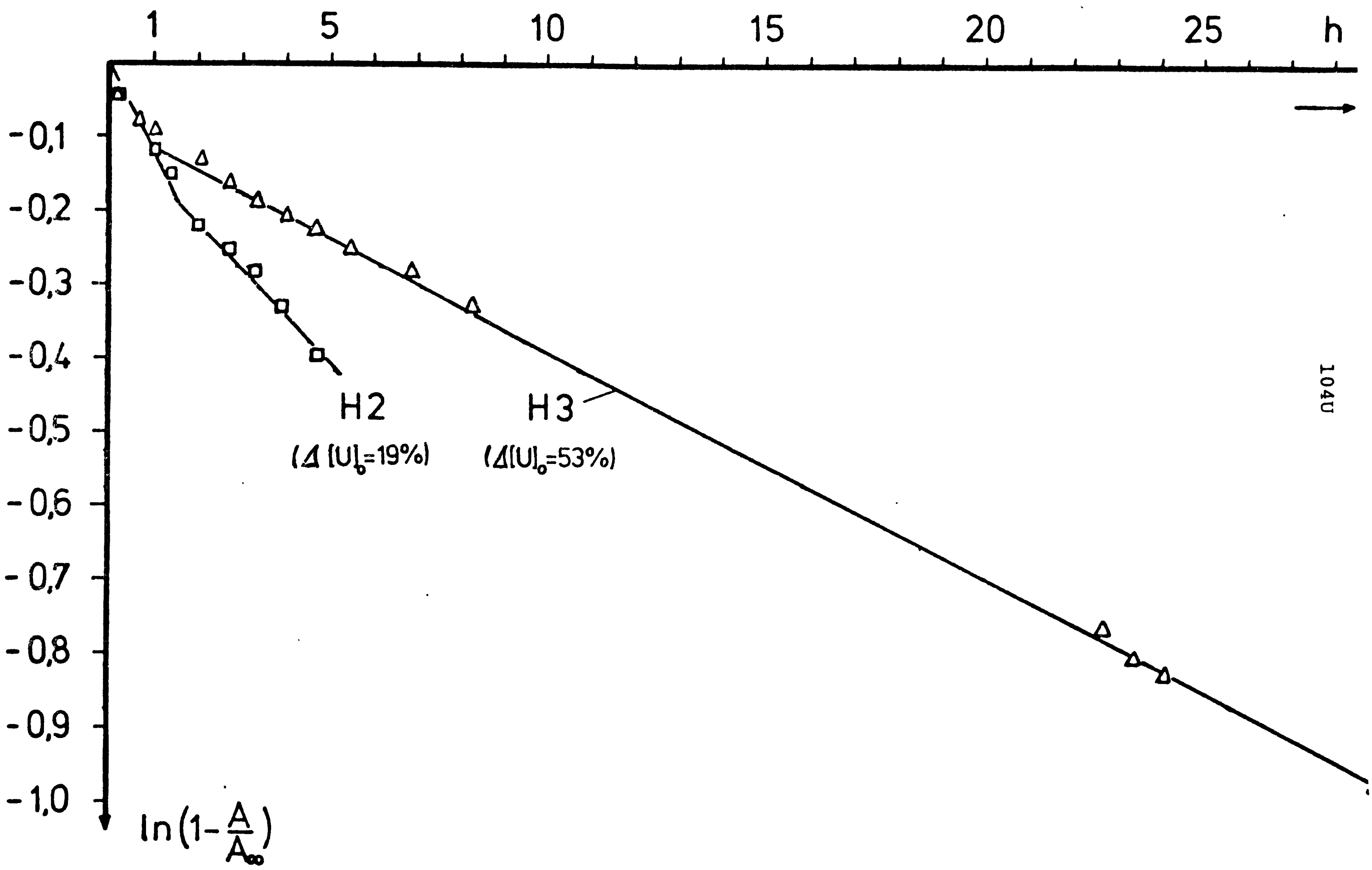
Fig. 5: Effect of flow velocity on the uranium accumulation kinetics of humic acids (fixed on Dowex resin),
$d = 0{,}4 - 0{,}5$ mm, $T = 18^{\circ}C$, $\Delta|U|_o = 19\%$, v(H2) = 0,33 cm/sec, v(H6) = 0,19 cm/sec

Figure 1

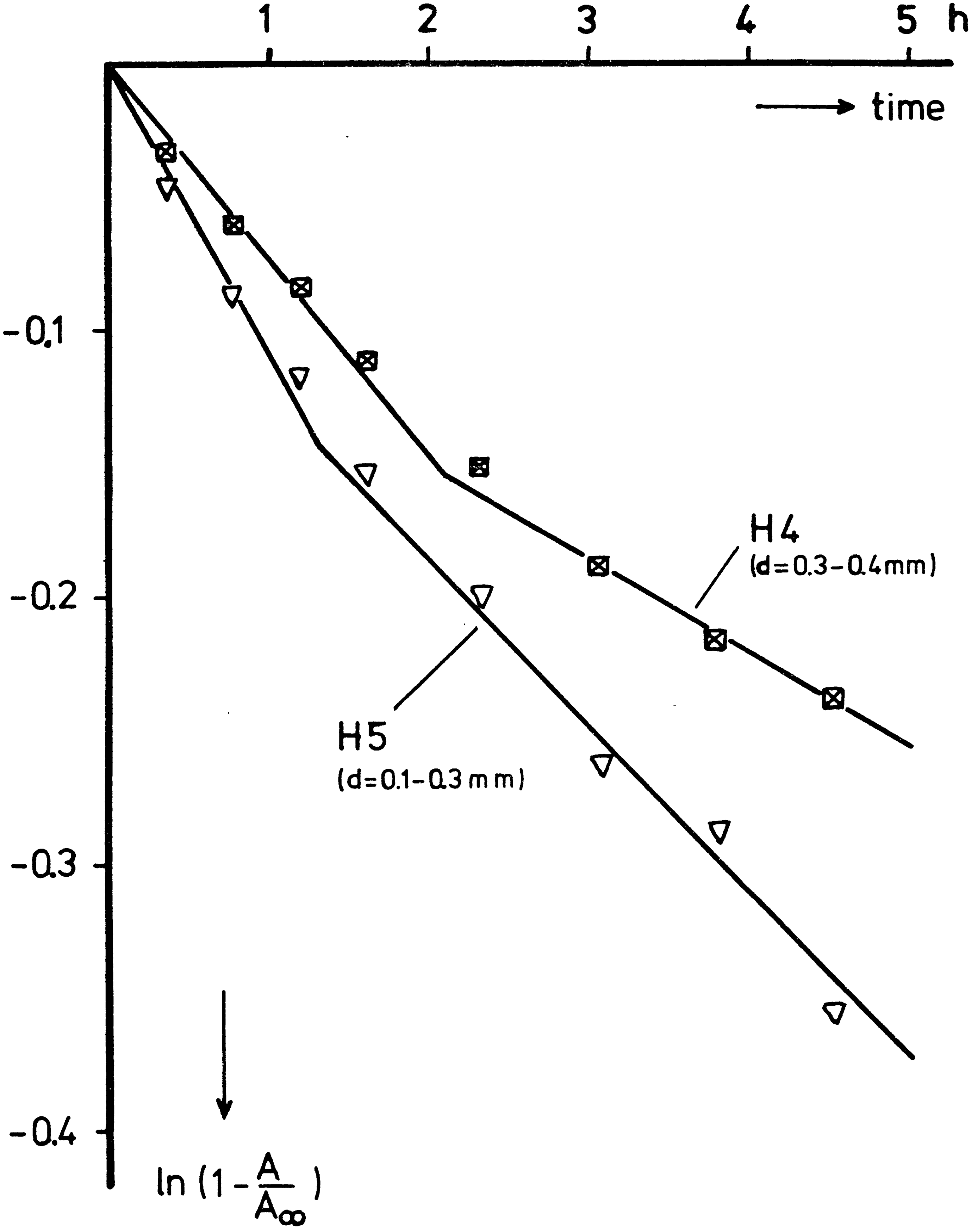


Uranium accumulation factor A
5·10⁴
4
3
2
1
HUMIC ACIDS (20°C)
HYDROUS TITANIUM OXIDE (28°C)
DUOLITE ES 346 (28°C)
HYPHAN (22°C)
time
1
5
hours

Figure 2



104U


1
2
3
4
5
h
time
-0.1
-0.2
-0.3
-0.4
$\ln\left(1-\frac{A}{A_\infty}\right)$
H4
(d=0.3-0.4mm)
H5
(d=0.1-0.3 mm)

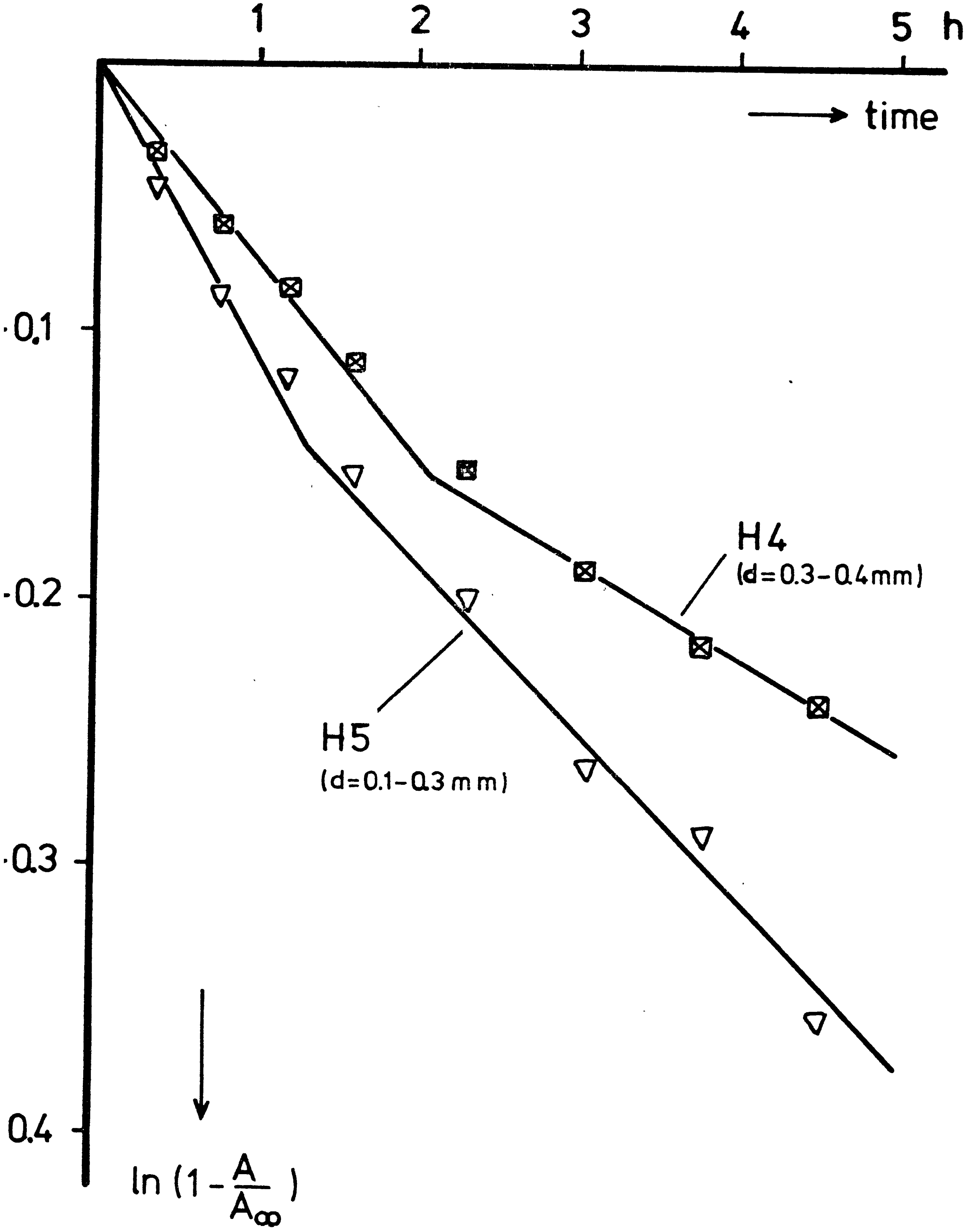
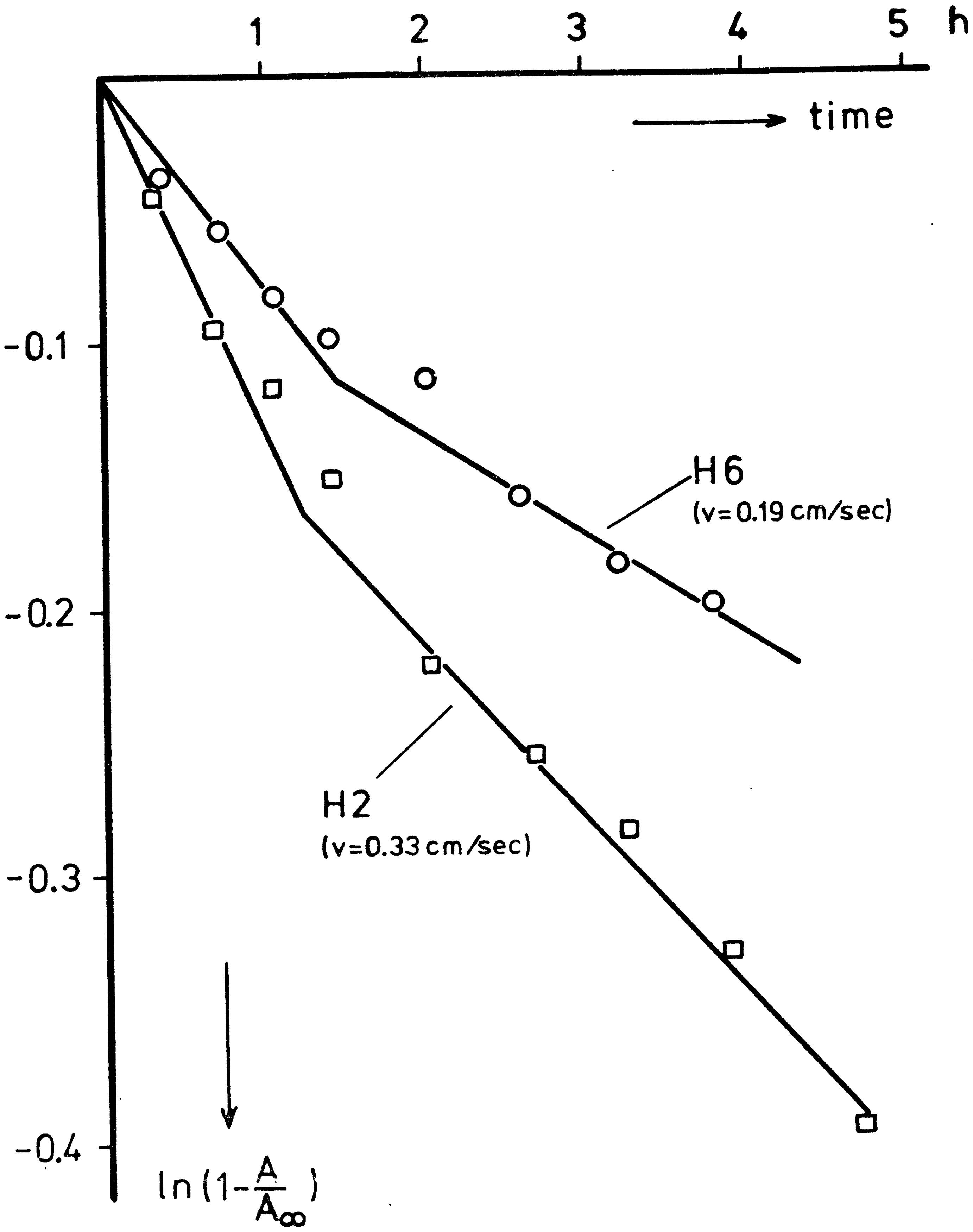

1
2
3
4
5 h
time
·0.1
·0.2
·0.3
0.4
H4
(d=0.3–0.4mm)
H5
(d=0.1–0.3 mm)
ln (1 - A/A∞)

Figure 5



Part B:

1) Design Parameter of a Recovery Plant

An uranium recovery plant consists of three separate units, the adsorption, the elution and the concentration unit. The following parameter study is only dealing with the adsorption unit, the most important and expensive part of the plant. In order to describe the adsorption system we have to consider a complex system of interconnecting parameters (figure 1): Plant parameters like production, adsorption area, flow velocity, etc. and adsorber parameters as adsorber diameter, kinetics, specific loading, bed height etc. The system is still more complicated than demonstrated in this picture and requires an extensive computer program for the optimization.

Our purpose is to pick up a few simple dependences of the parameters: production, adsorption efficiency, flow velocity and area of adsorption and to explain their influence on size and investments for the adsorption plant.

An uranium extraction plant is characterized by the following figures independent of the type of the used adsorber (figure 2):

- Uranium production per year (P)
- efficiency of adsorption (depletion of sea water) (η)
- flow velocity of sea water through adsorber beds (v).

For example, if the known uranium concentration of seawater (3,3 ppb) is combined with given values of the above parameters, like P = 500 tpa, η = 0,5 and v = 0,1 m/sec the area of the adsorber beds can immediately be calculated to F =96.000 m^2. This means that the total volume of sea water (in our case approx. 10.000 m^3/sec) has to pass through a square of 96.000 m^2. F represents one of the most important factors with regard to the size and investment costs of the plant.

The dependence of F and η - showing reverse proportionality - can be studied from the next graph (fig. 3), if production and flow velocity are kept constant. The smaller the efficiency the larger is the adsorption area and the greater is the increase of size and costs of a possible plant. But with respect to the slope of the curve a realistic plant concept requires efficiency values of 0,5 and more, shown as dotted region in the picture. As is known from the Exxon and Menai Straits Study these plants are designed with an adsorption efficiency of 0,8.

A similar interconnection is shown by F versus v, provided production and efficiency are kept constant (fig. 4). Low flow velocity needs large adsorption areas. The influence of kinetics and of capacity can be demonstrated very well in this picture. Referring to results of the Exxon Study a loading velocity of about 0,5 ppm U per hour (5 - 10 ppm U per day) can be achieved using titanium hydroxide granules at a flow velocity of 0,4 cm/sec. The effect of this low flow velocity leads to a large area of 1,4 Mill m^2 for the adsorber beds (outside of the range of the graph) and to high investment costs as will be shown later.

Using fast reacting adsorbents, like humic acid - values of approx. 10 ppm U per hour can be achieved - we are able to increase the velocity up to 0,1 m/sec and to diminish so the adsorption area down to approx. 100.000 m^2. But one has to emphasize clearly that the advantage of fast kinetics can only be really utilized if the adsorber material allows such a high velocity. On the other hand a high flow velocity favours the material exchange between liquid and surface of the adsorber because of the reduction of the hydrodynamic boundary layer effects.

The increase of the flow velocity enables us to operate a small, mobile and cheaper plant. Furthermore the amount of adsorber is reduced to 1/10 compared with titanium hydroxide and we save adsorber costs. According to our calculations the overall reduction of production costs is more than 50 %.

On the contrary, in case of a 10-times increase of the capacity of the adsorber, the plant size and the amount of adsorber material remain unchanged. The reduction of the costs is about 10 % due to a smaller elution unit and the minor number of cycles per year.

Until now we have mainly discussed the plant parameters, but will our adsorber material meet all these requirements? Let us go back again to the first picture. The adsorption efficiency represents one of the central problems as our plant is demanding for values of 0,5 and more together with a high flow velocity. In certain regions the efficiency can be controlled by the height of the adsorber bed altering the contact time between sea water and adsorber. But due to pressure losses and, of course, additional investment costs concerning bed structure and pumping system this influence is limited. And again one can imagine the positive effect of fast kinetics concerning the bed height.

From the first experimental results of humic acid we have calculated the bed height with regard to a constant flow necessary for different efficiency values (picture 5). But this important dependence has to be proved by further experiments. The dotted line marks the minimum amount of bed height without considering any effect of the depletion of uranium in the liquid phase. For example, from η = 0,1 to η = 0,5 we would enlarge 5-times our uranium production and need therefore 5-times the amount of adsorber height of the bed. However, according to our calculations, we need 8-times the bed height due to the influence of a diminishing uranium concentration to the kinetics. The results of our calculations led to a parabel shown in the picture 5.

Regarding the bed concept a fluidized bed system seems to be the single practical way of contacting the huge volume of sea water with the adsorber granulate at a high flow velocity. It seems unlikely to use a fixed bed because of the pressure losses. Thus, summarizing the prior figures an economic operating plant requires an adsorber granulate showing:

a) fast kinetics to recover uranium at a flow velocity of approx. 0,1 m/sec with at least 50 % efficiency

b) sufficient high specific weight to operate a stable fluidized bed at high flow velocity

c) and, what is most important, excellent mechanical stability and abraisive strength.

Unfortunately a lot of adsorber granulates, like titanium hydroxide, humic acid fixed on ion exchanger, etc. are showing reverse proportionality of kinetics and particle diameter (a, c) making the application of a fluidized bed more difficult.

Considering all the published data of titanium hydroxide we doubt that an economic use of this material can be achieved in the future. We hope that humic acid fixed on a suitable carrier will become a possible alternative.

2) The Exxon Concept: Humic Acid versus Titanium Hydroxide - a Cost Comparison

In order to give you an impression of the effect of using humic acid in a known and well elaborated model (Exxon Study) we have carried out the following cost estimations based on German conditions. But prior to this some remarks:

The Exxon Study was published in 1979 (fig. 6). The land based recovery plant applying titanium hydroxide should be erected on the island of Puerto Rico because of the demand for warm sea water. The adsorption area - as mentioned - is huge neeeding 1,4 Mill m^2 (125 beds) due to the low flow velocity of ~ 0,5 cm/sec. The plant is designed for 500 tpa production and for an adsorber efficiency of 0,8. The sea water is pumped and filtered before passing through the beds (pumping height: 5 m).

We introduced humic acid instead of titanium hydroxide in the concept and compared the cost figures (fig. 7 and 8) under the following assumptions:

- flow velocity v = 2 cm/sec and 10 cm/sec
- efficiency 0,3 (relatively unfavourable, but representing the first exp. values)

- adsorber losses: 0,1 % per cycle
- kinetics: 10 ppm U/h (exp. data).

a) We obtained a decrease of investment and production costs of about 50 %. Mainly responsible are the reduction of the adsorption area together with the land costs.

b) In case of humic acid use we have to consider a higher percentage of the energy costs, i.e. electric power consumption and investments for pumps,

c) However, the most important factor in our view is to diminish the plant size using fast reacting adsorber materials.

Our future work is concentrated on the fixation of humic acid on suitable carriers (heavy porous granulates or appropriate polymeric foam structures) as well as on the development of a floating and mobile recovery plant concept, the more, as it could be proved that there is no dependence of the adsorption efficiency of humic acid from sea water temperature.

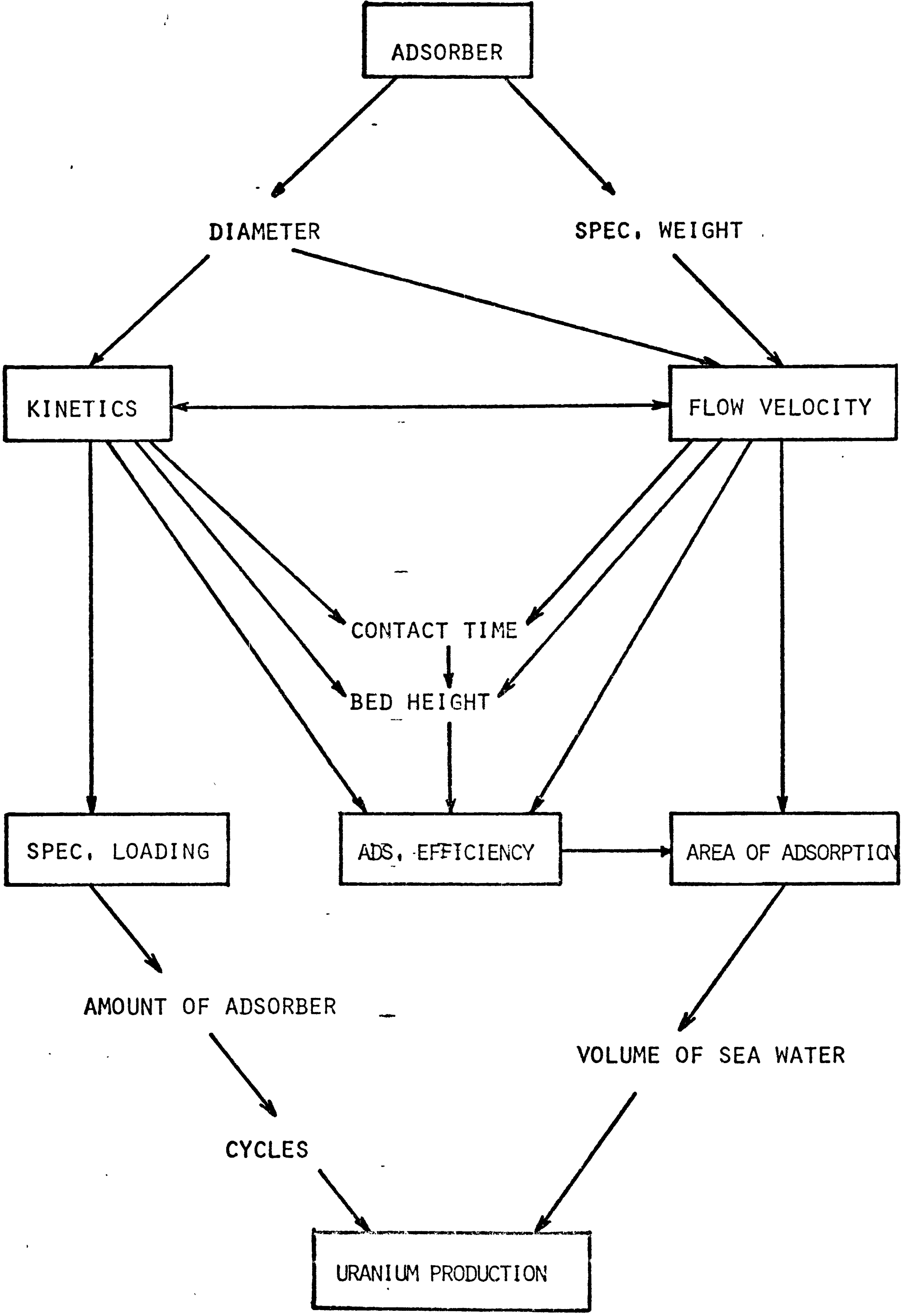

ADSORBER
DIAMETER
SPEC. WEIGHT
KINETICS
FLOW VELOCITY
CONTACT TIME
BED HEIGHT
SPEC. LOADING
ADS. EFFICIENCY
AREA OF ADSORPTIO
AMOUNT OF ADSORBER
VOLUME OF SEA WATER
CYCLES
URANIUM PRODUCTION

FIG. 2

KNOWN:	URANIUM CONTENT OF SEA WATER	3,3 MGU/M^3
ASSUMPTION:	P: URANIUM PRODUCTION PER YEAR	500 T
	η: EFFICIENCY OF ADSORPTION	0,5
	V: FLOW VELOCITY	0,1 M/SEC.
RESULT:	F: AREA OF ADSORPTION	96.000 M^2

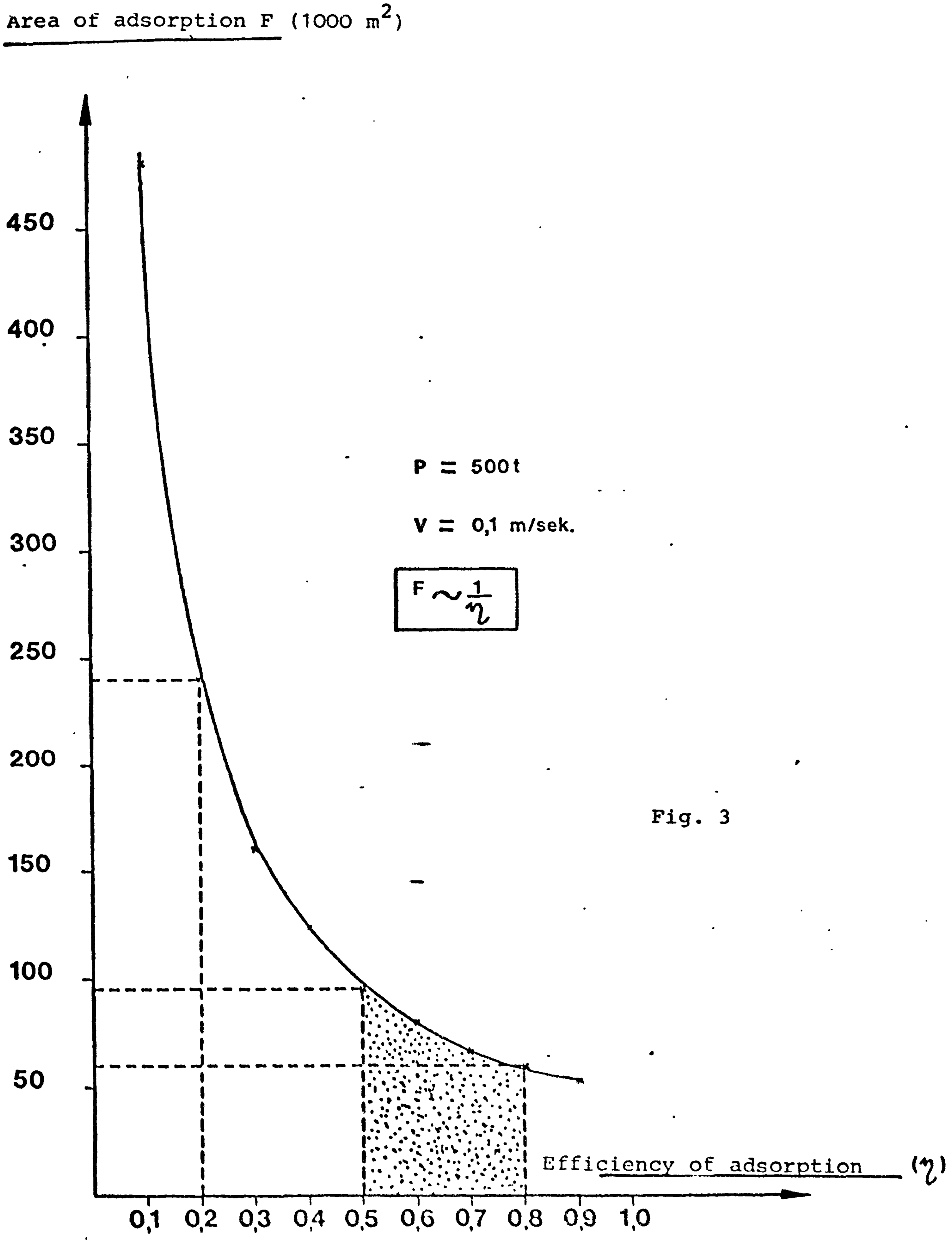

Area of adsorption F (1000 m²)
450
400
350
300
250
200
150
100
50
P = 500t
V = 0,1 m/sek.
F ~ 1/η
Efficiency of adsorption (η)
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1,0

Fig. 3

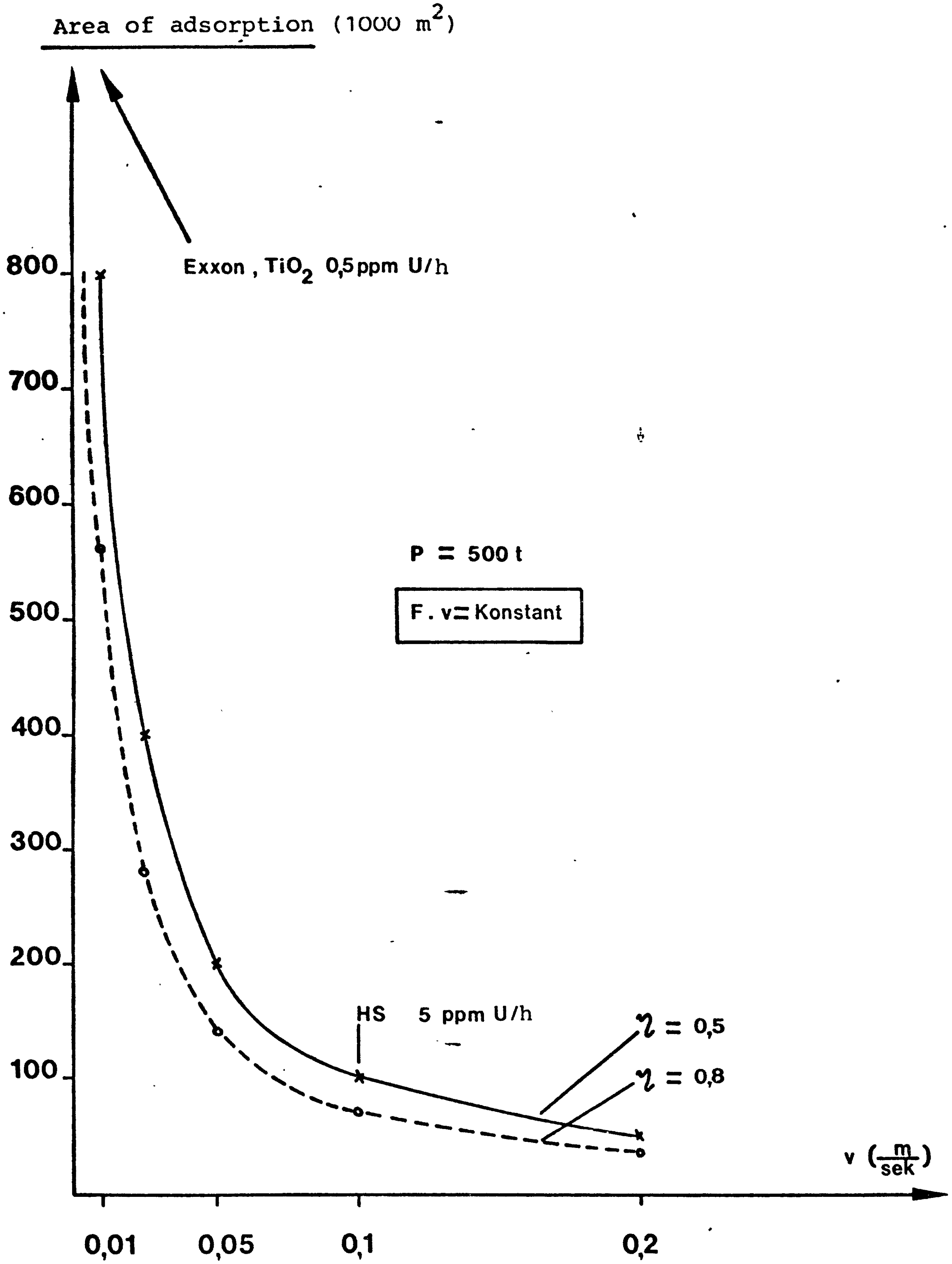

Area of adsorption (1000 m²)
800
700
600
500
400
300
200
100
Exxon , TiO₂ 0,5 ppm U/h
P = 500 t
F . v = Konstant
HS 5 ppm U/h
η = 0,5
η = 0,8
v (m/sek)
0,01
0,05
0,1
0,2

Fig. 4

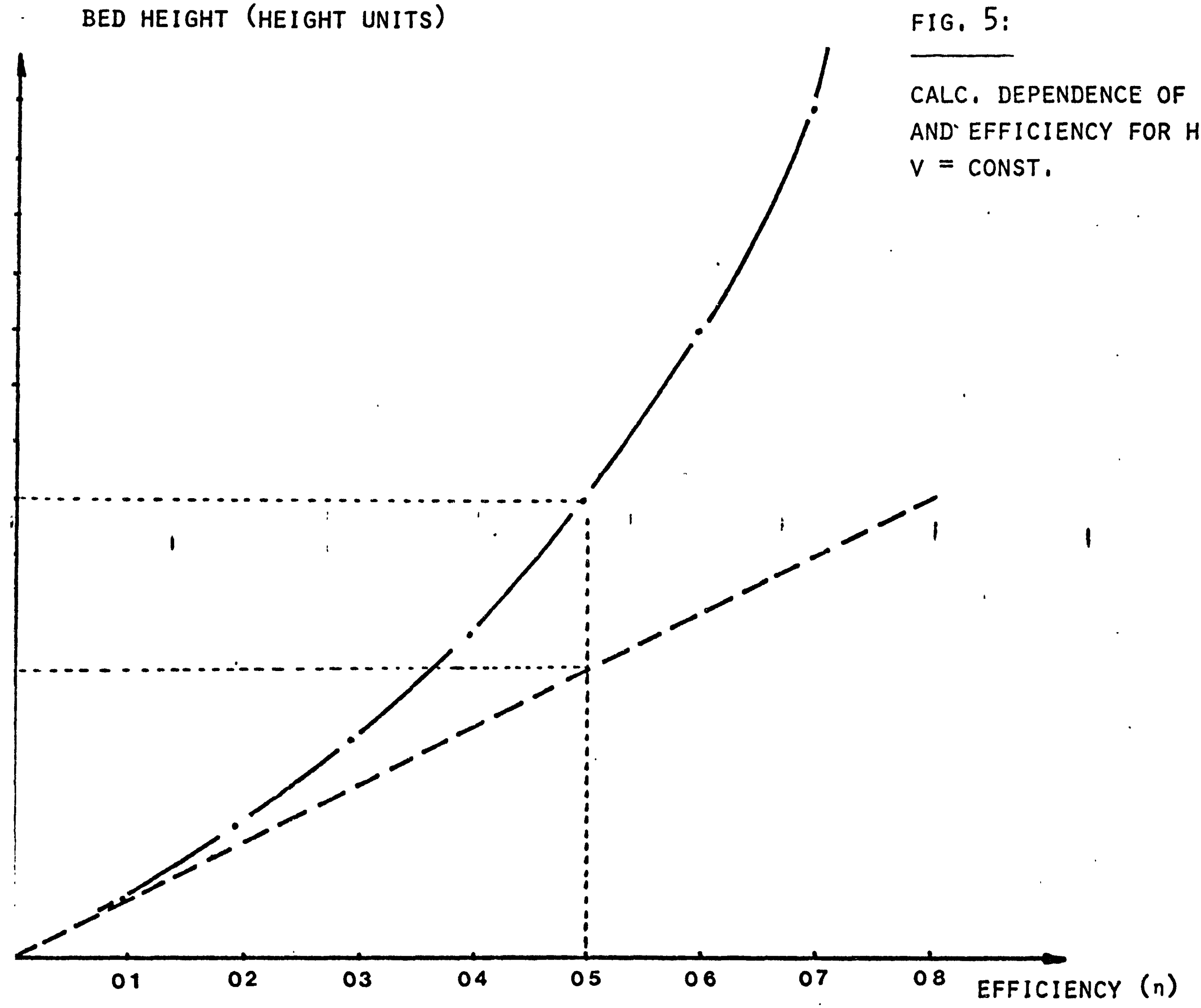


FIG. 5:

CALC. DEPENDENCE OF ADSORBER BED HEIGHT AND EFFICIENCY FOR HUMIC ACID
V = CONST.

EXXON STUDY

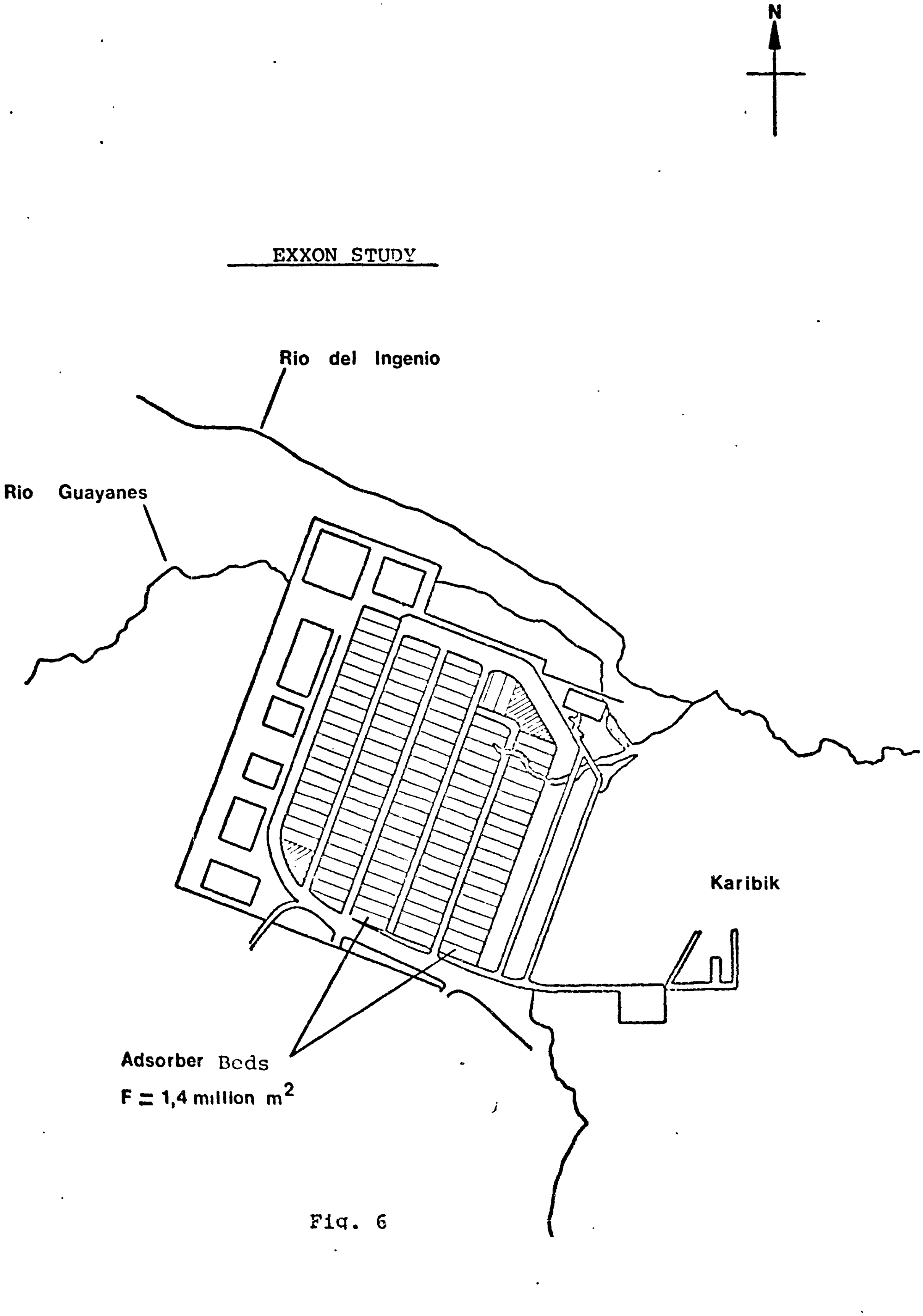


Fig. 6

FIG. 7

INVESTMENT COSTS MILL. DM (1980)	TiO_2-ADS.	EXXON-CONCEPT HS-ADS. (2 CM/SEC.)	HS-ADS. (10 CM/SEC.)
ADSORBER BEDS	6490	2160	430
LAND AND SITE DEVELOPMENT	2250	1130	450
SEA WATER HANDLING FACILITIES	3060	3360	3360
FRESH WATER HANDLING FACILIT.	250	340	340
ELUTION PLANT	780	1060	1060
CONCENTRATION PLANT	20	20	20
TOTAL	12850	8070	5660

FIG. 8

PRODUCTION COSTS PER YEAR MILL. DM (1980)	TIO_2-ADS.	EXXON-CONCEPT HS-ADS. (2 CM/SEC.)	HS-ADS.(10 CM/SEC.)
ANNUAL FIXED CHARGE	2010	810	570
CAPITAL REPLACEMENT, MAINTENANCE (CA. 3 %)	460	290	200
PERSONNEL	30	30	30
ENERGY	130	230	230
CHEMICALS	200	200	200
ADSORBER	60	60	60
TOTAL	2890	1620	1290
DM/KG URANIUM (PLANT EFF. 90 %)	6420	3600	2870

Discussion on Denzinger/Heitkamp Presentation

Dr. Morgan cited his impression that for practical systems the controlling step was mass transfer through the fluid film to the particle surface. Dr's Denzinger and Heitkamp pointed out that this resistance could be reduced substantially by increasing fluid velocity, hence the operating regime could only be characterized with reference to this parameter. Dr. Kelmers noted that the large effect of temperature observed in the case of adsorption by hydrous titanium oxide argued for the importance of the chemical step; and the fact that the uranium is concentrated on the surface of the sorber argues for solid phase mass diffusion as being a key step.

In the discussion Dr. Heitkamp noted that regeneration could be carried out using seawater, the material was readily available and that testing had shown no losses after 40 cycles. He also noted that the active sorber when fixed on peat was stable, implying that the carrier was the key. This was in response to a question by Dr. Fremery who asked whether peat had been compared to lignite. Dr. Heitkamp noted that only peat had been tested (ordinary, unprocessed black peat), but there were obvious problems with lignite in terms of solubility, the effect of oxygen, and decomposition. Finally he noted that the sorber was very selective with respect to uranium vs calcium or magnesium (coefficients of $\sim 8 \times 10^4$ for the former vs 6-20 for the latter pair).

Note that the paper by Drs. Denzinger, Schnell, Heitkamp and Wagener was delivered in two parts (see agenda in Appendix A), but is reproduced as one paper here.

THE RECOVERY OF URANIUM FROM SEA WATER BY CHELATION ON CHITOSAN

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INTRODUCTION

In 1968 we reported about the chelating ability of chitin and chitosan and the selective uptake of transition metal ions from brines, natural waters and organic and aqueous solutions: our data included uranium for which chitosan exhibits high collection capacity (1 - 5).

At that time, however, the knowledge on chitin was rather limited and chitosan was just a laboratory curiosity. Today, in view of the advances made in the field of these biopolymers (6 - 8), we can fully describe chitins and chitosans of various origins and evaluate their fitness for applications in various technological fields, one of which deals with the recovery of valuable metals.

Chitin and chitosan, the more or less acetylated polymers of glucosamine are, first of all, the only natural polysaccharides widely occurring in nature, which possess sharply basic characteristics: their basicity as well as their optical and structural properties are due to the presence of regularly spaced amino groups on the polyanhydroglucosidic chains. The difference between chitin and chitosan lies mainly in the acetylation degree, the chitin name indicating highly but not fully acetylated polymers, and the chitosan name indicating scarcely acetylated polymers.

The electron donor properties of the primary aliphatic amino group, the availability of electron pairs on oxygen atoms belonging to the same or to other chains, and the partially crystalline structure of the polymers are characteristics of chitin/chitosan favoring the instant chelation of transition metal ions under a wide range of conditions. High hydrophilicity and porosity of the polymer powders are physico-chemical characteristics of further advantage for this kind of applications. Another peculiar advantage is the indifference to sodium, magnesium and calcium ions which are not collected and do not disturb the fixation of transition metal ions.

The early reports about the collection of uranium on chitosan of animal origin were already aimed to the removal of uranium from the sea water, since low uranium concentrations in salt solutions and in sea water were used: thus, we reported the 100 % collection of uranyl ions on chitosan (200 mg, 100-200 mesh) from both distilled and sea water (50 mL) at the concentration of 0,44 mM, 20°C and pH 7.0 after 1 hr contact. Further data were obtained by radiochemical work on sea water collected at the depth of 600 m in the Mediterranean; it was filtered through a 0,45 μ Millipore filter on teflon supports. ^{233}U, 90 % isotopically pure, was added to the sea water and determined by liquid scintillation in order to study the behavior of uranium toward chitosan in sea water. A 60-mL fraction of a sample containing 5×10^{-6} g U was used for that measurement: 10 mL were taken for reference and 50 mL were shaken with 200 mg of chitosan. After a measured time, a 10-mL fraction was taken and centrifuged. The data obtained indicate that the adsorption of uranium on chitosan is total and rapid.

Uranium was easily recovered after collection on columns of chitosan, by elution with 0,5 M sodium carbonate with an overall yield as high as 96 %. Manskaya (9) published about the collection of uranium from solutions of uranyl sulfate by fungal and animal chitins; those data indicate that the two chitins used were not equivalent. The adsorption of uranium was later investigated with Chlorella dry cells suspended in artificial sea water containing 1 ppm U at 30°C for 20 hr under occasional stirring (10). The cell walls of the green alga Chlorella contain naturally deacetylated chitin, i. e. chitosan, and therefore those results are in connection with uranium fixation on chitosan. The extent of the adsorption was 81.7 %. Additionally, chitosan phosphate was found to recover 2.6 μg U / g chitosan phosphate from natural sea water containing 2.8 μg U / L, yield 93 %. Chitosan phosphate, however, is not so selective as chitosan because alkali metal ions are also collected.

We have recently given our attention to the chitosans now commercilly available in bulk quantities such as those obtained from the wastes of the fishing activities (crab and shrimp shells) [11], and of the fermentation industry (Aspergillus niger mycelia) [12], and to some samples of chitosans especially prepared in the laboratory by others and by us. We have submitted to viscometry, potentiometry, infrared spectrometry and x-ray diffraction spectrometry the polymers obtained in pilot plants, to define the best conditions for their production. We have then verified on these samples our early results about the uranium collection by chitosan.

EXPERIMENTAL

Chitosans. The ANIC chitosan was produced by ANIC, San Donato Milanese, Italy, from the shells of the norvegian shrimp Pandalus borealis. The Polyplate chitosan was obtained from prawn wastes by Polyplate, 41 Palace Court, 1 Kyd st., Calcutta, India. The Kypro chitosan, from Dungeness crab (Cancer magister) was supplied by Kypro Co., 4900 Ninth ave., NW, Seattle, Wash. The Kyowa chitosan, from crabs , was obtained from Kyowa Oil & Fat Co., Koike Shibayama-Cho, Sanbu-Gun (Chiba Pref.), Tokyo, Japan. The Rybex chitosan was supplied by Fisheries Central

Board, Foreign Trade Office, Rybex, Szczecin, Poland. The Kurifix CP-613 from crabs, was supplied by Kurita Water Ind., Ltd., Nishi-Shinjuku 3-chome, Shinjuku-ku, Tokyo, Japan. The Chesapeake chitosan was from the blue crab Callinectes sapidus of the Chesapeake area, USA.

Chitosan columns. The glass columns were filled with chitosan powder to the height of 10 cm (0.4 cm diameter). They contained 190 mg of animal chitosan and about 900 mg of chitosan-glucan. The flow rate was about 2 mL/min. Temperature 20°C.

Uranium determinations. Uranium was determined on 25-mL samples at pH 8.8 by colorimetry (425 nm) after complexation and extraction with 8-quinolinol in chloroform (10 mL, 1 %) or by fluorometry with the Galvanek-Morrison fluorometer Mark V manufactured by Jarrel-Ash, according to the fused pellet method (13). The pellets were obtained by using the sodium carbonate obtained after drying suitable aliquots of the uranium bearing carbonate eluates.

Viscometry. Measurements were done with the Haake Rotovisco RV 12 viscometer, equipped with a programmer and a Hewelett-Packard recorder; the temperature was controlled with a Haake thermostat. The rotor used was the SV1 for which factor G is 13920.

Alkalimetry. Titrations with 0.1 N NaOH were done under nitrogen on solutions of chitosan (0.5 g) in 0.3 N HCl (20 mL), with the aid of an Amel pH-meter and the results were worked out graphically.

Infrared spectrometry. The degree of acetylation was obtained according to our method, on KBr discs, with the Perkin-Elmer 299-B spectrometer, (14).

X-ray diffraction spectrometry. Chitosan powders were milled and sieved to pass a 200-mesh net and pressed to become self-sustaining in the frame for exposure to the primary beam of the Ni-filtered CuK_α radiation from a Jeol x-ray diffractometer.

RESULTS AND DISCUSSION

The data in Table I show that a careful study of the conditions applied in the preparation of chitosan can substantially improve its characteristics as indicated by the values of the ANIC sample. There are therefore means to produce chitosans of superior quality and performances, in terms of molecular size which would prevent undesirable degradation,

TABLE I. Characteristics of some commercial chitosans. Viscosity: the first line refers to data obtained under shear rate 456, the second and third lines refer to data under shear rate 114, acceleration and deceleration, respectively; standard deviations ± 40.7, ± 104.9 and ± 106.0, respectively. Infrared spectrometry: standard deviation ± 4.2.

	VISCOSITY, centipoises		ALKALIMETRY		I.R.	X-RAY
			NH_2 %	pK	Acetyl %	2 θ
	2°C	25°C				
ANIC	313 823	272 643 593	74	6.0	22	10°00' 19°58'
POLYPLATE	165 297 264	82	(92)	7.0	32	9°43' 19°58'
CHESAPEAKE	264 593 626	173 362 330	65	6.9	26	9°13' 19°58'
KYPRO	below limits		78	6.7	22	10°26' 19°58'
KYOWA Flonac	272 659 692	190 412 395	71	6.5	30	(10°13') 19°58'
RYBEX	231 593	206 494 461	58	6.6	35	8°58' 19°58'
KURITA Kurifix	230	160	71	6.2	(41)	(10°00') 20°00' 29°24'

acetylation degree and pK which would provide the best capacity for transition metal ions, crystallinity for its physical fittness in various operations such as the filtration of sea water.

Similarly, various chitosans of fungal origin prepared in our laboratory can be obtained in large amounts, with reproducible characteristics and superior performances.

As far as their ability to collect uranium from waters, brine and sea water is concerned, the data in Table II indicate that all of the chitosans of animal and fungal origin tested possess high collection ability for the uranyl ion, in water and brine.

The shaking time was 1 hr but there are evidences that the

TABLE II. Batch measurements on the uranium collection by chitosans. Uranium collection percentages ($\pm$ 3 %) of animal and fungal chitosans (200 mg) in uranyl acetate solutions (0.44 mM, 50 mL), after 1 hr shaking.

	Aqueous solution, pH 5.0	3.5 % NaCl brine, pH 4.5
ANIC	98	98
POLYPLATE	95	99
CHESAPEAKE	99	98
KYPRO	99	99
KYOWA Flonac	99	98
RYBEX	99	98
Aspergillus niger	95	84
Mucor rouxii, untreated	60	98
Mucor rouxii, NaOH	97	97
Choanephora cucurbitarum	91	97
Streptomyces	93	85

collection of most of the uranium occurs during the first minutes of contact. While the physical form of the animal chitosan is that of rigid and irregular particles, the fungal chitosan are filamentous and amorphous powders, therefore the comparison of the rates of uptake is not simple. However, the data in Table II indicate that the total amount of uranium present in solution is collected by nearly all samples. These measurements were carried out on solutions at relatively low pH values (4.5 and 5.0) because the uranyl ion concentration (0.44 mM) would promote precipitation at higher pH values; nevertheless, it was speculated that if collection occurs under these rather unfavorable pH conditions, its extent would certainly be very high from dilute solutions at pH values closer to the sea water value.

In fact, more dilute solutions, at 0.3900, 0.039 and 0.0028 ppm U in water and brine (the latter concentration being the one reported for uranium in sea water) at pH values close to neutrality (6.0 and 7.5) have been percolated through chitosan columns at rather high flow-rates; the results, shown in Table III indicate that uranium can be completely removed from water and NaCl brine when present at 0.3900 and 0.0390 ppm and can also be removed with very satisfactory yields (85 %) when present in NaCl brine at the concentration of 0.0028 ppm.

The recovery of uranium can be done either by elution or by ashing: elution can be performed with a dilute (0.33 M) solution of sodium carbonate, while ashing can be performed at relatively low temperature (for instance 650°C for 30 min).

The chitosan-glucan complex from <u>Aspergillus niger</u> is also suitable for the recovery of uranium from water and brine, however, in view of its higher mineral content and the presence in it of manganese, problems are encountered in the analytical determination of uranium by both the fused pellet and colorimetric methods. By running determinations

TABLE III. The recovery of uranium on chitosan.
Recovery percentages of uranium from water and 3.5 % NaCl brine, by using 10x0.4 cm columns of chitosan and chitosan-glucan.

Uranium concentration, ppm	Aqueous solution, pH 6.0	3.5 % NaCl brine, pH 7.5
ANIC chitosan		
0.3900, 1 L	94	100
0.1680 0.1 L	83	95
0.0390 1 L	108	100
0.0028 1 L	20	85
Aspergillus niger chitosan-glucan		
0.3900 1 L	122	117
0.0390 1 L	85	

on blanks, it is however possible to correct the high values obtained on these samples. The values in Table III are averages of 3 determinations.

CONCLUSIONS

The results presented for the best chitosans available implement and confirm our early results obtained twelve years ago. In view of its selectivity (indifference to alkali and alkali-earth elements) and its hydrophilicity, chitosan is quite suitable for the recovery of uranium from water and NaCl brine, thus it will certainly be applicable for the recovery of naturally occurring uranium from sea water.

Acknowledgements. This study was carried out under the auspices of ANIC, Divisione Chimica Secondaria, C.P. 3587, I-20100 Milan, Italy.

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Discussion on Prof. Muzzarelli's Paper

In response to a question Prof. Muzzarelli replied that chitosan was currently selling for approximately 5 $/kg in Japan and that a tentative price for a European facility was in the range of 4-5 $/Kg, but that larger scale use would reduce the price. He also noted the existence of an MIT report, written three years ago, on chitosan production.

He also indicated that amino group oxidation should not be a problem, and that while organisms can degrade chitosan, oceanographers had evidence that chitin deposited on the sea bottom takes a long time to decompose. The long term stability, however, should be verified.

In response to a question by Dr. Zakak, Prof. Muzzarelli indicated that highly concentrated carbonate solutions were used for elution. Chitosan is favorable in this regard because it is produced in a strongly alkaline solution and is therefore resistant to such conditions. In response to a related question he noted that while specific tests on the fate of the strong uranyl carbonate complex were not performed, the chelation reaction is obviously favored.

In response to a question by Dr. Morgan it was indicated that silver would be adsorbed by chitosan and indeed all transition metal ions would be (eg vanadium, molybdenum, etc..), also post-transition elements such as lead, and even precious metals. Prof. Muzzarelli noted that chitosan is used commercially in Japan for removal of copper from industrial effluents.

He also noted that the material particles are in the form of irregular granules, with some degree of crystallinity depending on the fibres provided by the living organism which served as the source of the chitosan.

MECHANISMS OF CHELATION OF HEAVY METALS BY CHITOSAN

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December 2, 1980

ABSTRACT

The concentration profiles of several heavy metal ions and anions have been measured in chitosan membranes immersed in dilute aqueous solutions. The shapes of the concentration curves for the metal ions is characteristic of a diffusion process in which the diffusion coefficient is a function of the concentration. The anion penetrates much more rapidly than the cation, however, and the concentration appears to be dependent on the reaction kinetics. We propose a mechanism whereby the metal ion bonds with the nitrogen in the functional amino group, with the bridging oxygen and with two hydroxyl groups in a neighboring glucose ring. The anion, on the other hand, bonds ionically to the metal-amino complex in order to neutralize the charge and to the protonated amino sites which have not reacted with the metal ion. In the case of uranium in sea water, it is probable that the uranium is present as a uranyl complex and that bonding with chitosan will occur by ionic bonding, that is, salt formation, rather than by covalent bonding to the amino groups. Uranyl complexes in dilute concentration will thus compete with chloride and the relative concentrations will be determined by the equilibrium constants.

INTRODUCTION

Muzzarelli and coworkers (1,2,3) have demonstrated that uranium in sea water can be recovered by chelation with chitosan. Chitosan is a glucosamine, and it can be prepared by a deacetylation reaction from chitin, which is a fundamental structural material in the exoskeletons of arthropods and insects, and which also occurs in certain fungi. The structures of chitin and chitosan are shown in Figure 1. The removal of the acetyl group leaves an active amino site, and it is the protonation of this site in aqueous solutions which causes chitosan to be a positively charged polyelectrolyte.

Chitosan is known to be an effective chelator of almost all of the heavy metals, other than the alkali and alkaline earth metals. The mechanism of this reaction has not been determined, however, and it has been assumed that the metal ions bonded, somehow, with the nitrogen in the amino complex. In the case of uranium in sea water, however, it is unlikely that the metal is present as a positively charged ion, but rather as a complex which is anionic. Yet uranium has been recovered from sea water by chitosan and it appears that other mechanisms were at play.

In this paper we report on our work on the reaction between chitosan and dilute solutions of copper sulfate. We postulate a mechanism for these reactions and suggest that the same mechanism carries over to uranium in sea water. This suggests certain limitations on the process which should be explored if chitosan is to be used for this purpose.

EXPERIMENTAL DATA

In our experiments we cast chitosan membranes from solutions of chitosan in dilute acetic acid (4). These membranes were approximately 100 μm thick. The membranes were immersed at room temperature in aqueous solutions of copper sulfate with copper contents which varied from 1 to 100 wppm. Membranes were sectioned after various exposures in solution, and the concentrations of copper and sulfur were measured in a scanning electron microscope by means of an electron beam microprone (5). Typical profiles of copper and sulfur are shown in Figures 2 and 3.

The copper profile appears to follow diffusion kinetics, with diffusion coefficients which are functions of the concentration. The penetration of the sulfur, which presumably indicates the sulfate content, is different. The penetration of sulfate is much more rapid than of copper and the profile seems to be determined by the reaction kinetics rather than by diffusion.

DISCUSSION

We also observed that the membranes became thicker and embrittled as the reaction proceeded. This led us to conclude that ions were entering between the chains, and that cross-linking was also occurring. These data thus suggest a mechanism in which the following sequence of events occurs:

1. the amino sites in chitosan are protonated rapidly in aqueous solutions
2. the anions then enter readily and neutralize the charge by means of a salt-like reaction.
3. The positively charged copper can then enter and bond with the nitrogen and probably the bridging oxygen and hydroxyl groups in a neighboring ring to provide a strong cross-linking.

Since the pH of the copper sulfate solutions was 5.8 and the pK_a value of chitosan is 6.3, this mechanism leads to complexes will have 4 glucose rings, one copper atom and 2.5 sulfate ions. On this basis, the maximum copper content would be 6.7 wt. pct. and the sulfur content 8.5 wt. pct. Within our experimental accuracy, this is what we observed.

CONCLUSIONS

Since uranium is probably present as a complex in sea water, rather than as a metal ion, it appears that the primary mechanism of bonding will be by ionic bonding in a salt-like compound, rather than as a covalently bonded amino compound. If this is so, the uranyl complex will compete with the chloride ion and the efficiency of chitosan as a chelator will depend on the relative values of the equilibrium constants. Chloride ions enter chitosan very rapidly, and if the uranium is present as a complex oxychloride, the reaction with chitosan could be very rapid and very efficient. Such a mechanism would make chitosan a very attractive material for the extraction of uranium from sea water. A considerable amount of experimental work is required, however, in order to establish the feasibility and practicability of this system.

ACKNOWLEDGEMENTS

The author would like to express his thanks to the MIT Sea Grant Program for the sponsorship of this work. We would also like to acknowledge the work of Amin Nakhla and Chee Wong in obtaining the data cited here.

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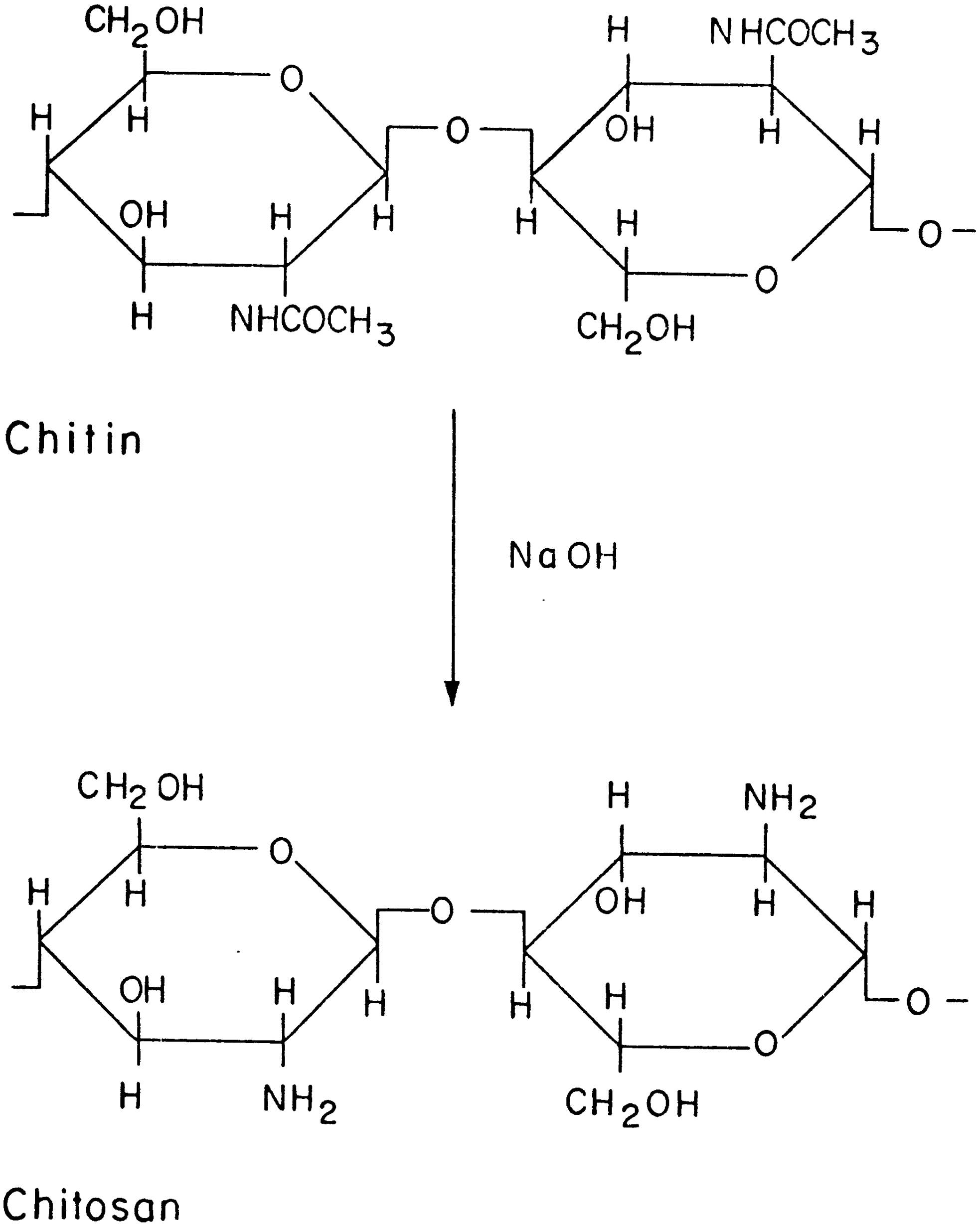

Fig. 1. The deacetylation of chitin to chitosan.

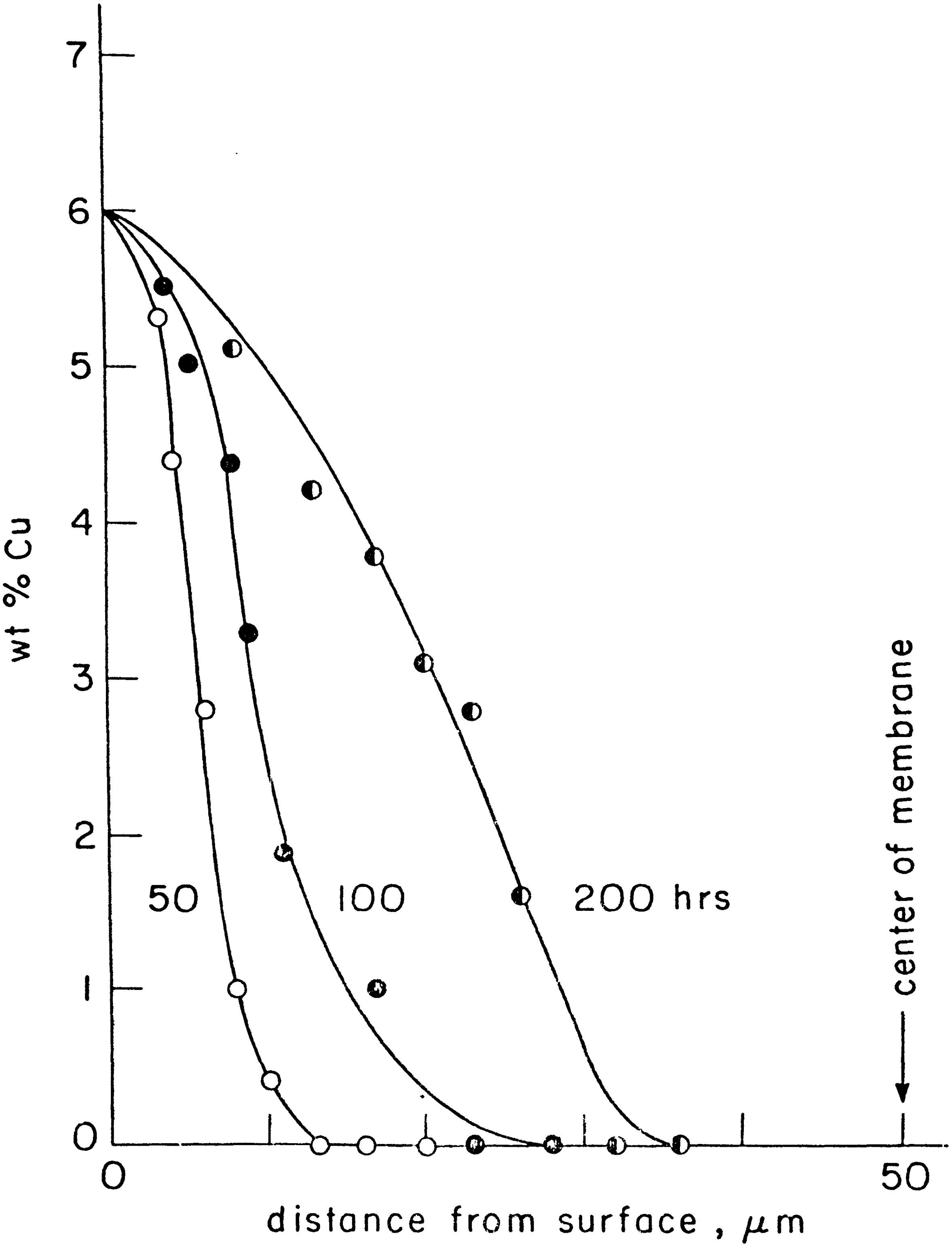

Figure 2. Concentration of Cu with depth in chitosan exposed to $CuSO_4$ solution with 10 wppm Cu.

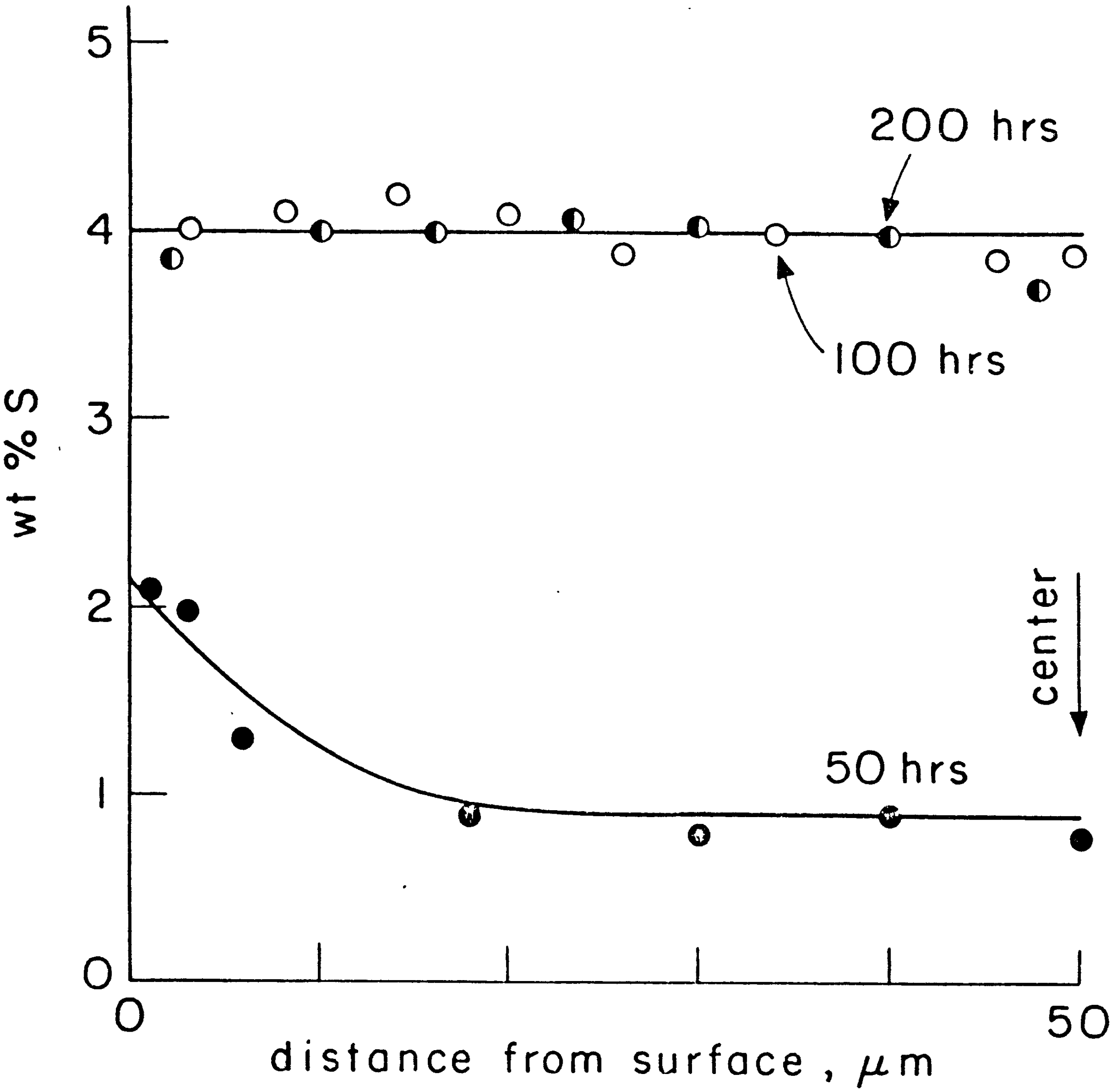

Figure 3. Concentration of S with depth in chitosan exposed to $CuSO_4$ solution with 10 wppm Cu.

Discussion on Prof. Averbach's Paper

In response to a question from Dr. Wang regarding the mechanism of binding for the uranyl carbonate complex, Prof. Averbach indicated that he felt salt formation was responsible, and that experimental data existed showing that many complexes bonded: chromates, dichromates, phosphates, etc.

It was noted that since chitosan could be made into membranes, it could probably be used to make coated particles. In this amorphous form, however, it was more susceptible to degradation.

Prof. Muzzarelli described an experiment using containers separated by a chitosan membrane. Ion transport across the membrane could be studied by putting various salts in one of the containers and measuring its concentration in the originally pure water in the other. Such experiments showed that sodium ions readily passed through the membrane, whereas copper did not.

Dr. Morgan asked whether chitosan could be manufactured synthetically. Dr. Averbach responded that while this should be possible, the problem was today that there was no shortage--there is no market for natural chitosan today in the U.S. Japan produces about 10^6 lbs/yr. A major problem is the lack of economies of scale due to the dispersed source of the natural materials, seasonal variations in supply and the like, which will make it difficult to improve upon 4 $/lb:

for example the chemical raw material costs alone amount to about 90¢/lb. Furthermore, one must process roughly 1 ton of shell to obtain 100 lbs chitin or 80 lbs chitosan.

Chapter 4

Recovery System Studies

Collected in this chapter are those papers which are principally concerned with the overall systems aspects of contacting sorber and seawater:

M. Kanno and K. Saito

"Recovery of Uranium from Seawater"

J. Bitte, M. I. Fremery and H. G. Bals

"On the UEB Concept of Uranium Extraction from Seawater"

B. Bjork and P. Vallander

"Recovery of Uranium from Seawater by Using Wave Power and Floating Offshore Units"

D. Gregg and F. Wang

"Lawrence Livermore Laboratory Concept for Uranium Recovery from Seawater"

M. J. Driscoll, J. L. Whaley, C. K. Nitta and F. R. Best

"Practical Constraints on Systems for the Extraction of Uranium from Seawater"

F. R. Best and M. J. Driscoll

"The Effect of System Improvements on Uranium Recovery from Seawater"

With the exception of the paper by Gregg and Wang, all are reproduced directly from texts supplied by the authors. This one paper is transcribed from the tape recording of the presentation (with the permission of the authors, who provided copies of their overhead projector transparencies)

The paper by Bitte, Fremery and Bals was presented in two parts (see Agenda, Appendix A)

Also see Part B of the paper by Denzinger, Schnell, Heitkamp and Wagener in Chapter 3, which describes the system used in their concept.

Recovery of Uranium from Seawater

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Recovery of Uranium from Seawater

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ABSTRACT

Japan depends most of her energy resources on foreign countries. Therefore, nuclear power generation is considered to be very important, but known domestic uranium resources are very rare. Hence, recovery of uranium from seawater has become of interest. To investigate the technical and economical feasibility of recovering uranium from seawater, a research programme has been carried out in the Metal Mining Agency of Japan,since 1975, sponsored by the Ministry of International Trade and Industry. In this programme, selections of the chemical processes, developments of adsorbents mainly on hydrous titanium oxide, the performance of continuous adsorption and elution process, the recovery of eluate by steam stripping or electrodialysis, secondary concentrations of uranium in the eluate by ion exchange or ion flotation etc., some site selections around Japanese coast, the conceptional designs of two types of commercial plants, the "pumping and fixed bed type" and the "direct sea current utilization type" and some tentative cost estimations have been carried out. Though several problems await solution, it has shown that it is technically feasible. Accordingly, the construction of a model plant with a uranium production capacity of about 10 kg/year will be started on October 1980.

INTRODUCTION

For the country like Japan, which has very limited energy resources, the essenciality of the development of nuclear power generation becomes enhanced, and it needs to ensure the uranium resources. If the scale of the nuclear power generation in Japan will increase favorably, the necessary demand of natural uranium

(U_3O_8 equivalent) will reach 3300 t in 1980, 8500 t in 1985, 15 000 t in 1990, 18 600 t in 1995, and 25 500 t in 2000.

To secure uranium supply, various policys like long-term purchase contracts etc. have been taken, however, the price of uranium seems to go up with the recent rise of the oil price and the restriction of the reprocessing of spent fuel by the uranium exporting countries and so on let us feel the necessity of exploiting domestic uranium resources. For this purpose, Japanese exploitation of overseas uranium deposites are being performed, but also the development of the techniques of extracting uranium from seawater which is estimated to be 4 Gt must be considered.

At present, the price of the uranium from seawater is supposed to be considerably higher than that of usual ore uranium, however, with the progress of the tightness of the relation between demand and supply, a rapid rise of ore uranium price is forecast, and seawater uranium will have some possibilities of competing with the ore uranium economically in future. If it is not the case, the percentage of the price of natural uranium among the nuclear power generation costs is as low as several percent, and an appreciable rise of the uranium cost could be easily absorbed in the total power cost.

Some experimental studies of the extraction of uranium from seawater have been carried out since early 1960's at the Japan Tobacco and Salt Public Corporation, Kyoto University, the Shikoku Government Industrial Research Institute, University of Tokyo and others. In 1975, a research programme was started by the Metal Mining Agency of Japan (MMAJ), sponsored by the Ministry of International Trade and Industry, and a considerable progress has been made. Japan has such favorable conditions that it is an island country surrounded by sea, Kuroshio Current is flowing near by, which high seawater temperature is advantageous for uranium adsorption and the current ensure an adequate supply of fresh uranium-bearing seawater and the removal of water that has passed through the plant. This paper attempts to describe the present status of the research on extracting uranium from seawater and identify the problems in satisfactorily designing and operating a demonstration plant in Japan.

URANIUM DEMAND AND RESOURCES

According to the report of the IAEA/OECD, "Uranium Resources, Production and Demand" (Dec. 1979), 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 were not included for USSR, Eastern Europe nor China. The maximum attainable production capacity of uranium shown in Fig. 1 was based on the all reasonably 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. 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 any cases, it indicates that some crossover between uranium demand and production rate will occur between 1995 and 2000. Therefore, some additional 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 seawater.

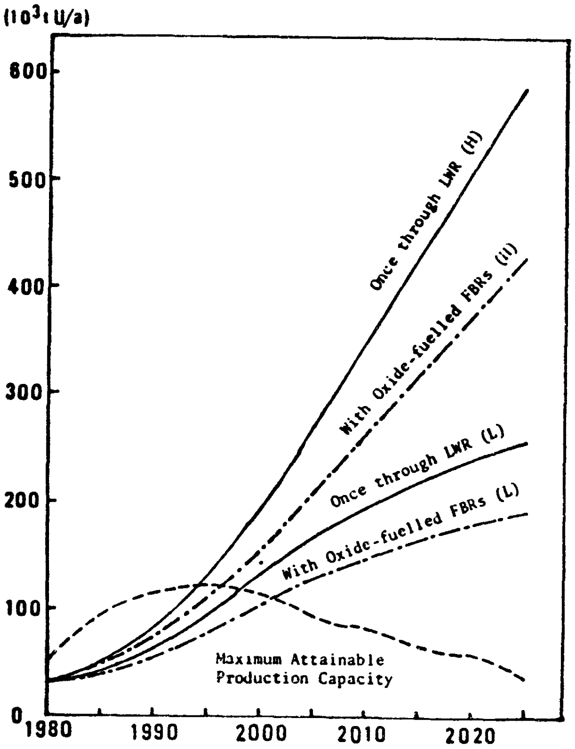

Fig. 1 Annual world uranium supply and demand

THE SEA AS A URANIUM RESOURCE

The concentration of uranium in seawater has been reported to be practically constant and the values have centered around 3.3 ppb. The slight difference of the concentration is said to be dependent on the salinity. The concentration of uranium in the sea near coastal river outflow and nearshore seems to be somewhat diluted. The chemical state of uranium in seawater is considered to be mainly complex form, $UO_2(CO_3)_3^{4-}$ and in dissolved state. It was also shown that less than about 0.1 percent of the uranium is associated with suspended matter.

In order to insure a maximum available supply of uranium, the extraction of uranium must always be done from unscavanged seawater. Therefore, the flushing time should be on the order of the plant's throughput time. This can be accomplished by a current consistently flowing in one direction, not necessary of high velocity. Another means as eddys, tides, waves, and other dynamic movement of the sea can force the mixing, however, the existence of the ocean current is most important. Major ocean currents in the world are shown in Fig. 2 (1)

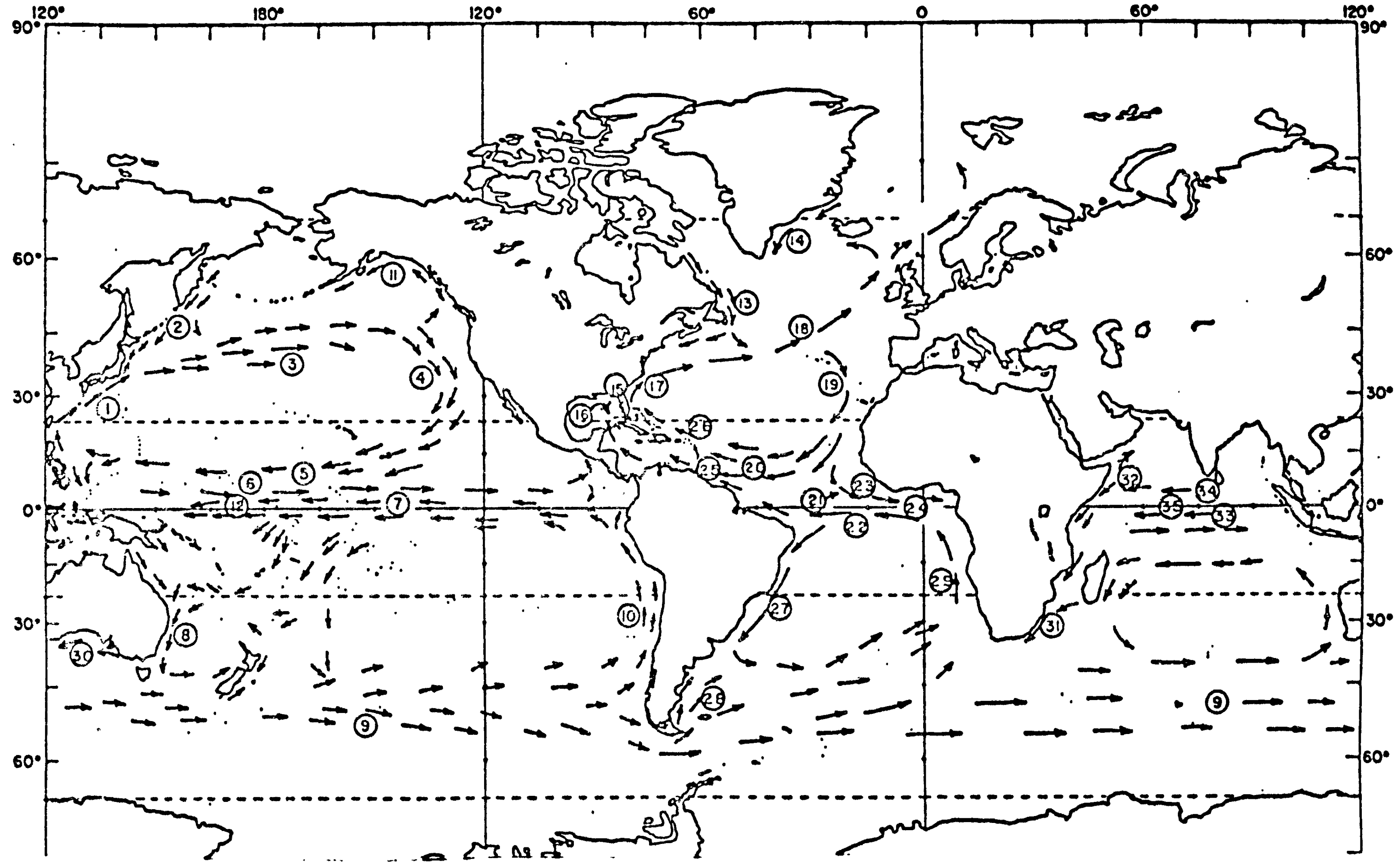

Fig. 2 Major surface currents of the open ocean

Key to current systems shown in Fig. 2

1. Kuroshio
2. Oyashio
3. Kuroshio Extension
4. California Current
5. North Equatorial Current (Pacific)
6. Equatorial Counter Current (Pacific)
7. South Equatorial Current (Pacific)
8. East Australian Circumpolar Current
9. Antarctic Circumpolar Current
10. Peru Current
11. Alaska Current
12. Equatorial Undercurrent (Pacific)
13. Labrador Current
14. East Greenland Current
15. Florida Current
16. Loop Current
17. Gulf Stream
18. North Atlantic Current
19. Canary Current
20. North Equatorial Current (Atlantic)
21. Equatorial Counter Current (Atlantic)
22. South Equatorial Current (Atlantic)
23. Equatorial Undercurrent (Atlantic)
24. Guinea Current
25. Guiana Current
26. Antilles Current
27. Brazil Current
28. Falkland Current
29. Benguela Current
30. Flinders Current
31. Agulhas Current
32. Somalia Current
33. South Equatorial Current (India)
34. North Equatorial Current (India: in summer opposite flowing monsoon current)
35. Equatorial Counter Current

Table 1 Characteristics of Major Ocean Currents and Uranium Resources

Current	Av. Speed (cm/s)	Transport ($10^6 m^3/s$)	Temperature (°C)	Uranium Resources (t/yr)
Kuroshio	125 - 225	50	18 - 26	53×10^5
Kuroshio Extension	125	100	16 - 18	106×10^5
Florida	210 ; 160	34	23 - 25	37.1×10^5
Gulf Stream	110	100	15 - 25	106×10^5
N. Atlantic		35	10 - 15	37.2×10^5
S. Equatorial (India)	10 - 30	40	27 - 29	42.5×10^5
Somalia	70	65	26 - 26.5	69×10^5
Agulhas	70	80	22 - 25	86×10^5

As seen in Table 1 (1), the advantage of Kuroshio current is clear. Another important factor is the temperature of the sea water. Theory and some experimental work indicate that warmer temperature increases the efficiency of uranium extraction. The whole year average seawater temperature distribution around Japan is shown in Fig. 3. In this respect, Japan is also favorable to extract uranium from seawater.

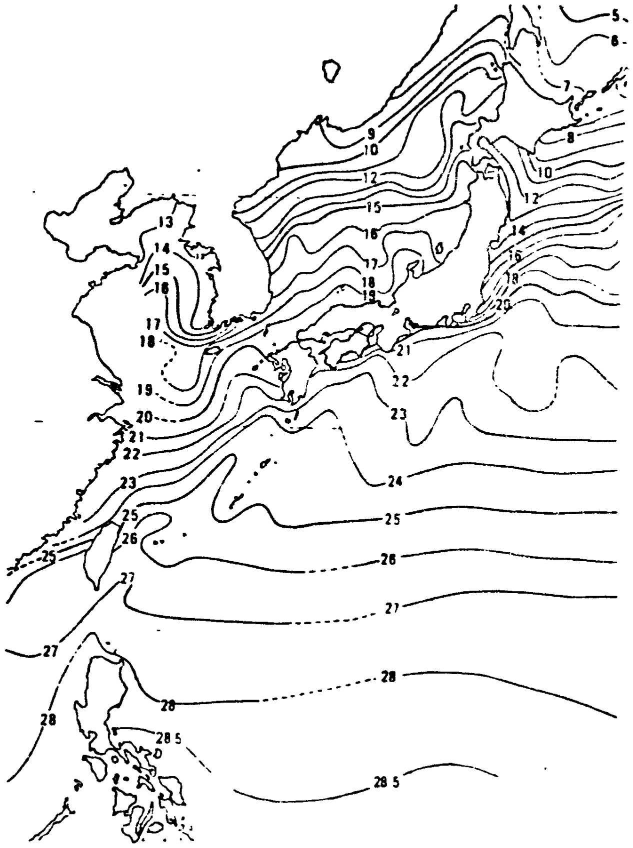

Fig. 3 Whole year average seawater temperature map around Japan

CHEMICAL PROCESS SELECTION

As the uranium in the seawater is in a strongly complexed form at extreme dilution in the presence of relatively high concentrations of such other ions as Na, Mg, Ca, Br and so on, it is considerably difficult to extract uranium from seawater economically. Various chemical processes which are considered to extract uranium from seawater are listed in Table 2. Some coagulation and coprecipitation methods were investigated by Ishibashi (2), Ogata (3) and Yamabe (4) in Japan, but the long precipitation times involved in this process are not suitable for the large volume flow rates of seawater. Adsorption with hydrous titanium oxide (titanium hydroxide or titanic acid) was much investigated (5) (6) (7) and is still thought to be the best adsorbent at present. Some details will be described later. PbS or galena showed some good adsorption capacity (8) (9), 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 uptake, but it was later found that its capacity was deteriorated in seawater (8). Recently, various kinds of chelating resins (10)(11) cyclic polyethers (so called crown ether), macrocyclic hexaketone etc. are being investigated. However, these seems to be still in the initial stages.

Though some flotation methods have been investigated (12)(13) these methods are not suitable because of the necessity of changing the pH of the seawater to acidic side.

Solvent extraction, although feasible, any suitable solvent has not been found because solvent losses by entrainment and solubility would make it prohibitively expensive.

Technique		Representative Materials	Criterion					
			Capability of Contacting with large volume of Seawater	Stability of Materials	Cost of Materials	State of Materials	Uranium Yield	Total
Co-precipitation		$Fe(OH)_3$,(2)(3) $Al(OH)_3$,(3) $Ti(OH)_4$(3), $Ca_3(PO_4)_2$(4)	△	○	○	×	○	×
Adsorption	inorganic	$TiO_2 \cdot nH_2O$,(5)(6)(7) PbS(8)(9) Basic Zinc Carbonate(8) Lead pyrophosphate(8)	○	○	○	○	○	○
	organic	condensation product of formaldehyde and resorcinol(8) Chelating resins(10)(11)	○	△	—	○	○	△
Flotation		$Fe(OH)_2$ and dodecyl sodium sulfate(12) Lauryl amine acetate(13)	△	△	—	×	○	×
Solvent Extraction		DBP, TBP(8)	△	×	×	△	○	×
Biological		Green Algae(14) Chlorella(15)	○	○	—	△	△	△

Table 2 Chemical process selection criteria

In the Nuclear Research Center Jülich, the extraction of uranium with mutated and selected algae was investigated (14). Some methods with chlorella were also studied in Japan (15). However, there is some problems of contacting these microorganism with seawater and their collections.

ADSORPTION BY HYDROUS TITANIUM OXIDE

Various kinds of preparation of hydrous titanium oxide including neutralization method, urea method and thermal decomposition method have been tested, and the urea method gave the best adsorption capacities and stabilities. According to the urea method, urea solution is added to a well stirred solution of titanium sulfate. The dense flocculent precipitate of hydrous titanium oxide is then washed, filtered and dried at appropriate temperature. 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 1600 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 agitating granulation, were carried out. The amount of uranium adsorption follows the Freundlich's adsorption isotherm. The uranium adsorption curves by fixed bed columns for two different average particle sizes obtained by MMAJ are shown in Fig. 4.

The adsorption capacity decreases markedly with increasing the

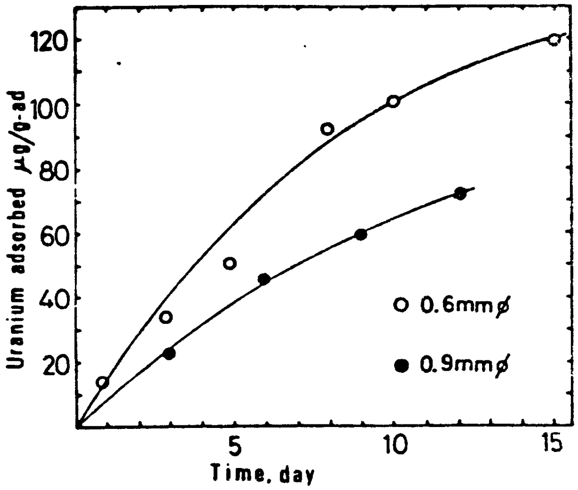

Fig. 4 Uranium adsorption curves by fixed-bed columns

granulating pressure, but appropriate pressure is needed to maintain some mechanical properties. Several kinds of binder, inorganic and organic, have been tested, however, the addition of binder usually decreases the adsorption capacity. When the granular adsorbent is used, it was shown that the adsorption capacity was proportional to the reciprocal of the granule radius as shown in Fig. 5. The effect of the temperature of the seawater on the adsorption of uranium was found to be conspicuous, as shown in Fig. 6. Therefore, we can't evaluate the capacity of the adsorbent without considering its particle size and adsorption temperature.

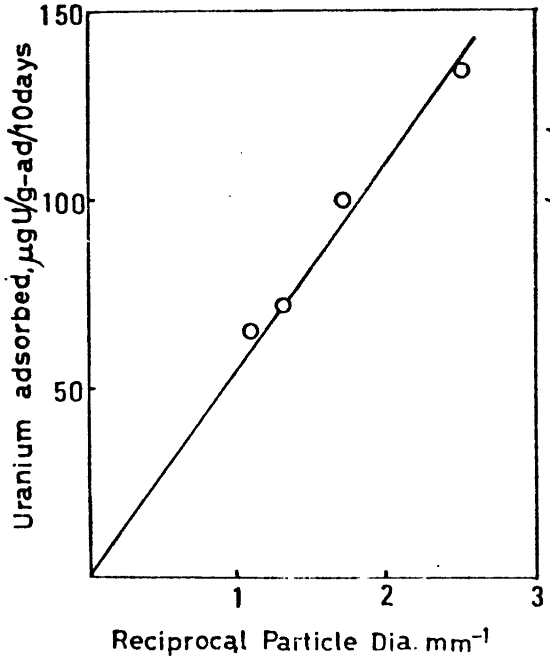

Fig. 5 Effect of adsorbent particle sizes on uranium adsorption

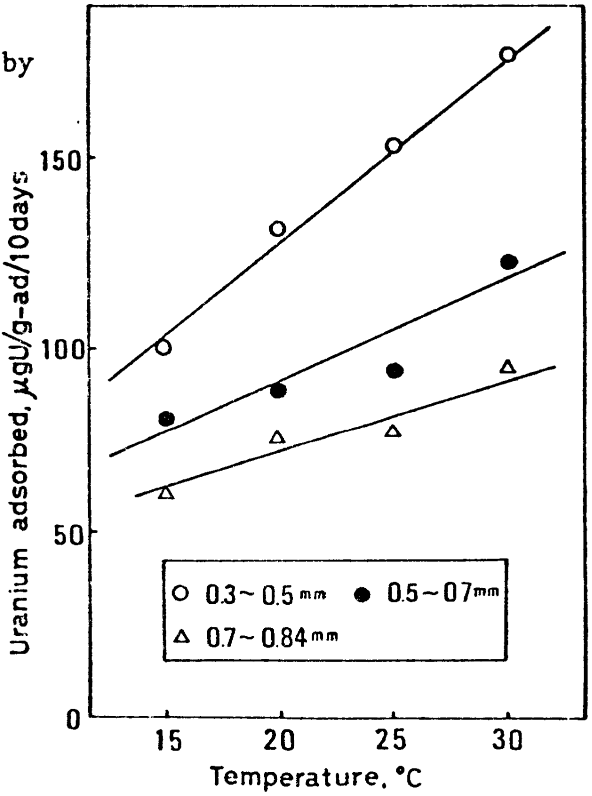

Fig. 6 Effect of temperature on uranium adsorption

ELUTION AND SECONDARY CONCENTRATION

In order to elute the uranium adsorbed on the hydrous titanium oxide adsorbent with concentrated acids causes granule breakage and dissolution of adsorbent, and the elution rate with low concentration acids has been slow. Therefore, ammonium carbonate was chosen as an eluant. For estimating the elution rate, some experiments with column were carried out with 1.0 N ammonium carbonate solution. It needed more than 48 hrs for eluting more than 90% of the adsorbed uranium at room temperature.

Prewash process is thought to be necessary to remove residual seawater containing calcium and magnesium that would otherwise precipitate during elution with ammonium carbonate solution. Such precipitation reduce the adsorption capacity for reuse. At least five bedvolumes of fresh water were found to be needed. Postwash process is also necessary for improving the uranium and carbonate recovery and preventing the deposite of calcium and magnesium carbonates.

The relatively expensive carbonate must be recovered for the recycle and for reducing the pH of the eluate for the following uranium recovery processes, and some experiments of steam stripping were carried out. According to the experiment with initial ammonium carbonate concentration of 1.1 mole/l, and outlet ammonium carbonate concentration of 0.1 mol./l, the heat efficiency of 82.3% was obtained, which showed that 0.387 t/m^3 (in terms of 7 kg/cm^2G steam) of steam was required to reduce the concentration.

Recently, by the view point of the reduction of waste effluent treatment of the ammonium carbonate processes, sodium carbonate and sodium bicarbonate solutions have been chosen as eluant. In these cases, the electrodialysis by using ion-exchange membranes has been studied. According to the experiments with 10 monovalent-ion-selective ion-exchange membranes of a effective area of 1 dm^2, employing a 1 mole/l sodium bicarbonate solution and circulating a 0.2 mole/l sodium bicarbonate solution in the concentration chamber, and applied voltage of 35 V, the concentration of uranium in the mother chamber was kept almost constant and apparent current efficiencies were 86.8% in the mother chambers and 73.2% in the concentration chambers.

The concentration of uranium in the eluate is the order of 10 mg/l as compared with that in the conventional ore leach solution which is the order of several grams per litre, and it is necessary to increase the concentration to use the conventional refining processes. The process is called the secondary concentration. For this purpose, the ion exchange method and the flotation method gave good results. For example, 1000ml of anion exchange resins were filled in a column with a diameter of 5 cm and 211 l of the eluate from the hydrous titanium oxide adsorption process with 0.1 mole/l ammonium carbonate and

13 mg/l of uranium were passed through the column with a specific velocity of 5 BV/min. The eluting solution was 1.84 l of 3 mole/l ammonium carbonate. As the result, the concentration of uranium in the final eluting solution reached 1.39 g/l and 93.1% of the recovery was obtained. According to the two step flotation experiments with surfactant of Zonyl-FSP for the first step and sodium laurate for the second step, 251 g of froth with 0.725% uranium was obtained from 150 l of primary eluate containing 13 mg/l uranium, and the recovery was 92.8%.

CONCEPTUAL DESIGN OF PRACTICAL PLANT

Several adsorbents and seawater contacting structures have been considered, and the conceptual designs of two types of commercial plants, the "pumping and fixed bed type" and the "direct sea current utilization type" have been carried out.

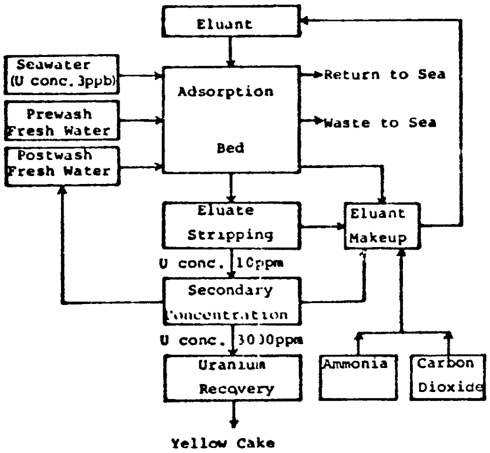

Fig. 7 Flow diagram of "pumping-fixed bed system with eluant of $(NH_4)_2CO_3$

Pumping and fixed bed system

The flow diagram of the pumping and fixed bed system is shown in Fig. 7. This system is thought to be most realistic because much experimentally approved conditions have been established. Some basic conditions of this system are shown in Table 3. A sketch of the conceptual design of this concept with the capacity of 1000 t U/y is shown in Fig. 8. The preliminary design showed that it needs 467 pumps of 80 m^3/s capacities, the siting of the total, 8.8 km x 130 m, electric

Table 3 Basic conditions of pumping-fixed bed system

1. Annual uranium production	1000 t-U
2. Concentration of uranium in seawater	3 ppb
3. Adsorption recovery	60%
4. Adsorption structure	Fixed Bed, multi-layered
5. Adsorption-elution cycle	10 days/2 days
6. Adsorbent	$TiO_2 \cdot nH_2O$
7. Adsorption capacity	200 μg-U/g·ad./10 days
8. Bulk Density	1.0 g/cm^3
9. Linear flow rate of seawater	60 cm/min
10. Granule size	1 mmϕ
11. Adsorbent loss	0.1 %/cycle
12. Bed thickness	10 cm
13. Elution recovery	95%
14. Elution temperature	Room temperature

15. Eluting solution	1 M $(NH_4)_2CO_3(NaHCO_3,Na_2CO_3)$
16. Uranium concentration in eluate	10 ppm
17. Decarbonation method	Steam stripping(Electrodialysis)
18. Secondary concentration	Ion exchange(Ion flotation)
19. Concentration recovery	95%
20. Final concentration of uranium in solution	3000 ppm

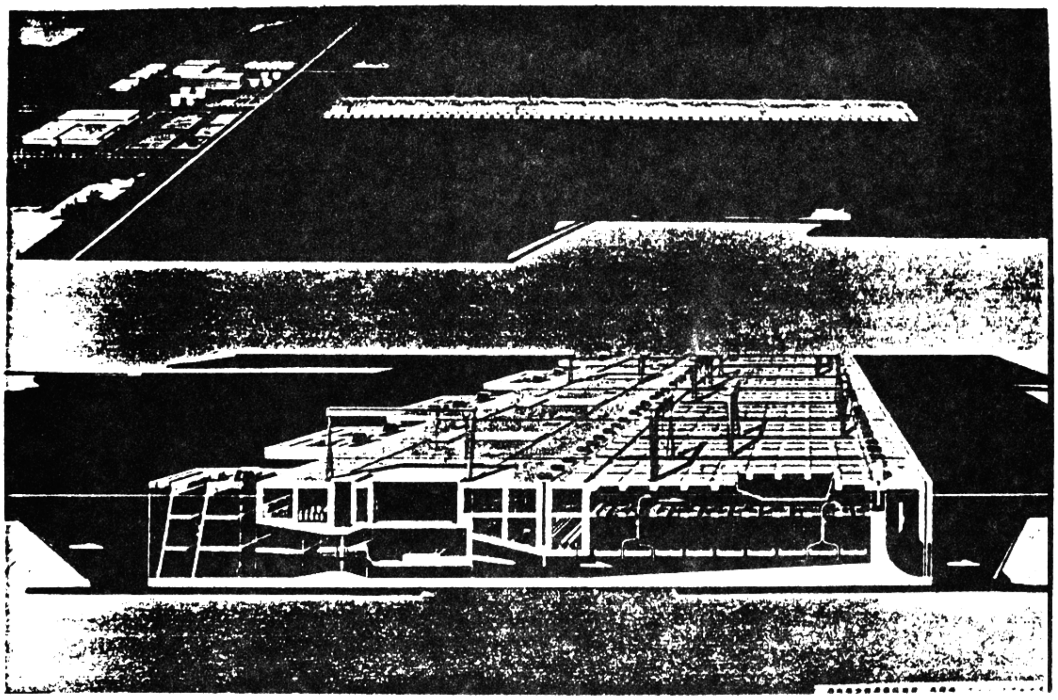

Fig. 8 Concept of "pumping and fixed-bed system"

power of 670 MW for the pumping, and 250 000 t of adsorbents, assuming 50% of adsorption efficiency and 80% of elution and secondary concentration efficiencies. The necessary fresh water for washing the adsorbent was 26 x 10^4 m^3/day.

Later, it was thought to be able to use 500 m^3/s pumps instead of 80 m^3/s pumps, the necessary number of the pumps was reduced to 60 for the recovering efficiency of 60%. The plant design shown in Fig. 8 is based on the latter conditions. The required electric power was also reduced to 570 MW. The pumps are arranged to be breakwater type and the total length of the structure is 3.8 km and the width is 254 m. In all these cases, the multilayer fixed beds with adsorbent were used.

Sea current direct utilization system Another concept was the sea current direct utilization system. Many marine structures with many fixed bed adsorption stacks immersed in the seawater are constructed in possibly flat offshore sea-bed, where the constant sea current is

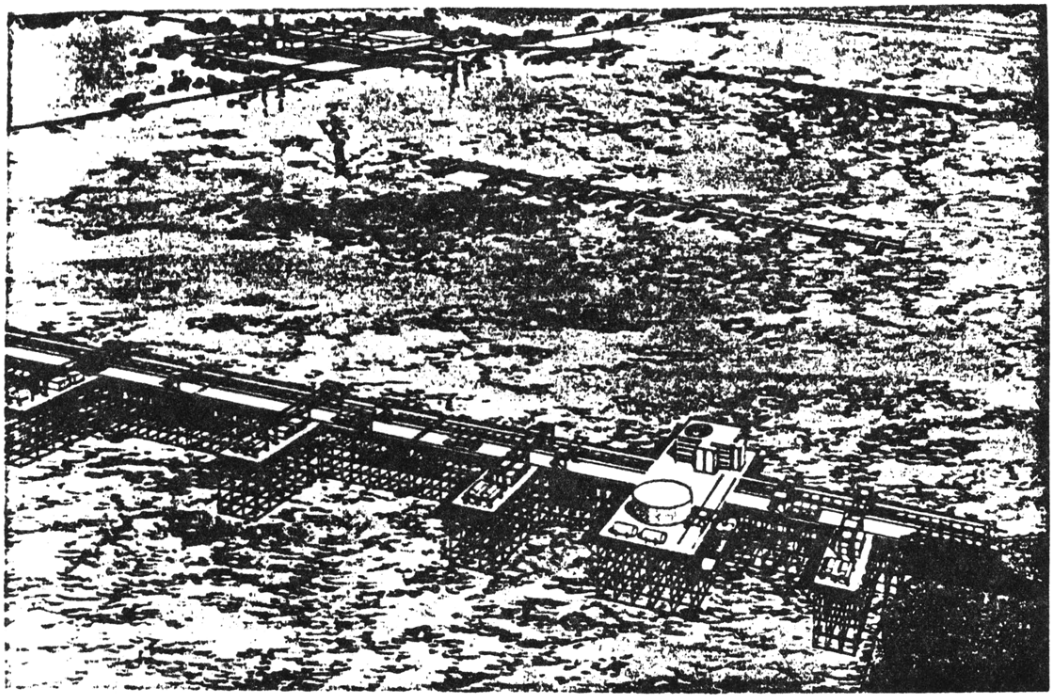

Fig. 9 Concept of "Sea current direct utilization system"

flowing. The sketch of the system is shown in Fig. 9. One adsorption stack is composed of three 5 m x 5 m x 5 m adsorption blocks. These stacks are held in one unit of 17.3 m in width, 45 m in height and 1.7 km in length and it is built in the sea at the depth of 35 m.

Each unit has several substations where the adsorption blocks are brought in and the elution is performed. The unit has one station with two tanks for eluant and eluate storages. The loaded eluate is transported to the processing plant onshore through the sea-bed pipelines. For the production rate of 1000 t U/y, 20 sets of the unit were needed and arranged in a zigzag type and the occupied area might be 5.5 km x 5.5 km.

COST ESTIMATIONS

The cost of the extraction of uranium from seawater is much dependent on the systems and also there are much uncertainties. So, it is only a presumption. According to the Exxon's report (16), for the pumping and fluidized-bed system at Puerto Rico, the uranium production costs from seawater have been estimated to be $ 2614/lb U_3O_8 (1995 price) and $ 1436/lb U_3O_8 (1978 price). Even in the hypothetically best conditions, the cost may be $ 845/lb U_3O_8 (1995 price) and $ 475/lb U_3O_8 (1978 price).

However, these costs are based on the adsorption capacity of about one quarter of our projected capacity with the relatively low seawater

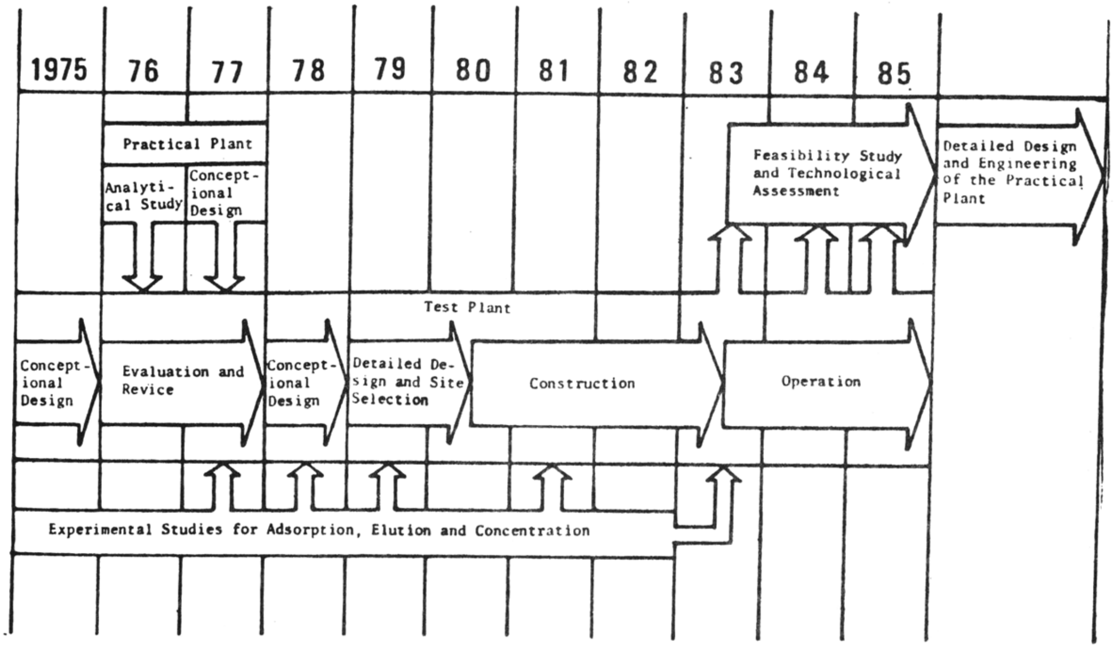

Fig. 10 Development schedule for extraction of uranium from sea-water in Japan (It will be changed by the budget)

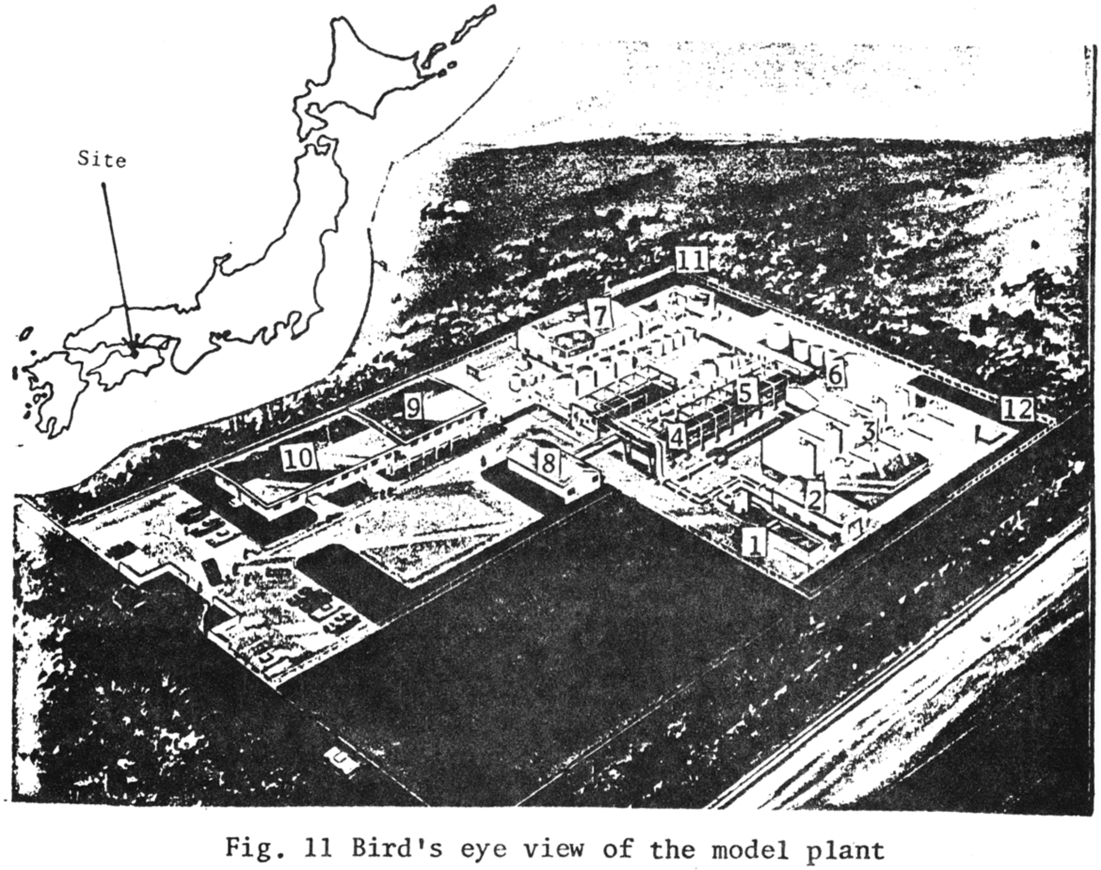

Fig. 11 Bird's eye view of the model plant

1. Intake Cell 2. Pump Room 3. Sand Filter 4. Adsorption Cell
5. Elution Cell 6. Experiment Room 7. Concentration Room
8. Storage 9. Analysis 10. Administration 11. Waste Water Treatment
12. Effluent Cell

linear flow rate of 24 cm/min compared with our 60 - 80 cm/min, and especially on the use of single layer adsorption beds instead of our multilayer beds. This results in making the necessary facilities and site larger. We think the cost may be the order of $ 200 - $ 400/ lb U_3O_8.

DEVELOPMENT SCHEDULE IN JAPAN

The research programme for the future include the collection and compilation of basic data for various processes, improvement in unit processes, study of equipment for the plant scale-up, development of plant control methods for long-term stable operation and solutions of problems caused by natural seawater suspension and living creatures and others. Many of these will be carried out by the model plant operations. The long term development schedule in Japan is shown in Fig. 10. The construction of the model plant for producing about 10 kg U/yr. will be started in Fall 1980. The bird's eye view of the model plant is shown in Fig. 11. It will be completed within three years.

CONCLUSIONS

Among various adsorbents, hydrous titanium oxide seems to be most promising at present. Small scale continuous extractions with these adsorbents have been carried out successfully. However, for a large scale extraction, large scale productions of adsorbents, their long term stabilities, some preventions of the blockage of the adsorption bed, systematic studies of the adsorption, elution and secondary concentration, the recycle of the reagent etc. must be investigated. In parallel with these investigations, some exploitations of new types of adsorbents are also desirable.

As the contacting system of adsorbents with seawater, the pumping and fixed-bed system is thought to be most realistic at present, however, some problems remain unsolved. Many experimental and modeling studies of not only the pumping and fixed-bed system but also other various systems must be carried out. Besides, the effect to the environment by processing a large amount of seawater with large scale facilities must be assessed.

Japan is blessed by the Kuroshio Current, and some techniques of extraction of uranium from seawater has been developed. With the completion of the model plant, Japan must promote this programme by the cooperation of the fundamental field of researches with the engineering field.

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Discussion on Prof. Kanno's Paper

Prof. Kanno explained the reasoning behind choice of a 10 Kg U/yr facility for their test program; that this size is needed to provide sufficient material to test the elution and secondary recovery processes. He also opined that the next step should be a 1-10 ton/yr facility, to be considered in several years, followed by a 1000 ton/yr production plant around the year 2000.

Prof. Kanno indicated that in the longer term elution would be done in place, but that some thought was being given to transfering the material in the pilot plant.

He also repeated his estimate of a 200-400 \$/lb U_3O_8 production cost, the range depending heavily on the economic environment assumed. The cost of the 10 Kg/yr test facility is estimated as $\$12 \times 10^6$. Prof. Kanno referred several questioners to his second paper at this conference (which see).

Kanno noted that the Japanese hydrous titanium oxide sorber was currently performing at capacities approximately four times that in the older English work. He felt that this was due in part to the difference in starting materials, in the Japanese case a mixture of titanium and ferrous sulfates from ilmenite, treated with urea (as opposed to others who have frequently used titanium chloride and ammonium hydroxide). The efficiency of the urea-based process is still low, however: about one-tenth of the theoretical yield.

Finally, Prof. Kanno explained that they do not plan to use carbon-impregnated with hydrous titanium oxide -- a material which they have tested in the past -- because of its low capacity per total sorber weight and its poor mechanical strength.

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Uranerzbergbau-GmbH

ON THE UEB CONCEPT
OF
URANIUM EXTRACTION FROM SEAWATER

by

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THE RECOVERY OF URANIUM FROM SEAWATER

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ABSTRACT

The UEB-concept, a (semi-)submersible current driven adsorption unit using fluidized adsorber beds with hydrous titanium oxide (HTO) is introduced. Based on the properties of the HTO adsorber, a design is described for the complete chemical process involved in the extraction of U_3O_8 from seawater. A technically feasible procedure to manufacture the adsorber is also given.

1. INTRODUCTION

The research and development work at UEB in the area of "uranium extraction from seawater" is carried out under the sponsorship of the German Ministry for Research and Technology (BMFT).

It began in 1975, when BMFT awarded a research contract to UEB to study and document the state of the art in the field of the extraction of uranium from seawater. This study was finished in the first half of 1976. Already during this investigation UEB began to look at alternative technological solutions to the recovery of uranium from seawater, since the examined technological concepts did not seem to provide a sound basis for an economic large scale industrial production plant.

Thus UEB produced its own concept and received another research contract from BMFT in 1976 with the goal to study the feasibility of a large scale uranium extraction plant on the basis of this UEB concept.

At that time the concept was unprecedented in its characteristic operation principles and had to be based primarily on physical intuition and a great deal of technical imagination.

In the meantime, however, the essential process steps of the UEB concept could be verified through comprehensive hydrodynamic and chemical experiments in the laboratories. Intensive qualitative and quantitative analyses with numerical and experimental optimizations have been carried out and the results were extrapolated to full scale. Because of the many parameters involved, some of the basic investigations are not yet completed and will still take some time in the future. However, all results obtained to date indicate an optimistic and positive overall picture of the concept.

The following paper is intended to introduce this UEB concept, to describe its characteristic features and to show the status of its development.

2. THE UEB CONCEPT

Since the uranium occurs in the sea only in very low concentrations (i.e. 3.3 ppm) - however, in a remarkably uniform distribution - large quantities of seawater have to be processed in a prospective production plant. This represents one important design parameter. Another one arises from the fact, that out of the several possible ways to extract uranium from seawater, the adsorption process is commonly chosen as the most promising at the present time. This means, that the design criteria for a uranium production plant center around the two problems of, first, developing the best and most selective adsorbing system and,secondly,establishing the most economic method of contacting large quantities of seawater with such an adsorbing system.

As to the first problem, it has been found by many independent research groups all over the world, including ourselves, that granulated hydrous titanium oxide (HTO) is probably the best choice of the many different adsorber materials tested in recent years. Besides this, only organic ion exchange resins seem promising. For this reason, the HTO adsorber has been adopted for use in the UEB concept and later in this paper you will hear more about the stage of its development.

With respect to the second problem Fig. 1 (see appendix) may illustrate the enormous flowrates of seawater to be processed. One can see that they depend solely on the efficiency of the adsorption and elution cycle, once the production rate of the plant has been fixed. In search for the most economic method of handling these large quantities the UEB concept is aimed at utilizing the natural ocean currents to transport the seawater through the adsorption chambers. In addition it was realized that these adsorption chambers had to consist of fluidized beds with freely moving granulated adsorber particles of suitable size to ensure a high adsorption probability at a minimal energy consumption. Therefore the UEB concept may be characterized as a current driven, fluidized bed HTO adsorption system. Other characteristics are listed in Fig. 2 and will be discussed in greater detail during the course of this presentation.

In the following paragraphs the operating principle of the UEB design shall be explained. A key role in this concept is played by the adsorption module shown in Fig. 3a. It consists of a diffusor, a settling chamber and the fluidized adsorber bed. Its operational mode is illustrated in Fig. 3b. The kinetic energy contained in the oncoming ocean current is caught in the diffusor and is converted - by deceleration of the flow - into a static pressure gain.

This static pressure gain is then used to overcome the resistance imposed on the flow by the adsorption bed and the supporting perforated plate underneath. Or, in other words, the kinetic energy of the ocean current is utilized to fluidize the adsorption bed and to keep the adsorber granules suspended and freely moving in the vertically deflected sea current.

Several of these adsorption modules are then connected and arranged as shown in Fig. 4 forming a huge wash-board like adsorber bed area which constitutes the main part of the UEB uranium extraction concept. Another key feature within this concept, which was already pointed out in Fig. 2, is the possibility of an economic transverse transport of the adsorber granules within the adsorber bed. The fluidized adsorber behaves like a fluid with somewhat increased viscosity, allowing the adsorber granules to migrate from the feeding to the discharge stations at right angles to the flow (see Fig. 5). This transverse or horizontal transport together with the diffusor-fluidized bed combination permits to take the entire process energy required for the adsorption from the ocean current.

However, it shall be pointed out here that the economic advantage of this concept does not only lie in the energy saving as compared to an actively pumped system, but also and even to a greater extent, in the much lower investment and maintenance costs due to the greater simplicity of the concept.

Continuing in the overall production plant lay out, the staggered adsorption modules are then suspended from a main carrier unit, housing the rest of the chemical extraction apparatuses as the elution and concentration installations. A variety of possible carrier units as for example shown in Fig. 6 has been investigated to date. However, the configuration shown in Fig. 7 is believed to be the most promising, most economical and most elegant solution. It has been investigated in more detail in the past and has been critically examined especially from marine technological viewpoints. We will report on the outcome of these investigations at a later date. It is intended that such an adsorption plant be moored in a natural ocean current, preferably 30 - 40 m beneath the sea-level to minimize surface wave effects and to avoid regions with higher water impurities.

Intensive experimental hydrodynamic tests have been carried out by the Institute for Aeronautical and Aerospace Engineering (ILR) of The Technical University of Aachen. Four staggered adsorption modules were investigated in a towing tank with and without wave motion (see Figs.8 and 9). The results were very favorable and will also be published at a later date.

It was learned from experiments, such as the above, that an ocean current with a velocity of 1.3 to 1.4 m/sec. would be sufficient to fluidize the adsorber beds in the adsorption modules. This offers a variety of ocean currents to be used for uranium extraction purposes. Since the adsorption efficiency sharply increases with water temperature, the warmer ocean current, such as the Gulfstream, are to be preferred. A typical example of ideal conditions in that respect is given in Fig. 10 for the Florida current.

3. THE CHEMICAL PROCESS

Although in principle our plant design is considered to be independent of the kind of the adsorber used, its process design described here was determined by utilization of hydrous titanium oxide HTO-gel as the adsorber material. In spite of the fact, that this gel has a lower adsorption capacity towards uranium than organic adsorbers, it has the considerable advantages of being available in large quantities at relatively low costs and has acceptable marine-ecological properties - including the kind of elution media incorporated in the adsorber unit.

The chemistry of the adsorption/desorption (elution) process for uranium utilizes the well-known equilibrium which depends upon the carbonate ion concentration:

$$(-O)_2Ti(OH)_2 + \left[UO_2(CO_3)_3\right]^{4-} \rightleftharpoons (-O_2)TiO_2UO_2 + CO_3^{2-} + 2\ HCO_3^{-}$$

The hydroxy groups of the $TiO(OH)_2$ matrix can be considered to be the active adsorption centres, whereby the labile protons on the HTO-surface are exchanged for uranyl cations (as well as other metal cations) after cleavage of the uranyl carbonate complex anions which are present in seawater. The increase of the carbonate concentration leads to the reformation of the uranyl carbonate cations and the free HTO.

This phenomenon forms the basis for the elution of uranium from the adsorber employing alkaline, saturated carbonate solutions.
The complete process involved is represented by the following scheme (Fig.11):

Besides the adsorber-manufacture and the final precipitation of U_3O_8 from the uranyl carbonate concentrates, all processing steps are employed within the submerged adsorption unit.

The operational procedures for these steps are determined primarily by the throughput quantity of the adsorber in the elution stage, the conditions at the site of operation, the ecological tolerance prerequisites and last but not least the operational costs.

The throughput quantity of all process-flows is necessarily dependent upon the properties of adsorber employed (see summary) and the desired production capacity of the submerged adsorber unit.

Properties of the adsorber:

Composition:	hydrated titanium oxide gel, 50-54 % H_2O, remainder: TiO_2	
Particle size :	1.5 - 2.5 mm (cylindrical, Ø = L)	
Bulk density (in seawater):	0.88 g/ml	
Particle density:	1.47 g/ml	
Adsorption capacity:	250 ppm U_3O_8 (max.)	(Objective with
Elutable quantity:	200 ppm	particle size 1.5 mm)
Adsorption period:	20 days	
Elution period:	7 hours	
Eluant:	1.5 mol $NaHCO_3/NaCO_3$ in partly desalinated seawater	

The type of HTO particular suitable for application in the process which we have developed is obtained by alkaline precipitation of an aqueous solution of either titanium oxichloride in hydrochloric acid or titanium oxisulphate in sulphuric acid under specific conditions. These conditions are chosen such that a salt-free HTO-gel can be reproducibly obtained.

The actual starting material for the above mentioned titanium oxi-salt solution is the widely occuring, readily available mineral, Ilmenite, which is a mixed oxide of iron and titanium. The mineral is preferably broken down by sulphuric acid treatment and the resultant titanium oxisulphate solution is purified simply by precipitation methods via titanium dioxide.

Currently the use of primary ore solutions containing up to 10 % iron sulphate are being investigated to see if a cheaper starting material can be employed for the manufacture of adsorber which, as we shall see, has to be used in quite considerable quantities.

After obtaining the HTO-gel by precipitation and subsequent sedimentation washing and filtration, the gel solidification and pelleting are carried out simultaneously.

The HTO is unstable in acidic media; progressive cross-linking via oxigen bridges occurs with elimination of water, resulting in gel contraction. The cross-linking leads on the one hand to increased internal chemical stability (which can theoretically lead to the formation of anatase), but on the other hand it causes a reduction of the hydroxy groups necessary for the ion exchange activity.

Consequently it is necessary to find a compromise between the adsorber exchange capacity and the pellets' mechanical stability and density.

Our experiments have shown that the minimum value of the water content of the gel is about 45 % H_2O (based on TiO_2). Generally we limit the autogenous acid-catalyzed internal dehydration to 50 % H_2O by exchanging protons with sodium ions; thus the alkalinity of the storage solutions is raised to and held at pH 8.5.
For completeness it should be mentioned that the HTO adsorber must be stored in water continuously.

The pellet-forming process strongly influences the adsorption effectiveness of the adsorber. Numerous experiments were undertaken to investigate the technically feasible possibilities for the cheap mass production of the adsorption pellets and currently cylindrical form pellets are favoured. These can be produced at relatively low cost (at little technical means) by either press moulding or extrusion of the acidic gel paste, which is obtained at pH 6 and has a water content of approx. 80 %, followed by air drying to give an irreversible water content of 50 % by subsequent storage in aqueous sodium carbonate solution. Corresponding developments for subsequent large-scale production are currently under consultation with industrial manufacturers, well experienced in the technical scale handling of inorganic oxide pastes.

As mentioned before the typical pellet shape has a height to diameter ratio of 1.0 at a height of 1.5 mm. The correct pellet size is to some extent determined by the conflicting demands of the chemical engineer and the designer of the construction of the submersible adsorber bed. Fig. 12 shows a gross simplification of the dilemma in the relation between the HTO pellet size and adsorption capacity:

As previously indicated we are satisfied within the design proposal presently with an uranium adsorption content of 250 ppm based upon the weight of the adsorber. Experiments which have been carried out at Fowey Rocks, in the biological laboratories on Heligoland and also on the adsorber float of the GKSS research centre showed that optimal loading is already achieved within a maximum of 20 days as demonstrated in Fig.13 for HTO.

The most economically viable period for adsorption has yet to be determined.

Other problems pertaining to the development of the adsorption process are:

1. Improvement of the adsorption capacity
    1.1 by adding oxides or sulphides of certain transition metals before coprecipitation
    1.2 by increasing the surface area of the pellets
2. Improved selectivity towards uranium
3. Long-term recycling procedures
4. Biostability

For the continuance of the experimental investigations it was necessary to carry out further experiments mainly at the experimental station at Fowey Rocks in the Florida Current and at the BAH on Heligoland. Fig. 14 shows the typical experimental equipment applied at both stations.

The fluidized bed is clearly distinguishable in the adsorber column,shown in Fig. 15.

Prefiltered seawater (20° - 28°C) with a flow rate of 3 cm/sec - equivalent to that for a large scale plant - is passing upwards through the adsorber bed which has a bulk density of 0.88 and exhibits a swelling factor of 1.3.

Fig. 16 shows again a typical HTO adsorber pellet which is used in the Heligoland plant.

Fig. 17 shows the same pellet after an adsorption period of 30 days.

Having discussed the problems associated with the adsorption process the design of the adsorber unit will now be discussed:

For a projected production capacity of 150 tons p.a. of U_3O_8, 8.3 tons must be extracted within the previously mentioned adsorption period of 20 days. Since the elutable fraction recoverable from the adsorber contains 200 ppm of U_3O_8 (based on the weight of the adsorber) it is necessary to circulate a total of 42,000 tons (48,000 m^3) of adsorber per 20 days cycle, that is eighteen times a year.

This is equivalent to an hourly plant throughput of 100 m^3 of adsorber. At the same time a five-fold volume of the eluant solution - 500 m^3 - is used for the recirculation.

The adsorption plant consists of two rows of nine adsorption modules arranged in the pre-described stepwise fashion indicated in the diagram, each bed is 24 m wide and 150 m long and is positioned lengthways across the current flow. Each of these eighteen independent modules is connected to an adsorber elution unit; these are each constructed to take a circulating throughput of 5.6 m^3 of the adsorber with 28.0 m^3 of eluant solution per hour. The elution units consist again of several elution columns which are connected to the corresponding bed module such that during the operations of charging and discharging the adsorber, the adsorber bed is transferred across the direction of flow of the seawater.

The rate of adsorber flow through the adsorber bed , the column-charging times and the elution times are all determined by the uranium adsorption time, i.e. 20 days for 2 x 150 m at a speed of 0.6 m/h (Fig. 5).

The duration of the complete elution procedures are shown in Table 1.The process is divided into four steps, each of differing time requirements.

Table 1

Duration of one complete elution cycle per column:

Charge of column with adsorber	5 min
Elution of adsorber	420 min (7 h)
Washing of adsorber	50 min
Discharge of adsorber	5 min
Total time required	8 h

Since a total of 8 h is required between the charging and discharging of the 5.6 m³ of the adsorber, eight elution columns, each 12 m long with an internal diameter of 0.8 m are required for an elution unit in order to maintain the quoted 5.6 m³ hourly throughput of adsorber per module (Fig. 18):

For the elution, the loaded adsorber pellets together with the water required for fluidization are drawn into the seawater filled elution column from the fluidized bed module by means of a seawater conveyer pump; the displaced water is expelled.

The operation of this conveyer pump, together with the valve groups and the screen-"Butterfly" is operated automatically for filling and discharging the elution columns by means of seawater as a hydrodynamic transport medium.

The eight columns of one elution/adsorption - unit (which again is one of the total 18 units in the submersible) are positioned in the lower stabilization section of the submersible - central hull as shown in the following diagram for one column (Fig. 19):

This cross-sectional part should only present a scheme of the elution arrangement which is integrated into two process- loops or -cycles:

1. The adsorber pellets / seawater cycle by means of the conveyer pump and the valve groups. Each of these loops is connected to one adsorption column.
2. The elution cycle through several or all of the elution units. This is operated from the central pumping system (Fig. 20):

   Each of the adsorption columns is connected via a pipe network into the cycle through its individual valve group. The valves are controlled by means of a timer system set according to the duration of the elution.

For the technical processes described above, various different fludized bed systems may be utilized; however, a high mechanical stability for the adsorber pellets is a prerequisite.

The type of elution plant employed is determined fundamentally by the adsorber/eluant system involved. In this case the adsorber consists of cationic loaded hydrated titanium oxide with a U_3O_8 content of approx. 250 ppm, whilst the eluant consists of a partly desalinated, saturated, aqueous solution of $NaHCO_3/Na_2CO_3$ (ratio 1:1.5) at pH 9.5. This solution contains a residual uranyl carbonate content of $\leq$ 20 ppm.

The desorption characteristics of the system are such that the uranyl carbonate concentration may be represented as a function of the throughput quantity of the eluant (Fig. 21):

This shows that the eluant solution which passes through the adsorber bed (five-fold the volume of the adsorber bed) contains the highest concentration of uranyl carbonate in the second and third volume fractions (volume fraction = adsorber bed volume).

Accordingly these eluant fractions are separated from the remaining eluate in a volume ratio of 1:2.5 and then they are concentrated further by membrane permeation (R.O.). In the remaining eluate fractions (the larger part), the uranyl carbonate concentration tails off to a low value and this part of the eluate remains in the elution cycle. The first volume fraction of the elution unavoidably contains seawater from the filling procedure. It is displaced by the actual eluant solution and pumped away.

The elution is complete when five bed volumes of the eluant plus a bed volume of rinse water have been passed through the column bed.

The permeated solution with its residual uranium content collects behind the R.O. membrane during the concentration of the eluate and is returned together with partly desalinated seawater to make up the original volume into the elution cycle. Addition of NaOH and CO_2 is required to bring the solution back to a pH value of 9.5 and its original carbonate concentration.

During the elution, a suspension of calcium and magnesium carbonates forms in the eluate. The pellets adsorb Ca und Mg ions form the seawater which dissociate from the gel matrix during elution and due to the high carbonate concentration precipitate as carbonates. The suspended material is removed from the eluate solution and from the recycle solution by filtration. The resultant sludge is filtered under pressure to remove water, pressed into blocks and then deposited on the sea-bed.

After a fourth or fifth cycle (80 - 100 days) an - under elution condition - irreversible build-up of Ca and Mg ions occurs within the $TiO(OH)_2$ adsorber matrix, which reduces its adsorption capacity for uranyl ions. Therefore a regeneration of the adsorber after every fifth cycle is necessitated; regeneration is carried out by treating the pellets in the elution column after the washing stage with dilute hydrochloric acid until the circulating solution maintains a pH value of 5 for one hour.

This regeneration should not require more than 8 h, after that the adsorber is transferred back ot the fluidized bed.

The fractions of the eluate containing the highest uranium concentration (200 ppm) are further concentrated prior to precipitation (Fig. 22).

This is effected by employing three successive R.O. modules fitted with special membranes, each of which has to achieve a retention of $\gg 80$ % of the uranyl carbonate complex anion at a maximum working pressure of 10 bar and a 1:6 concentrating rate. A prerequisite for the effective function of the R.O. is an input solution free of suspended $CaCO_3$ and for this purpose each module is fitted with a filter. The final concentrate from the third module, with a uranyl carbonate content of >2 %, is transferred from the submersible ashore for precipitation of Yellow Cake.

The permeated solution contains the major part of the remaining ions, Na^+, HCO_3^- and Cl^- being present in the predominant concentrations. This solution is regenerated by addition of NaOH and CO_2 such that the $NaHCO_3/Na_2CO_3$ content reaches the 1,5 M concentration necessary for reuse. (Analogously, the $NaOH/CO_2$ addition to the recycle current in the elution is also necessary since Ca/Mg CO_3 precipitation occurs). The regeneration is controlled through monitoring the pH value of the solution.

The repeated recycling of the permeated solution leads to a build-up of an extraneous metal ion concentration. Consequently a purge of the recycle stream is unavoidable; it is replaced by the rinse water from the elution.

In this paper the described process design - beginnung from the adsorption and ending with the final concentration step by the R.O. - has been aligned to the application within a submersible.

The scheme is of course adaptable to any type of adsorption unit based on fluidized adsorber beds - as well to any type of adsorbers - organic or inorganic - which, however, may require different eluant solvents and R.O.-membranes.

The total unit must be designed for automatic operation in order to maintain a minimum of personnel with maximum safety. Thus, no more than 10 technicians per shift - in addition to the staff requirement for maintenance and the infrastructure of the submersible - should be planned.

The total energy-input for the operation of the complete process-units(e.g. conveyer pumps, R.O.pumps, pressure filters, block presses, stirring tanks, M & R-installations, compressors etc.) amounts to 1,5 MWh excluding the other requirements of the submersible.

No particular complications are expected with regard to the choice of material to be applied for the construction of the process units. Here Polythene or PVC as well as PVC-coated steel for the pressurized elution- and R.O. - units appear suitable.

4. FUTURE PLANS

UEB's future plans for the development of a production plant are based on the assumption that due to the increased demand for uranium in the future, the new technology should be available in the first decade of the new century. This requires that a full scale demonstration plant needs to be in operation by this time (comp. Fig. 23) and that a reduced scale pilot plant should be designed and put into operation in the nineties. Before this time a couple of experiments in a semi-technical scale should be prepared and carried out as far as the UEB concept is concerned.

In the direct future, i.e. within the next three years, UEB plans to test a free floating single adsorption module in the marine environment of an actual ocean current. The unit - called MOD. 1 - shall have an adsorber bed area of $F = 50\ m^2$ and shall produce $\mathring{U} = 10$ kg of uranium during 75 days of continuous operation. Total weight is estimated at about $W = 55$ t including 15 t of adsorber. Fig. 24 shows a cross-sectional view of MOD.1 and in Fig. 25 the proposed mooring system of MOD. 1 behind a supply ship is indicated.

5. ECONOMIC ANALYSES

Ever since the idea was born to extract uranium from seawater a variety of analyses have been carried out to estimate the economy of the extraction process. Some of the better known analyses are listed in Fig. 26. It can easily be seen from this summary that there exists quite a difference in opinion about the possible uranium production costs, ranging from 11 to

1400 \$/lb U_3O_8. This considerable span underlines the difficulty and the uncertainty of such analyses and points out how cautious their results have to be interpreted. It is very difficult, almost impossible, with simple means, to compare different production methods objectively because of varying assumptions, different simplifications and boundary conditions underlying each individual ease.

Under these circumstances the goal of such an analysis may not primarily be seen in the prediction of the correct price for a certain production method on an absolute scale, but more on a relative basis, allowing to pinpoint and improve the cost-intensive steps within a certain production method.

In this sense we have carried out a sensivity analysis of the uranium production costs for the UEB concept (see Fig. 27). In four alternatives (I-IV) we have investigated the influence of increased

a) plant investment costs (II to I)
b) adsorber performance (II to III)
c) adsorber price (I to IV)

on the specific uranium production cost. Since the effect of adsorber performance is inversely proportional to the influence of the adsorber price, there are only two major factors dominating the uranium price. First, the plant investment or capital costs plus the corresponding maintainance costs and, secondly, the adsorber price and performance costs.

It is seen from the curves in Fig. 27 that e.g. additional 50 Mio \$ plant investment costs would increase the uranium price by \$ 40/lb U_3O_8 and that a 3.5-fold increase in the adsorber costs would raise the uranium price by \$ 160/lb U_3O_8. The estimated uranium price for the UEB concept would lie in the order of \$ 220/lb U_3O_8.

Finally it should be pointed our in this context, that an increase of the uranium price by \$ 250/lb U_3O_8 would have very little effect on the specific electricity price - i.e. less than a 0.01 \$ increase - as shown in Fig. 28. Under these circumstances electricity produced from nuclear energy, with uranium extracted from the sea, would still be much cheaper than coal or oil produced electricity.

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8) N.N. "Recovery of Uranium from Seawater". Atoms in Japan, August 1980

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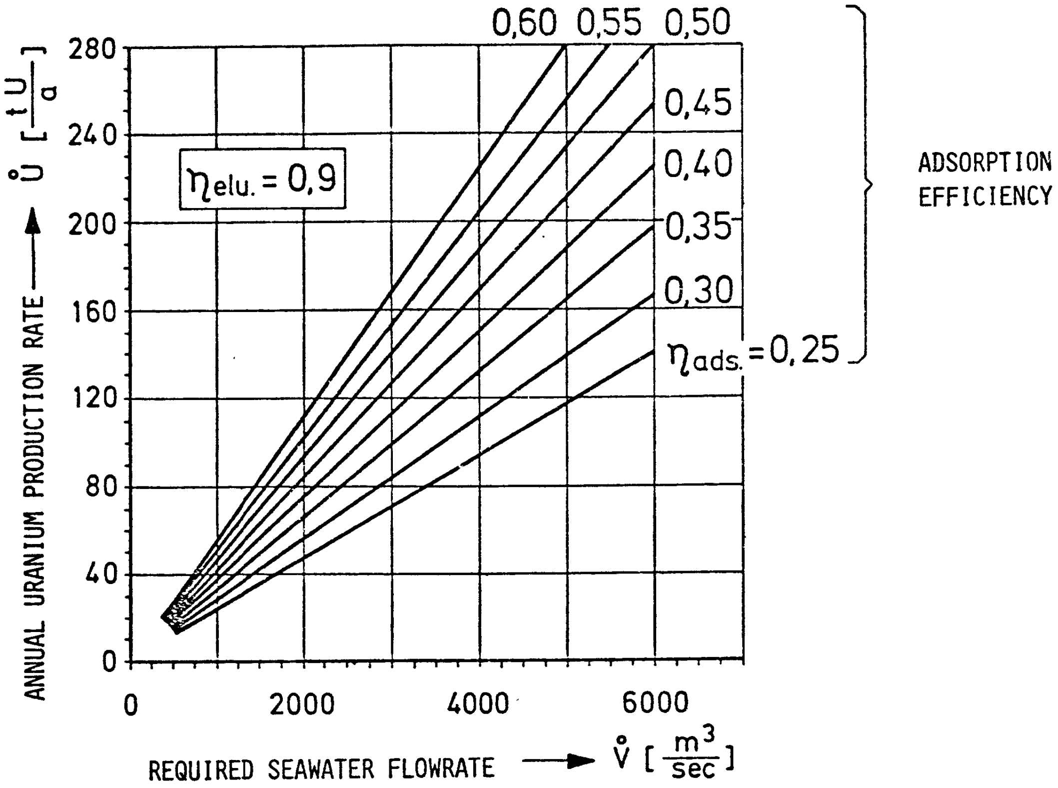
ANNUAL PRODUCTION RATE AS A FUNCTION OF REQUIRED SEAWATER FLOWRATE

FIG: 1



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CHARACTERISTICS OF THE UEB - CONCEPT

FIG: 2

- MOBILE SUBMERSED UNIT
- OCEAN CURRENT DRIVEN
- FLUIDIZED BED ADSORPTION
- ENERGY-SAVING HORIZONTAL TRANSPORT IN ADSORBER BED
- HTO ADSORBER WITH NON-POLLUTING ELUTION AND CONCENTRATION PROPERTIES

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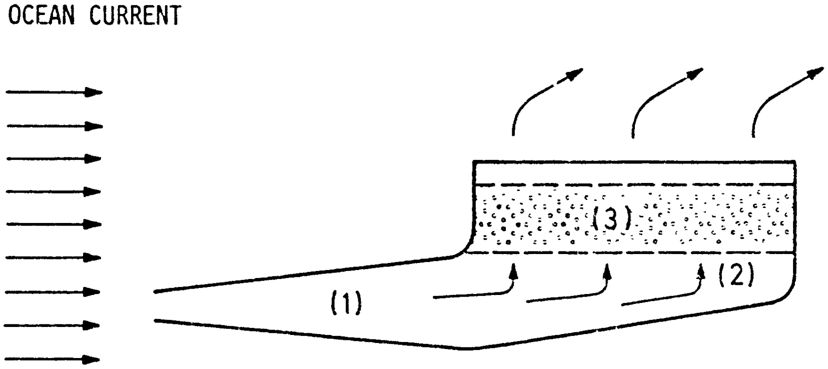
PARTS OF ADSORPTION MODULE

FIG: 3A



(1) DIFFUSOR

(2) SETTLING CHAMBER

(3) FLUIDIZED BED

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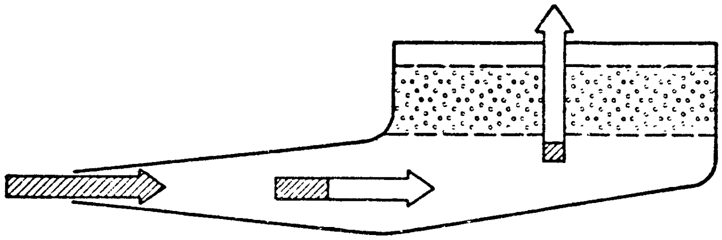
OPERATION PRINCIPLE OF DIFFUSOR

FIG: 3B



☐ PRESSURE

▨ VELOCITY

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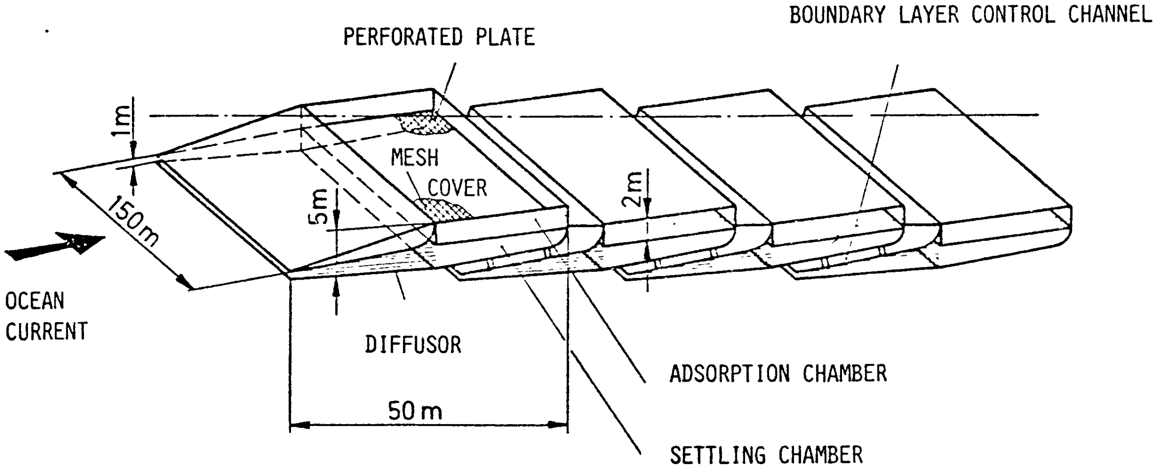
ARRANGEMENT OF ADSORPTION MODULES

FIG: 4



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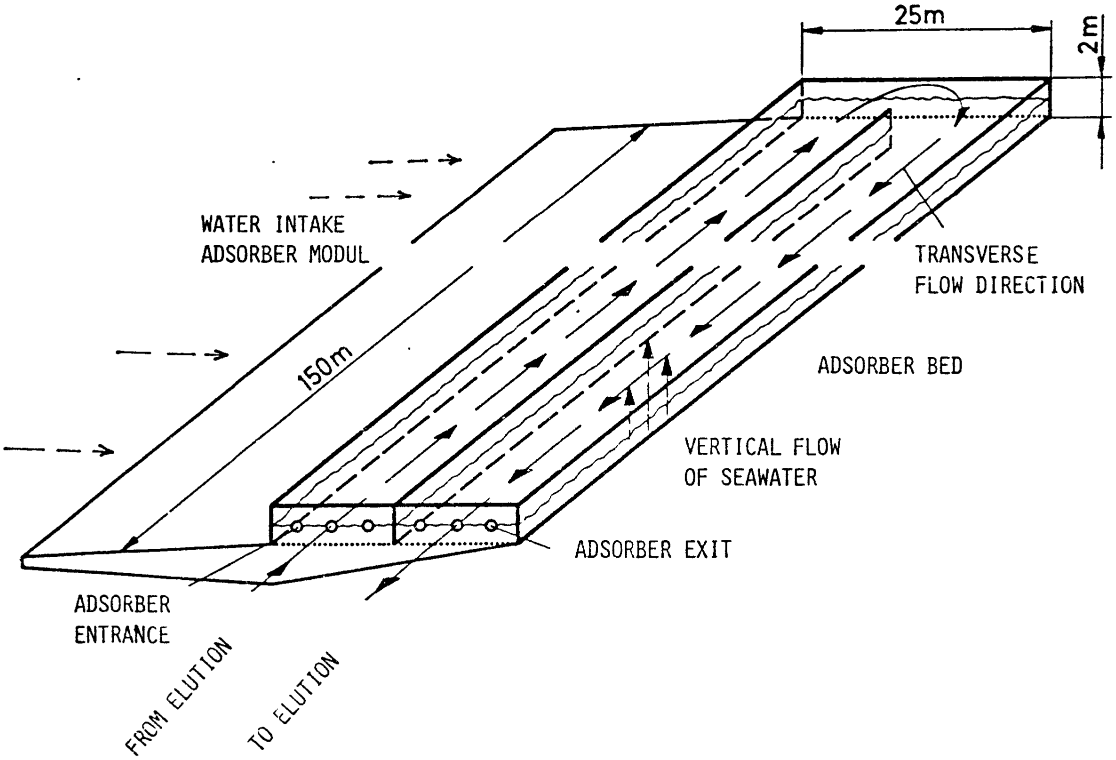
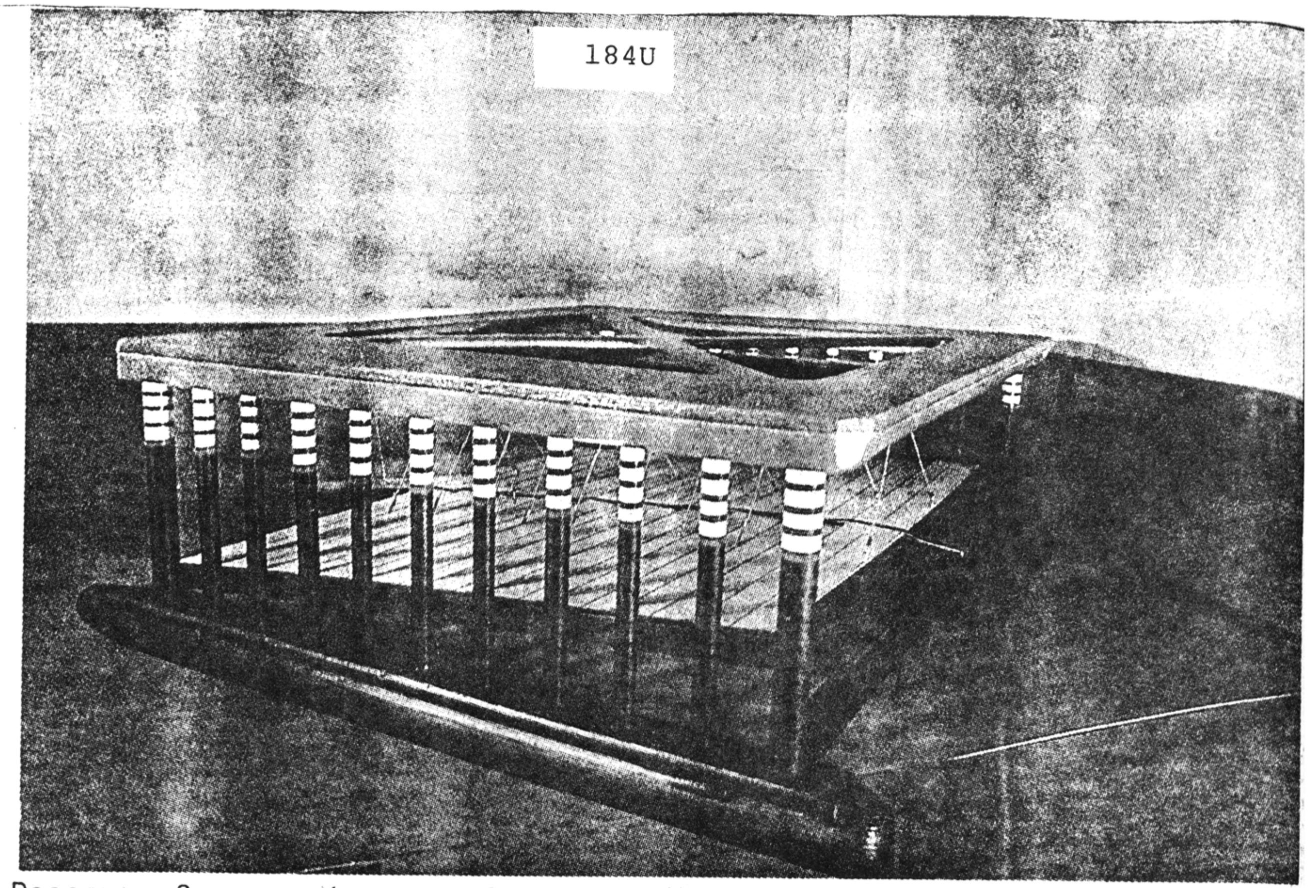
TRANSVERSE FLOW OF ADSORBER GRANULATE IN FLUIDIZED BED

FIG: 5





POSSIBLE CARRIER UNIT FOR ADSORPION-MODULES

FIG: 6

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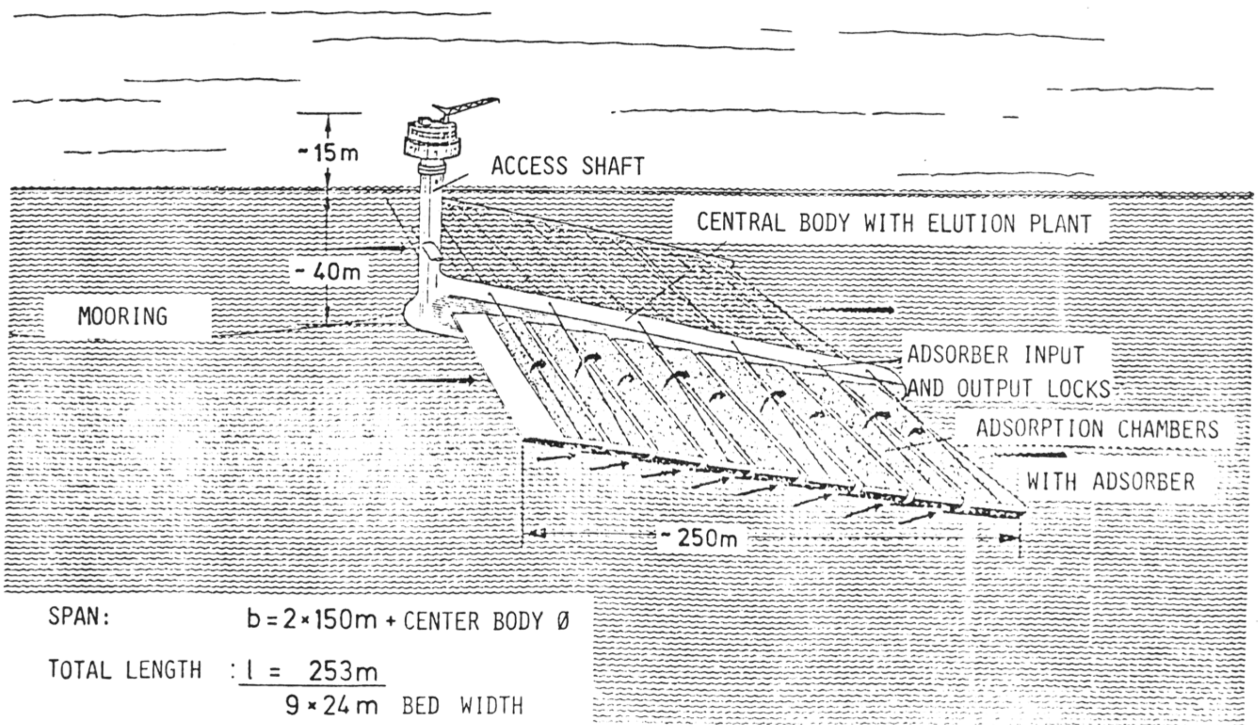
ADSORPTION PLANT

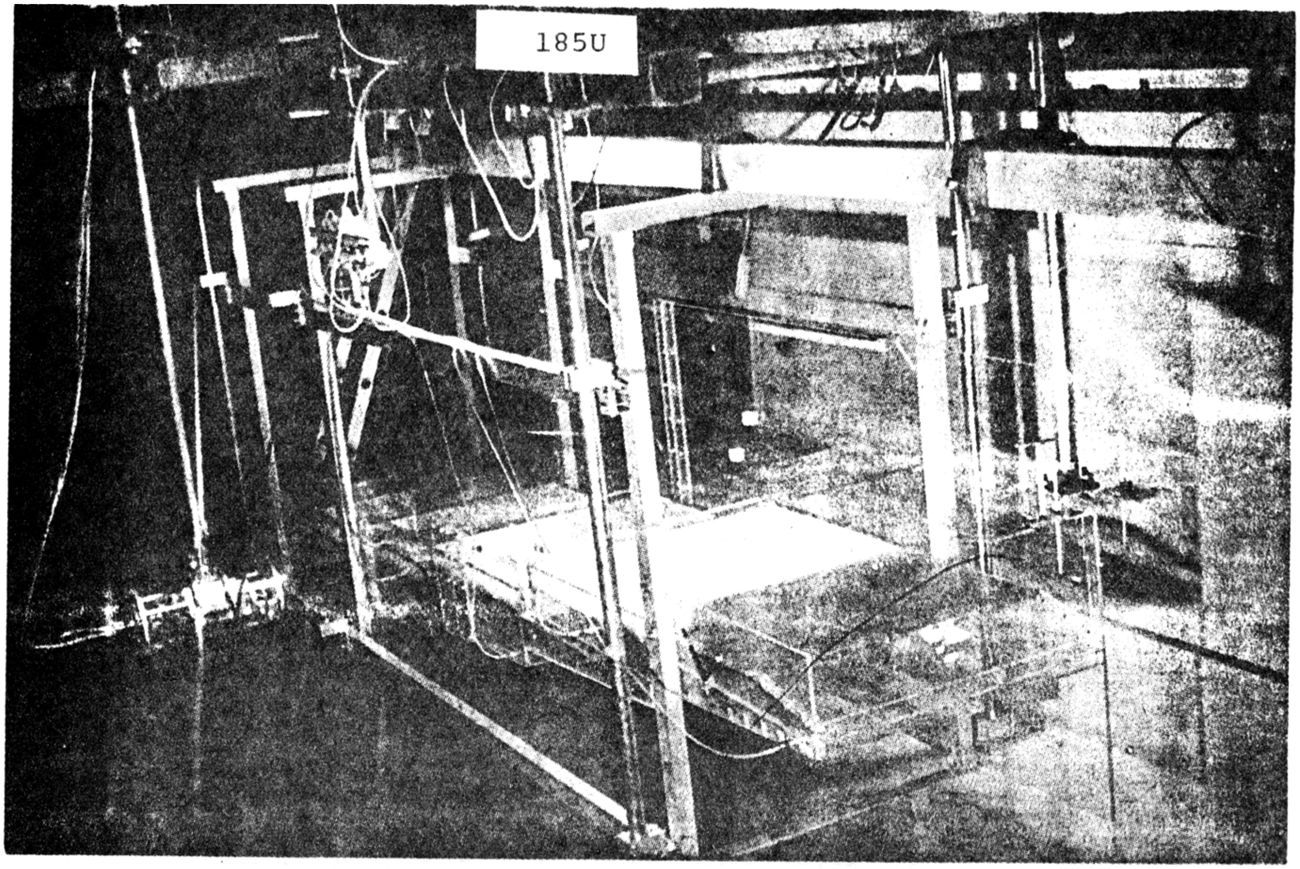
FIG: 7



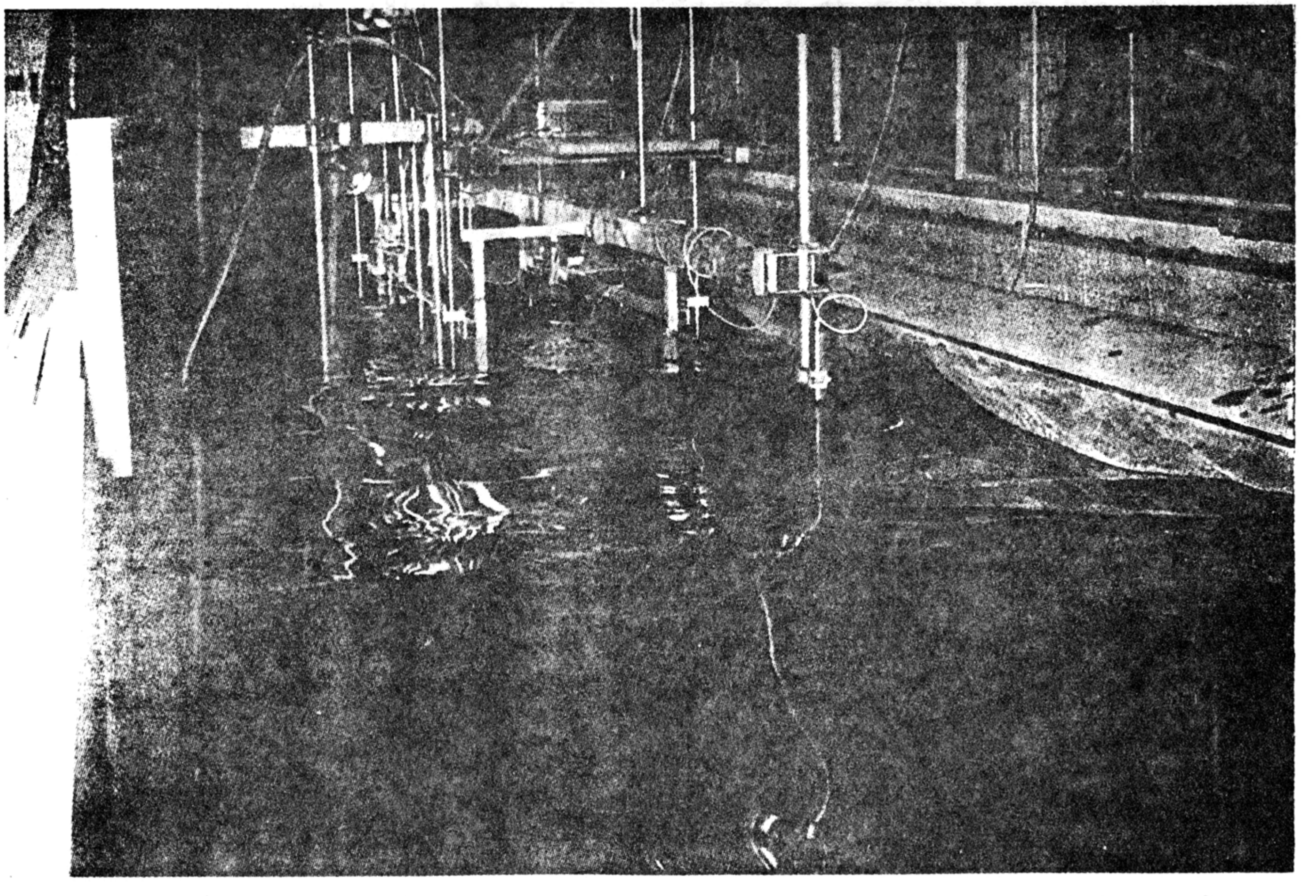
SPAN: b = 2 × 150m + CENTER BODY Ø

TOTAL LENGTH : l = 253m

9 × 24m BED WIDTH
8 × 1,5m B.L.CHANNEL
1 × 25m DIFFUSOR



TOWING TANK MODEL OF FOUR STAGGERED ADSORPTION MODULES FIG: 8
(MODEL SIZE 360 MM X 70 MM)



TESTING OF ADSORPTION MODULES UNDER WAVE INFLUENCE FIG: 9

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VELOCITY AND TEMPERATURE DISTRIBUTION IN THE FLORIDA CURRENT (CALANUS-POSITION)

FIG: 10

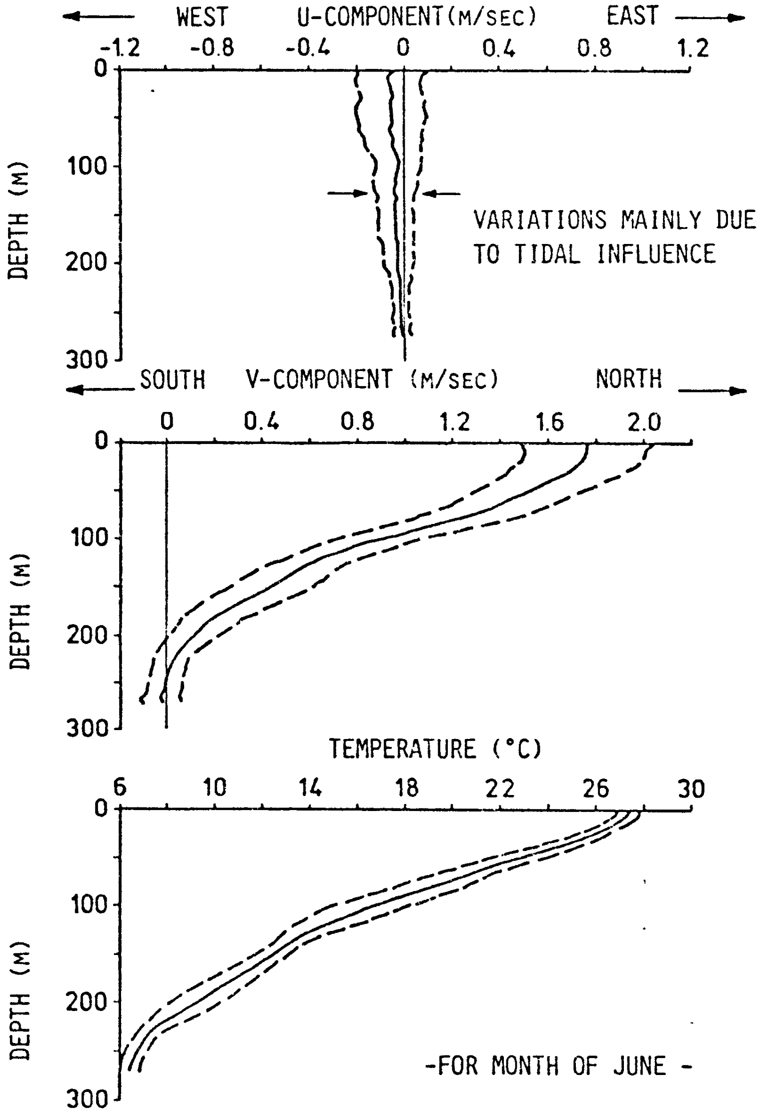

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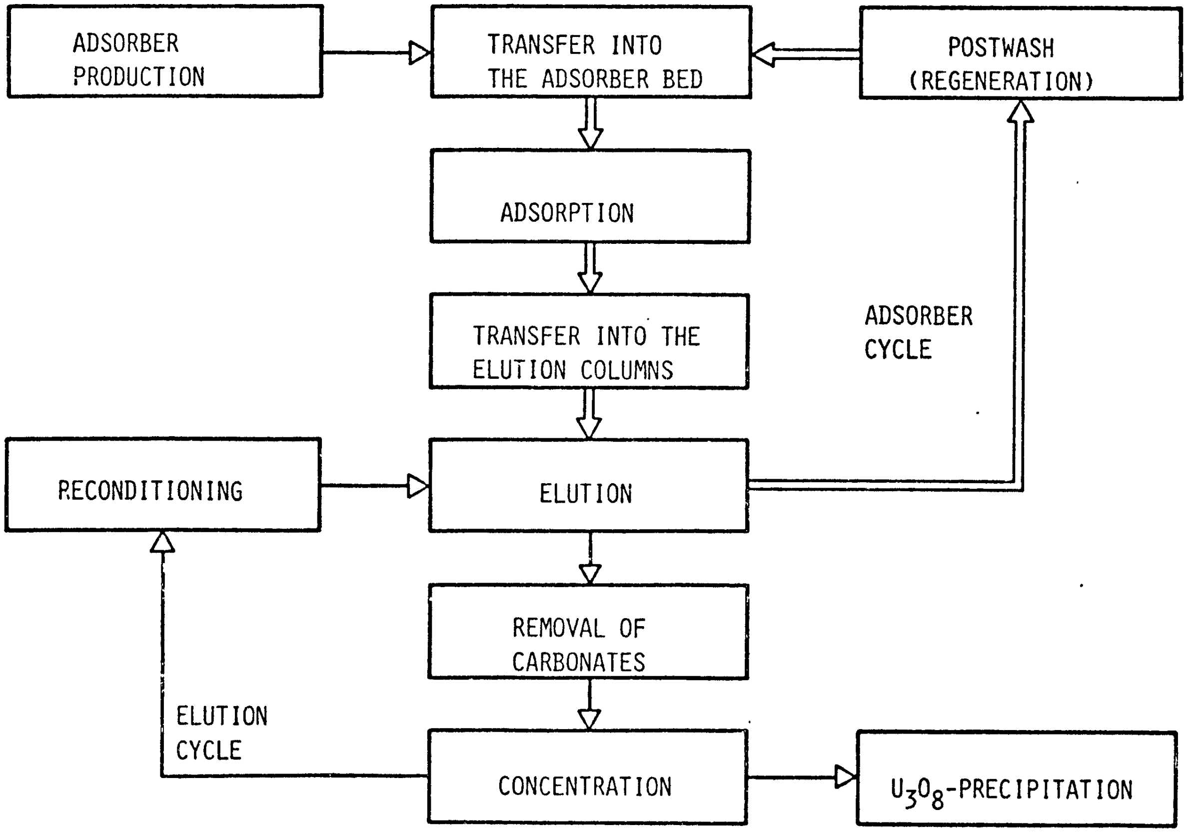
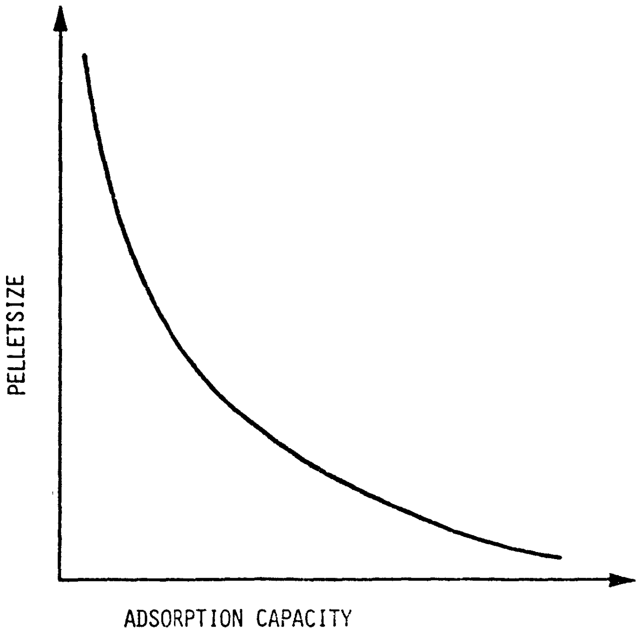
DIAGRAM OF THE COMPLETE PROCESS CYCLES

FIG: 11



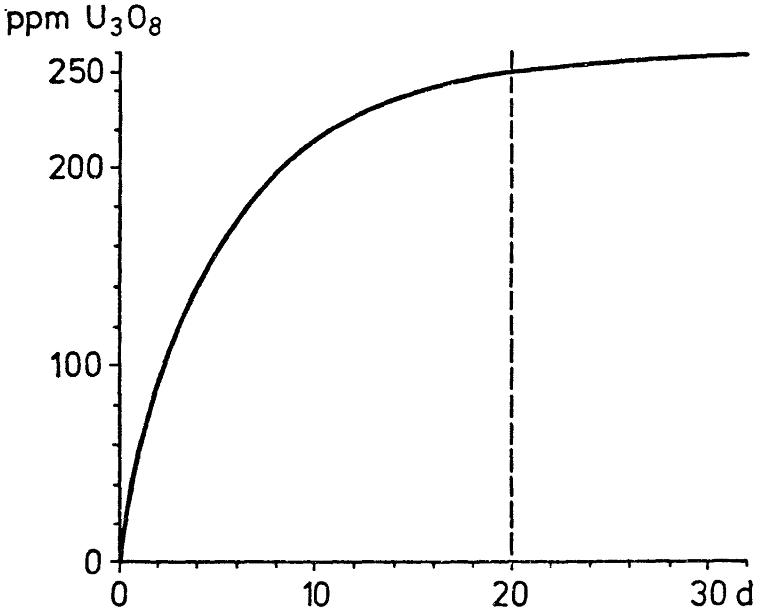
RELATION BETWEEN HTO - PELLETSIZE AND CAPACITY

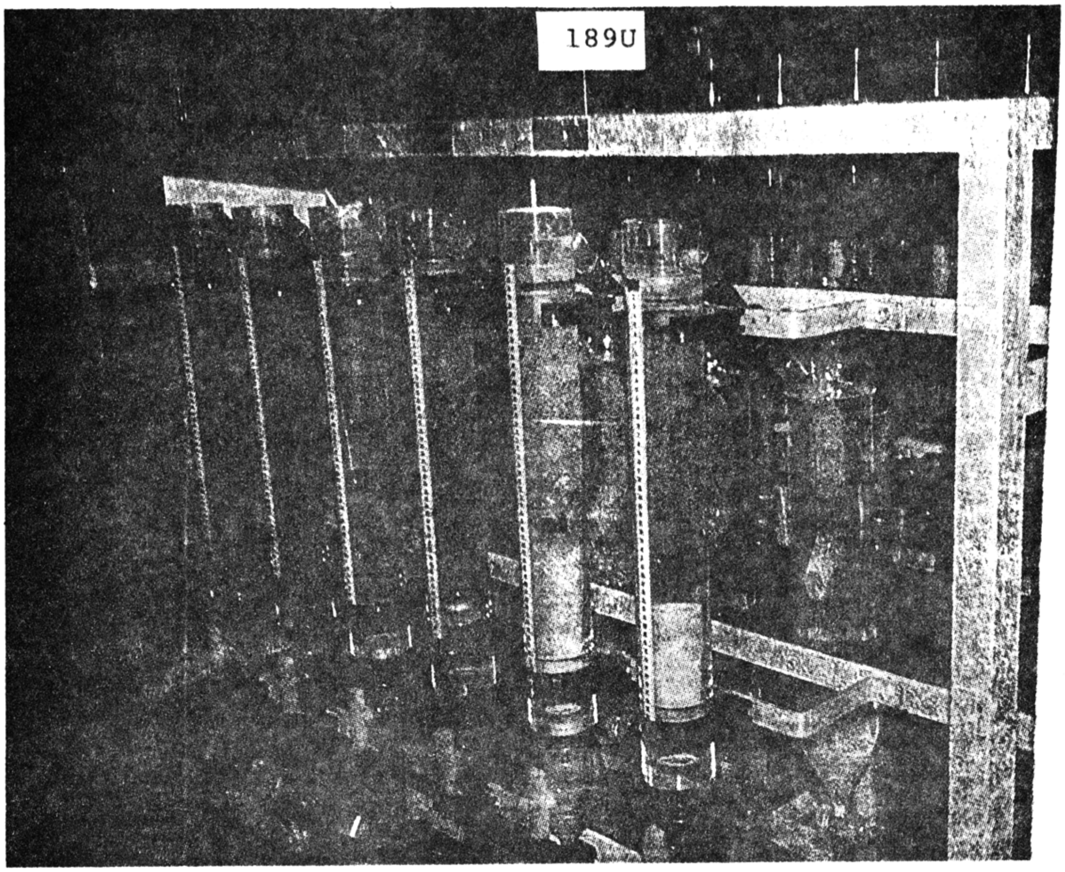
FIG: 12



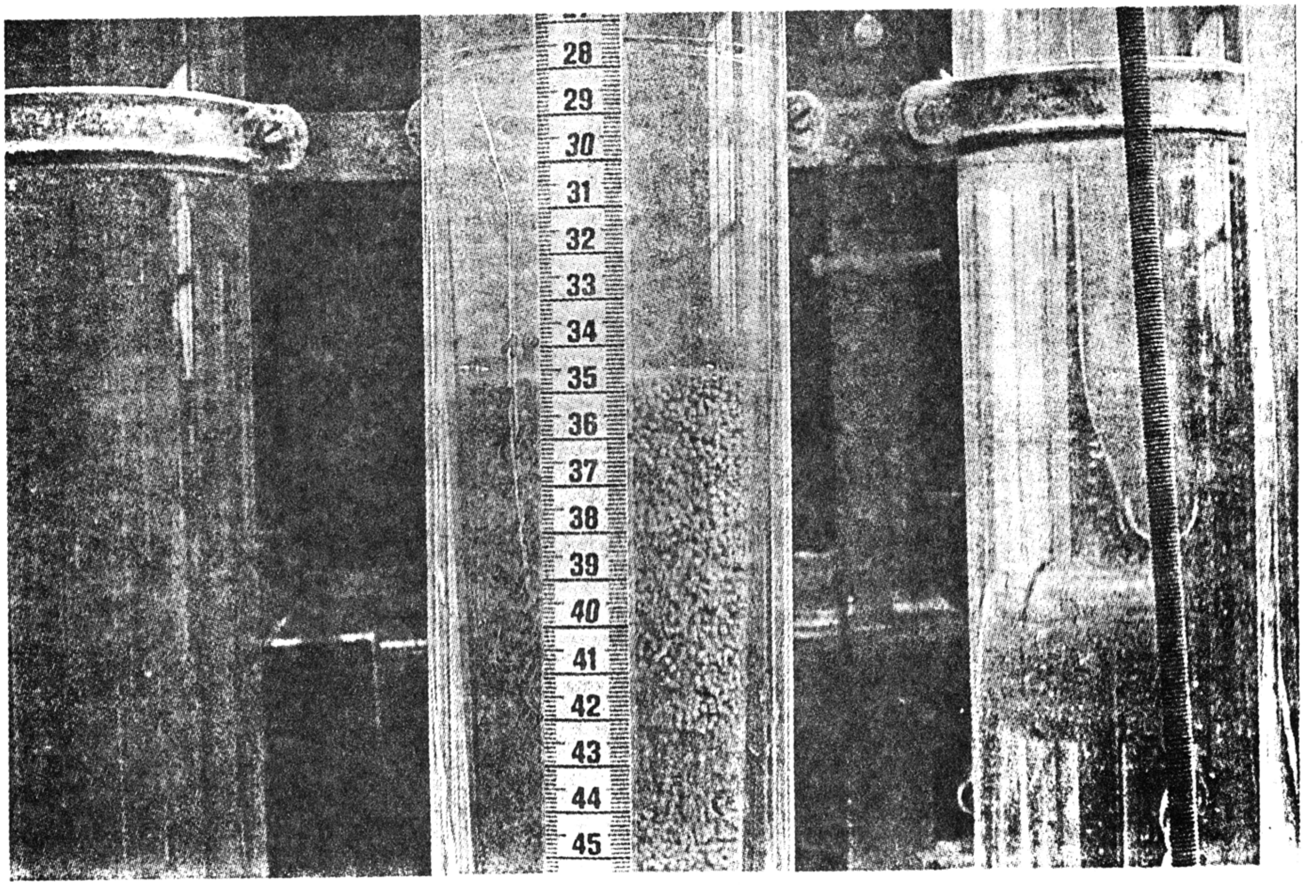
RELATION BETWEEN LOADING DEGREE AND -TIME

FIG: 13

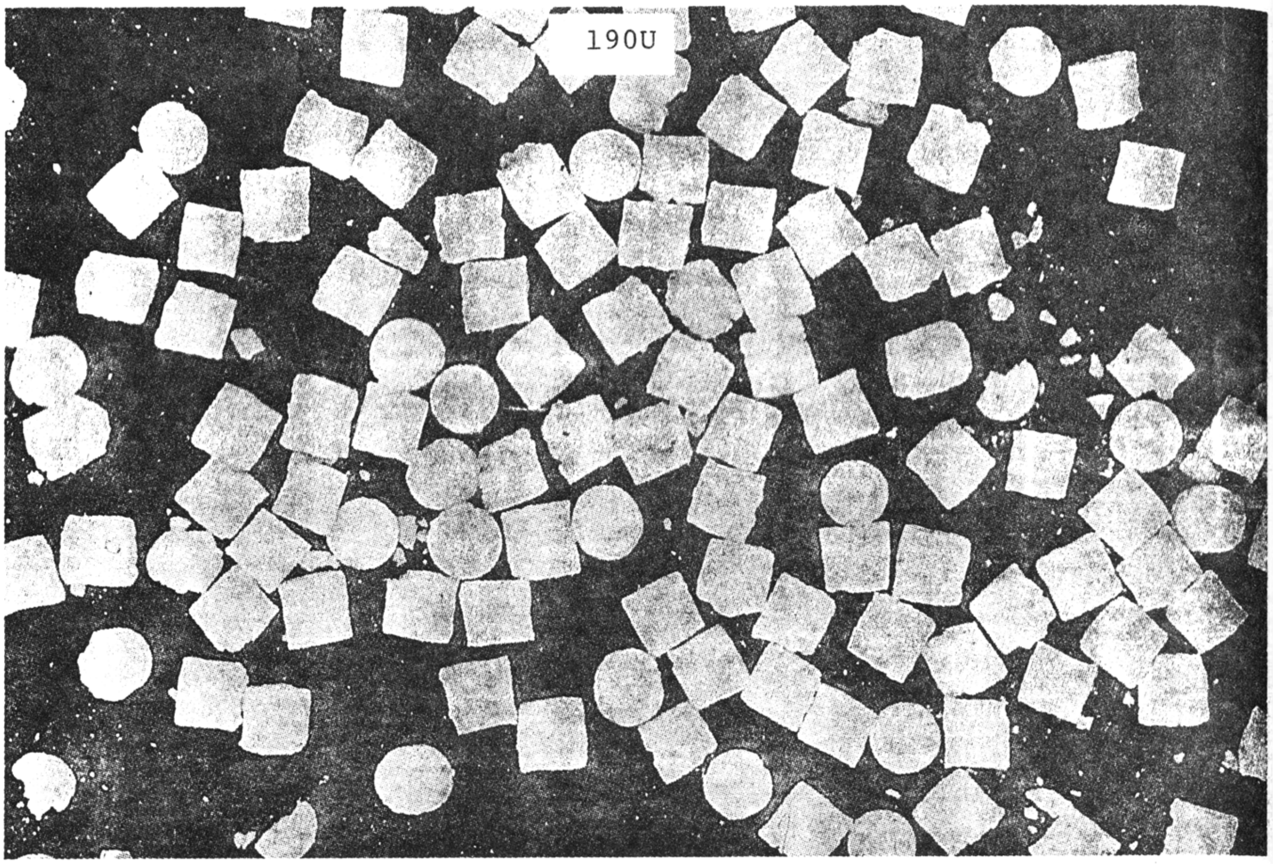




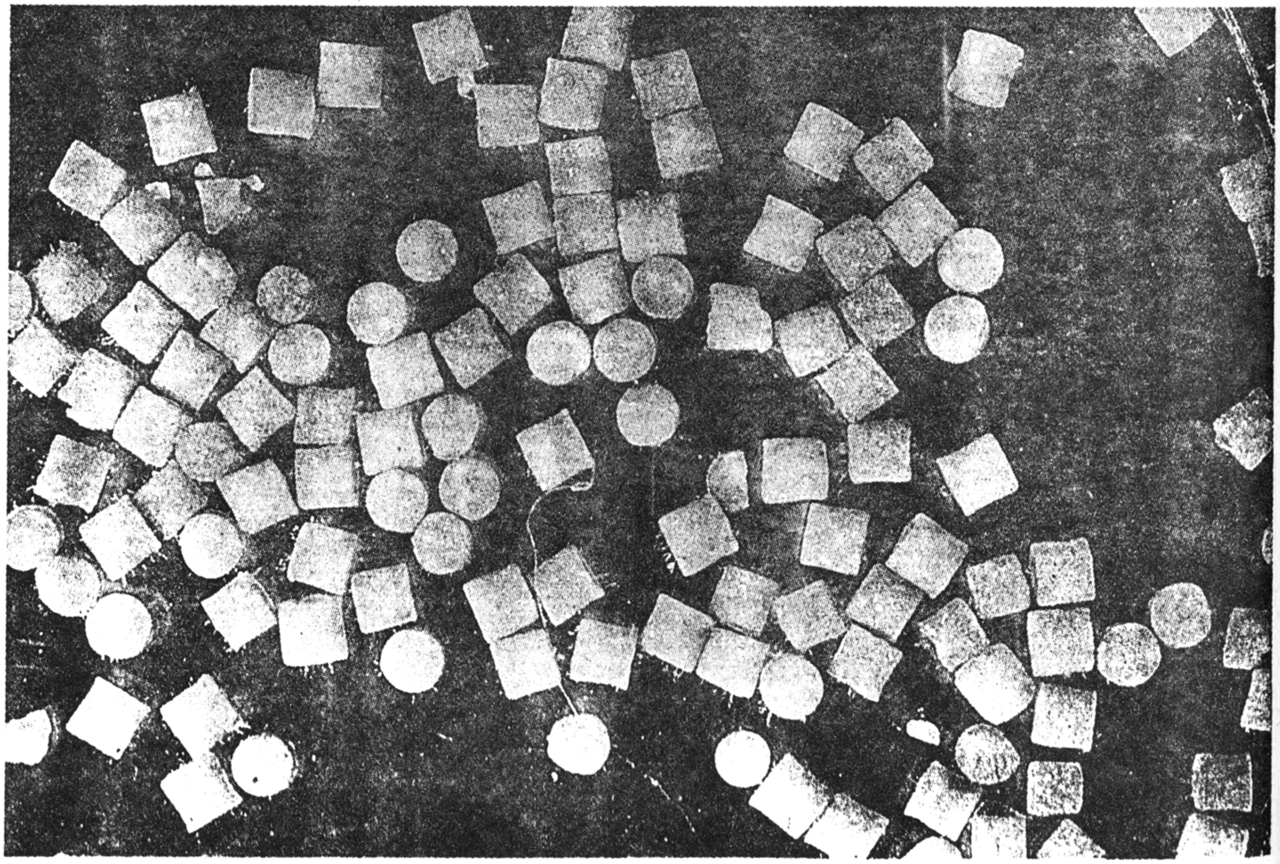
200 ML ADSORBER TEST UNIT IN A SEAWATER STATION FIG: 14



CLOSE UP OF AN ADSOBER TEST COLUMN FIG: 15



HTO PELLETS BEFORE ADSORPTION FIG: 16



HTO PELLETS AFTER 30 DAYS OF ADSORPTION FIG: 17

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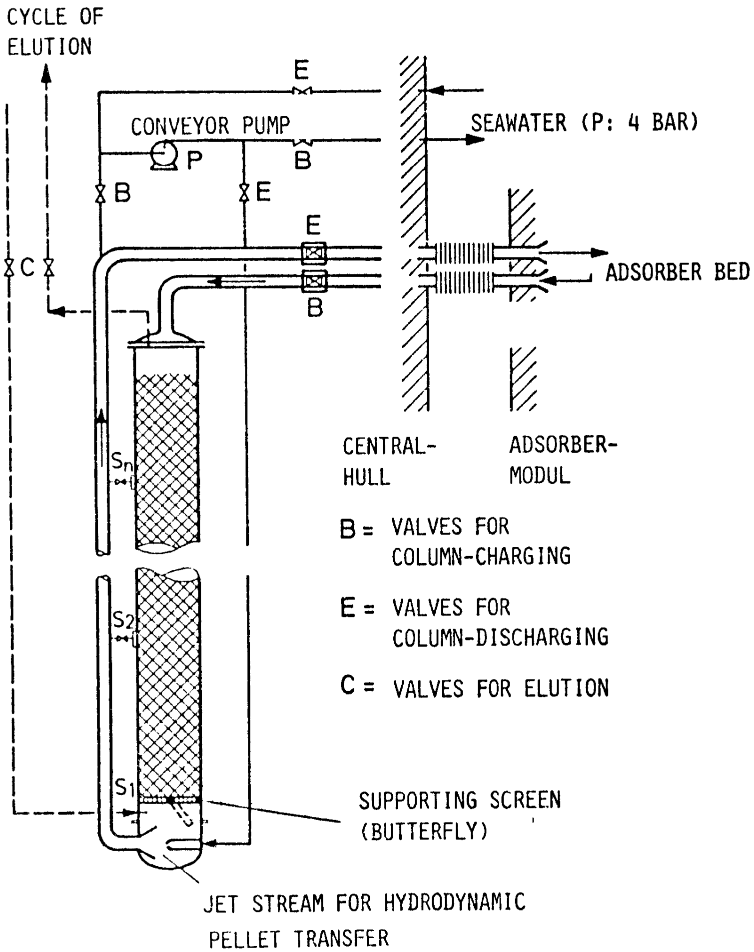
ADSORBER TRANSFER INTO/FROM AN ELUTION COLUMN

FIG: 18



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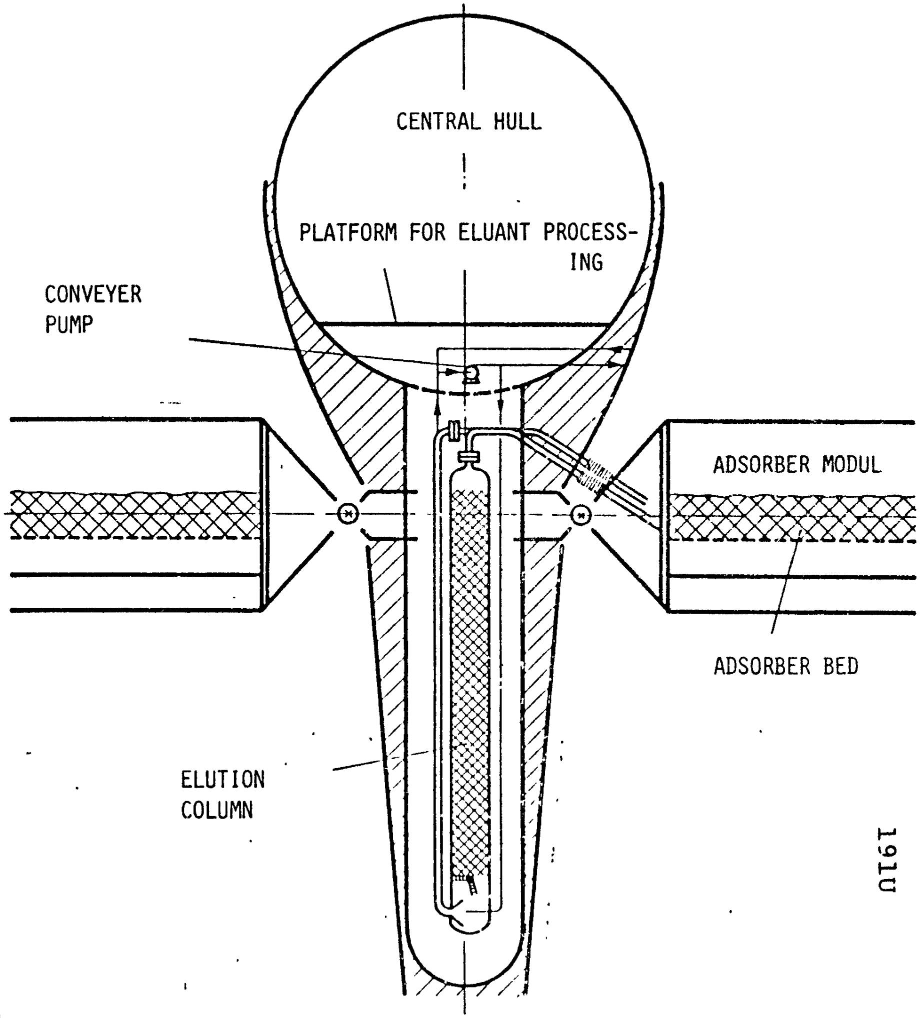
POSITION OF AN ELUTION COLUMN IN THE SUBMERSIBLE

FIG: 19



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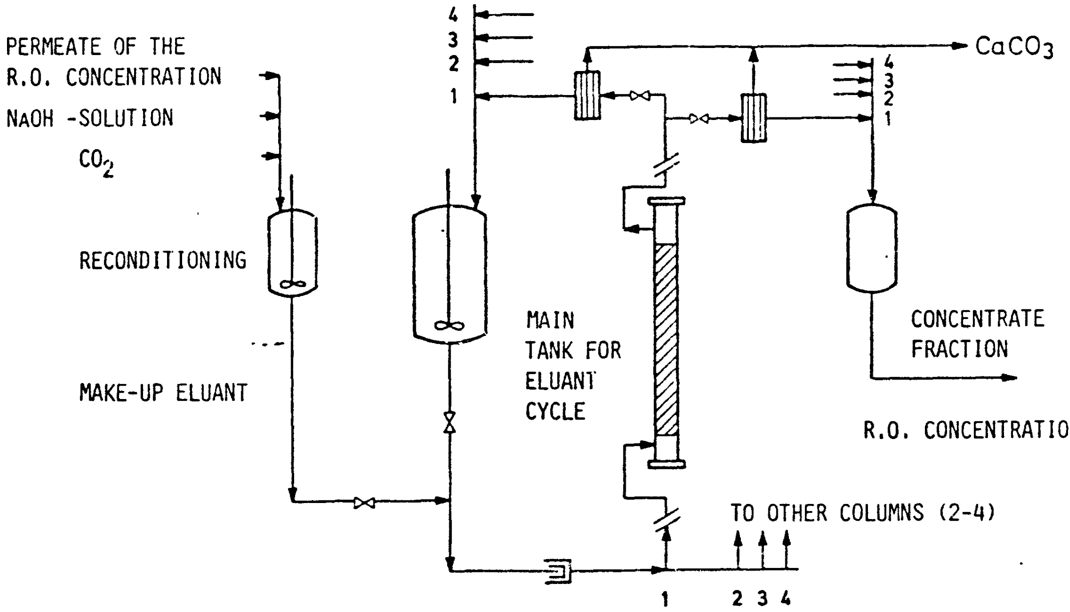
FLOWDIAGRAM OF THE ELUTION CYCLE

FIG: 20



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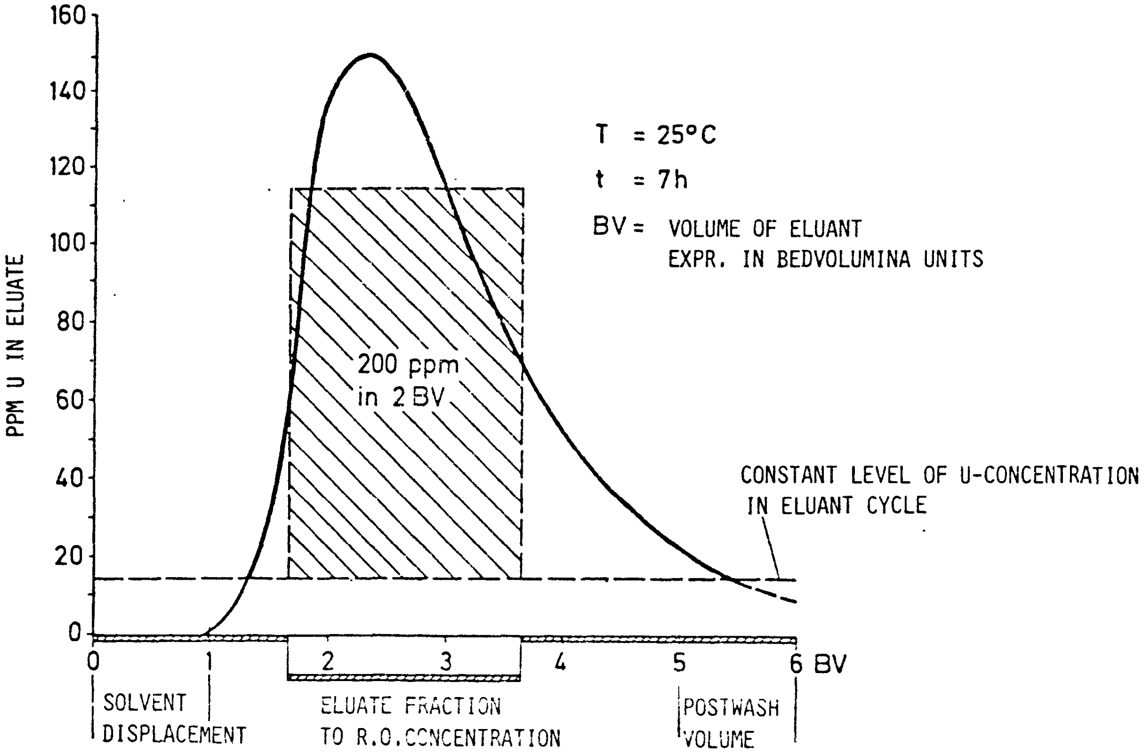
RECOVERY OF U FROM ELUATE

FIG: 21



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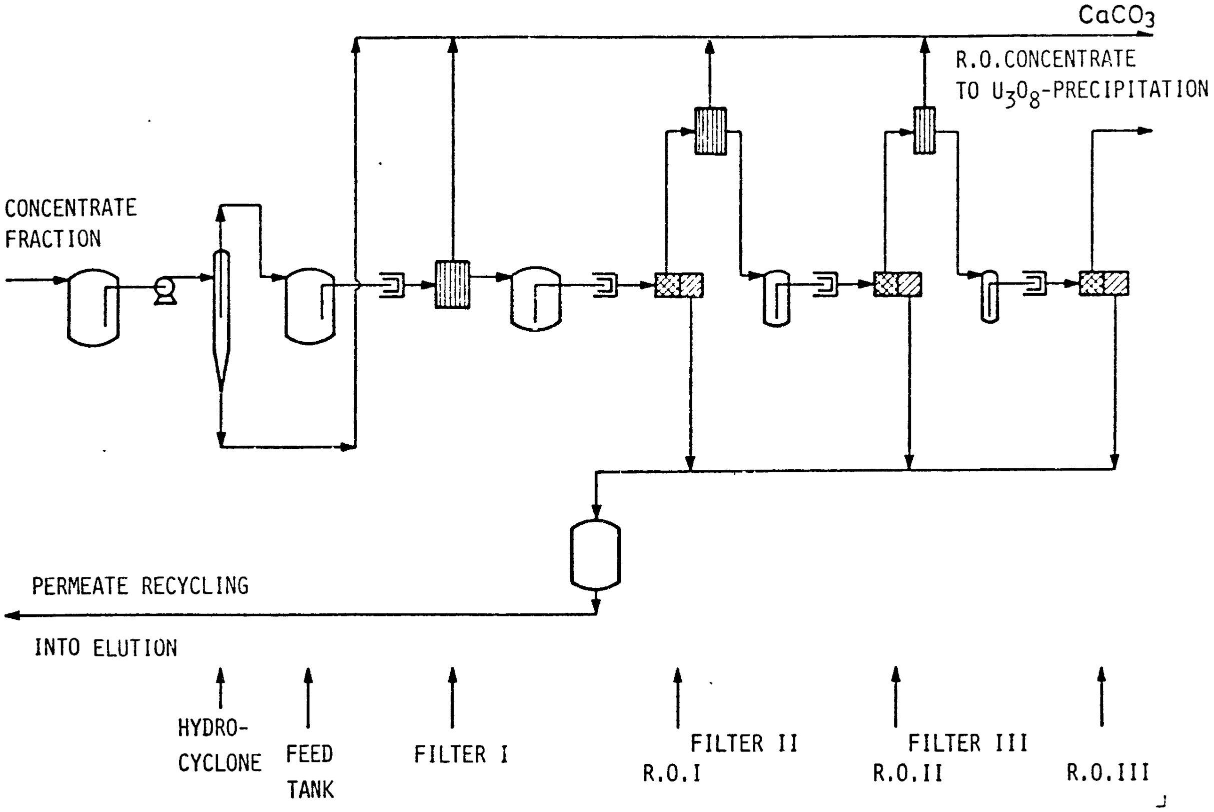
FLOWDIAGRAM OF FINAL CONCENTRATION STEP BY R.O.

FIG: 22



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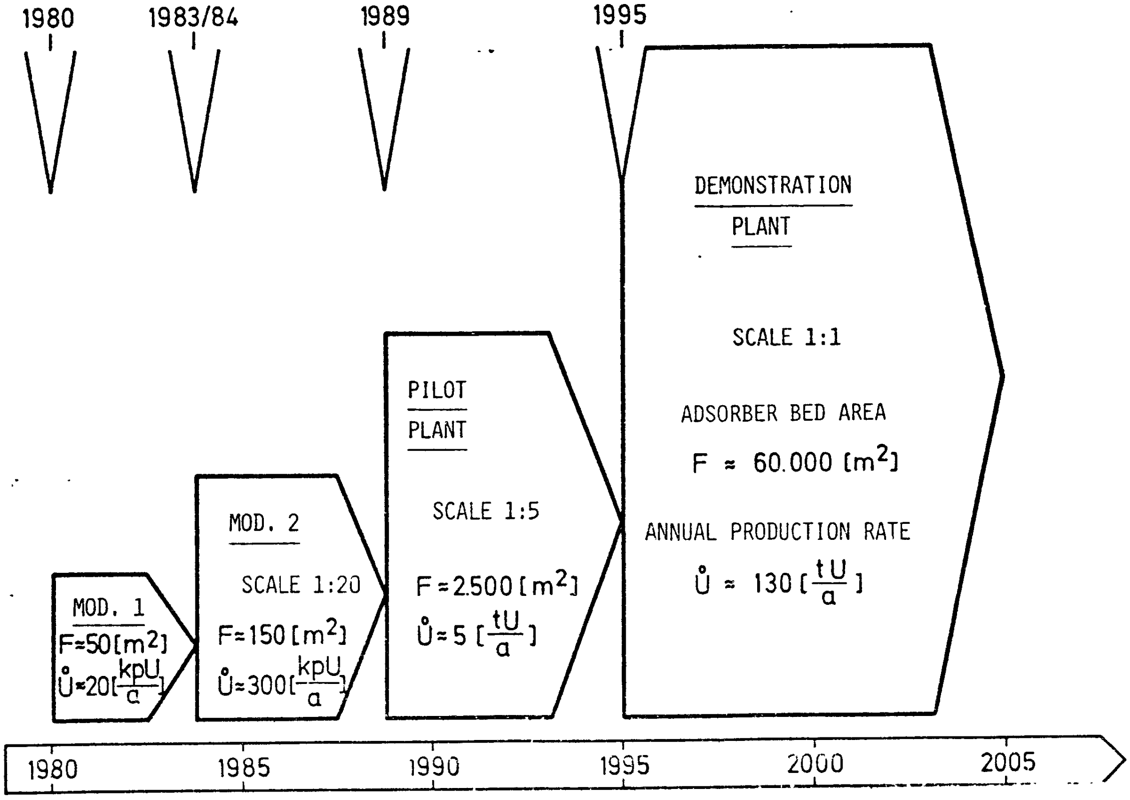
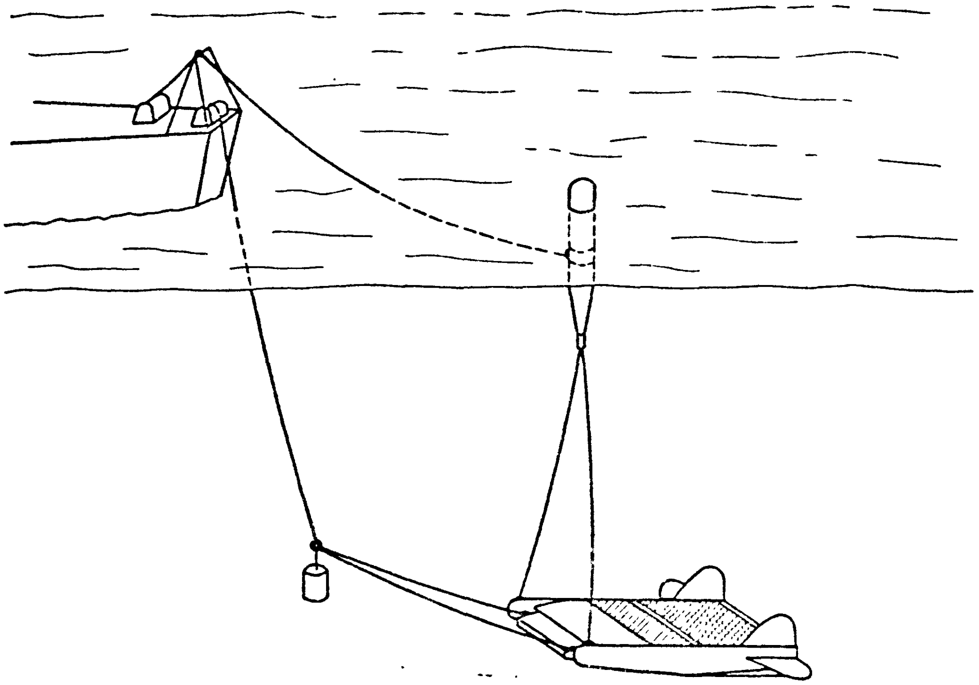
LONGTERM PLANNING

FIG: 23



MOD.1 IN ACTION

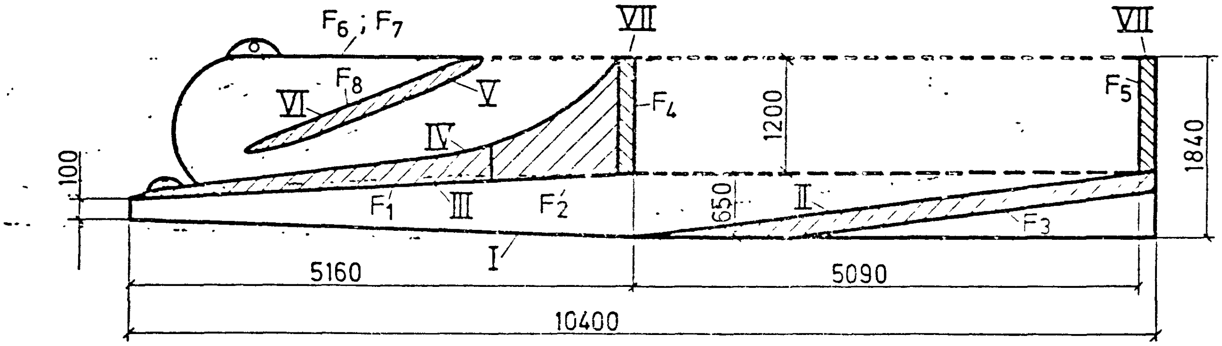
FIG: 25



CROSS-SECTIONAL VIEW OF MOD. 1

FIG: 24

WIDTH = 10.000 [mm]



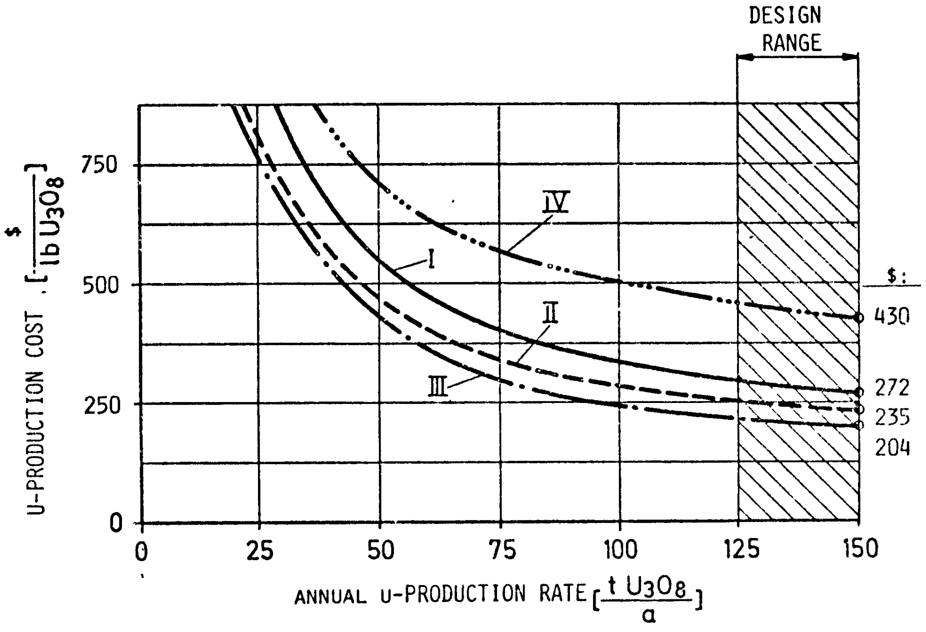
URANIUM PRODUCTION COSTS OF VARIOUS ECONOMIC ANALYSES

FIG: 26

Name [Ref.]	YEAR	PRICE $\$/lb\,U_3O_8$	
Spence (Harwell)	1955	20	
Davies et al. [1] (Harwell)	1964	11-22	
Harrington et al. [2] (ORNL)	1974	> 255	
Oser [3] (UEB)	1978	340	150 ppm TiO_2
Ogata et al. [4]	1979	150-300	
Campbell et al. [5] (Exxon)	1979	1400	100 ppm TiO_2
Best [6] (MIT)	1980	316	105 ppm TiO_2
Best [7] (MIT)	1980	150 50	420 ppm TiO_2 ION EXCHANGER CAPACITIES
NN [8] (Japan)	1980	"Competitive with terrestr. U-prices"	

SENSIVITY OF URANIUM PRODUCTION COSTS

FIG: 27



I 200 MIO INVESTMENT; STANDARD ADSORBER

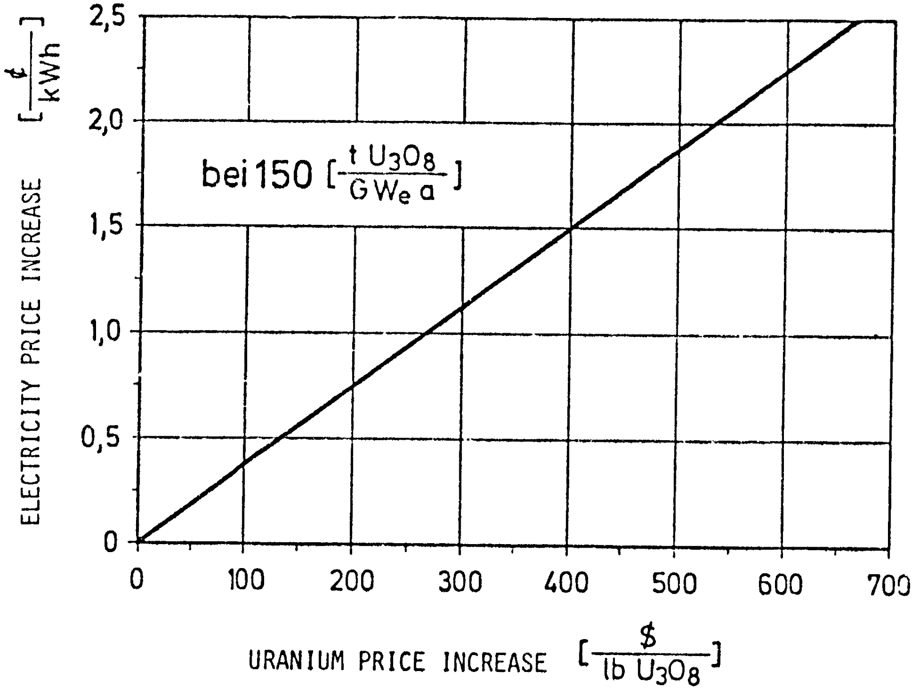
II 150 MIO INVESTMENT; STANDARD ADSORBER

III 150 MIO INVESTMENT; 100% IMPROVED ADSORBER

IV 200 MIO INVESTMENT; 3.5 TIMES INCREASED ADSORBER PRICE

ELECTRICITY PRICE INCREASE DUE TO URANIUM PRICE INCREASE

FIG: 28



Discussion on Dr. Bitte's Paper

Dr. Bitte in response to a question regarding the estimated cost of product showed a slide summarizing cost estimates to date, and made several points:

(a) The MIT estimates published by Best used sorber prices 3 or 4 times higher than those projected by UEB, hence the MIT values would fall to as low as 200 \$/lb U_3O_8 using UEB sorber costs

(b) The UEB costs, while they should be regarded as more of a sensitivity study than a firm estimate at the present time, showed costs as low as 208 \$/lb U_3O_8, but the most probable cost range should be taken as 250-300 \$/lb.

(c) Absorber price and efficiency trade-off directly in the cost evaluation process, hence one can compensate for the other

(d) Cost estimates have gone through several phases in the past: euphoric, skeptical/critical, and had now progressed to the "critical/optimistic" phase.

(e) When considering costs one should look at the effect on the price of electricity; even at 300 \$/lb U_3O_8, electricity generated in a LWR would be competitive with coal in Germany today.

Discussion on Dr. Fremery's Paper

In response to a question by Dr. Best regarding the uniformity of fluidization in thin beds over such large areas, Dr. Fremery noted that the fluidization had been quite uniform in laboratory scale models, but larger scale experience remains to be obtained. He pointed out that the unit would be operated at depths of around 100 ft where both the direction and velocity of the current would be quite stable. It was also noted that stability was obtained by designing the unit to have a certain ratio of retention mesh to bed pressure drop, and that the bed could accomodate fluctuations by collapsing and dilating.

Drs. Fremery and Bitte noted that the forces on the unit had been studied by the Ocean Engineering Division at the Technical University of Aachen using a computer model which had been benchmarked against experimental data. Attention was called to the flexibility of construction and the use of bearing-type joints. This reduced stress by several orders of magnitude. Flexible hoses were also used for material transfer.

In response to a question by Mr. Campbell, Dr. Fremery noted that their adsorber pellets could be produced in one of two ways: by extrusion and cutting as in the case of catalyst production, or using a pellet molding press having plastic forms. He confirmed a previous observation that star-shaped pellets having a greater surface area could be made in this manner.

In response to several questions as to how the large structures would be deployed and returned to port for maintenance, Drs. Fremery and Bitte noted that it was still too early to be definitive, but that the modules could be disassembled and individually replaced, the central housing floats and can be towed, and that the rig was equipped with trim tanks to adjust flotation. In the event of severe storms one might even contemplate increasing the submergence depth and allowing the unit to rest on the bottom.

In response to a question by Prof. Kanno, Dr. Fremery indicated that their design was based on 20 days adsorption followed by an 8 hour elution.

RECOVERY OF URANIUM FROM SEAWATER BY USING WAVE POWER AND FLOATING OFFSHORE UNITS

Abridged English translation from the Swedish original.

By Bo Björk[1] and Per Vallander[2]

1. DESCRIPTION OF THE PROJECT

1.1 Introduction

The demand for ores and minerals is ever increasing, whereas the supply from land deposits is decreasing. Extraction of ores and minerals from the sea is becoming a viable alternative to mining on land and the technical aids required are being developed rapidly. Up to now magnesium, calcium and potassium, which are dissolved or suspended in seawater, have been recovered. These substances are supplied to the seas by rivers, which have always been carriers of minerals.

Since the 1960's, the possibility of recovering uranium from seawater has been investigated. The estimated amount of uranium in the world's seas is about 4.5 billion tonnes, whereas the figure for land deposits is in the range 2 to 4 million tonnes.

Uranium can be recovered from seawater by using solid adsorbents arranged in filter beds or suspension chambers. Research has shown that at present the most adsorbent material known is titanium oxide with grain sizes from 0.2 to 2 mm. The adsorbent is directly loaded with the seawater, and uranium (U_3O_8) and other substances will be slowly recovered. The uranium is removed from the adsorbent material in an elution process, most conveniently utilizing ammonium carbonate. The adsorbent, and also the eluant, are recovered for reuse. The uranium will be concentrated in ion exchangers.

Since the concentration of uranium in seawater is only about 3 ppb, very high seawater discharges will be required in order to reach profitable levels of the uranium uptake. To date, water discharges from streams, tidal movements and electrical pumping have been studied.

It has been shown that the velocities of the streams of seawater are too low to reach the discharges required and that the waters where tidal movements are feasible, have among other things, temperatures which are too low to be useful for extraction purposes. In a feasibility study carried out by EXXON, it was shown that the costs of pumping seawater into the adsorbent was dominant in terms of the final cost of the uranium.

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In the present project, the feasibility of a floating unit for the recovery of uranium from seawater is studied. The seawater is supplied to the adsorbent inside the unit by means of wave energy. The wave energy transformation method derives from a Swedish patent, and is based on the principle that waves will rush up on a sloping plane, which is partly submerged in the water, and fill a reservoir with seawater to a level which is higher than the still water level in the sea. This difference in water level will create a pressure head which can be utilized to force seawater through filter beds, see Fig. 1.1.

1.2 Scope of the project

The scope of the project has been the production of a technical and economic evaluation of the feasibility of floating units for the extraction of uranium from seawater. The seawater is supplied by wave energy and received by a sloping plane. A processing plant on land and build up of adsorbent beds are not included.

The work has comprised the following:

- waves, streams and water temperatures available at sea
- uranium uptake
- optimization of a plant
- conceptual layout of a floating unit
- dynamic response of a floating unit
- costs

The project has been sponsored by the National Swedish Board for Technical Development (STU) and the work has been carried out in collaboration with STU and the Department of Nuclear Chemistry at the Royal Institute of Technology, Stockholm, Sweden.

2. FUNCTION

2.1 Chemical process

The chemical process for the separation of uranium from seawater can be divided into four operations.

i) Direct loading of the adsorbent with seawater. The operation is stopped when the adsorbent uptake capacity is reached. The adsorbent will then be prewashed with fresh water.

ii) Eluation of the adsorbent with an eluant. Chemically, this means that the adsorbing mechanism during the first operation is reversed due to an excess of carbonate and bicarbonate in the eluant (ammonium carbonate). The adsorbent will then be postwashed with freshwater.

iii) Steam stripping of the eluate to extract the uranium and to recover the eluant for reuse.

iv) Preparation of the solid uranium product by filtration and use of ion exchangers.

2.2 Adsorption processes

Four methods of bringing the adsorbent into contact with seawater can be distinguished. The methods can be categorized into two basic concepts, static beds and dynamic beds.

The static bed systems are batch operations with the washing and elution of the adsorbent occurring in situ within the contact structure. The dynamic bed systems are continuous operations. The bed material is then continuously transported to a separate washing and eluation area for processing and then recycled to the contact structures.

2.3 Selection of adsorption process

The technically most feasible contacting systems are static upflow beds and dynamic, continuous slurry beds. In the first concept, the seawater flows upwards through the beds with a velocity high enough to fluidize the adsorbent material. In the second concept, the adsorbent is discharged from one end of the bed as slurry. Flows of seawater and adsorbent slurry will cross within the contact structure and the slurry will be washed and eluated in separate continuous operations.

The static upflow beds, in contrast to the continuous slurry beds, will require less extensive installations and reduce the energy demand for pumping slurry. The layout is simpler.

For the conceptual design of the floating unit in this project, the static upflow bed system has been selected.

2.4 Capacity of hydrous titanium oxide

The uranium uptake capacity of hydrous titanium oxide is a function of the major parameters, seawater temperature, seawater discharge and pressure head available.

In this project, the capacity of hydrous titanium oxide has been defined at the Department of Nuclear Chemistry, the Royal Institute of Technology, Sweden, in accordance with the graphs shown in Fig. 2.3.

2.5 Other properties

The prewash will require about three adsorbent bed volumes of fresh water and the eluation process about four bed volumes of ammonium carbonate. For the postwash about five bed volumes of freshwater will be required. This water can be utilized for prewashing in the following eluation process without treatment. The prewash water can not be recycled.

The adsorbent bed area required is 167 m^2/m, based on a discharge of 1 m^3/s, m and a flow velocity of 0.006 m/s, and the height is 0.4 m when not fluidized. These figures have been chosen by the Department of Nuclear Chemistry.

The eluation process will need to take place about once every fortnight.

3. THEORETICAL URANIUM UPTAKE AND SITING OF FLOATING UNITS

3.1 Introduction

In order to find a feasible site for a plant, data on oceanographic conditions have been collected and theoretical annual productions of uranium have been calculated for the purpose of comparison.

3.2 Feasible sea areas

3.2.1 Criteria for selection

The most important parameters of the oceanographic environment for the uranium uptake in the project's floating unit are water temperature, current speed and wave energy available.

The criteria for site selection have been:

- annual mean water temperature of at least 15°C
- annual mean water current speed of 1.5 to 2.0 knots
- high waves all year with small variations in mean wave direction

3.2.2 Sea areas

The seawater temperature criteria limits the feasible areas to a belt approximately between latitudes 35°S and 45°N.

On the basis of current speed criteria, seven feasible areas were selected. They were the coasts of: southern and eastern Florida, USA; northern Brazil; eastern South Africa; Somalia towards the Indian Ocean; eastern Philippines, eastern Taiwan and southern Japan.

According to the oceanographic studies undertaken, three areas are feasible as regards the wave climate, namely the Bahamas, South Africa and Japan. The waves off the South African coast have two major directions, whereas those off other areas are more multidirectional.

3.3 Calculated uranium uptake

The fundamental mode of interaction between the waves and the floating unit, as well as the notations used below, are shown in Fig. 3.2.

Every wave which rushes up the sloping plane of the floating unit creates a certain seawater discharge into the water reservoir of the unit. The water surface in the reservoir will have a mean level which is higher than the surrounding still water level.

The vertical distance d between the still water level at sea and the lower edge of the sloping plane was kept equal to 2H (H= deep water wave height) for the calculation of the uranium uptake. Since the highest discharges will be obtained for a slope of 1 vertical to 1.5 horizontal of the plane, this slope was kept constant during the computations.

By means of the graphs presented in Fig. 2.3 and the calculated relationships between inflow of seawater, wave height and water reservoir level the uranium uptake could be related to the significant wave height, as shown in Fig. 3.3. It is clearly demonstrated by the graphs that the uranium uptake will be far higher off the Bahamas and South Africa than off Japan for waves of equal height. This difference is explained by differences in seawater temperature. The difference in uranium uptake between the Bahamas and South Africa, these areas having about the same mean annual water temperature, is explained by differences in wave steepnesses.

By multiplying the durations of the specific wave heights during the year at each site with the corresponding uranium uptake figures and taking the sum totals, annual uranium uptake was determined. This was:

- the Bahamas	2.4 tonnes/yr, 100 m
- South Africa	4.1 "
- Japan	2.3 "

The reason why more uranium can be produced off South Africa than off the Bahamas is that there are higher frequencies of higher waves off South Africa. The reason why there are similar production levels off the Bahamas and off Japan is the higher frequencies of relatively high waves off Japan.

The true uranium uptake at the sites will be lower than the figures presented above due to hydraulic losses, the dynamics of the floating unit, directional spreading of the component waves relative to their mean direction and obliquely incoming wave systems. These aspects are dealt with further in Clause 7.

3.4 Siting

The area finally selected is located off the South African coast, since this area offers the highest theoretical potential uranium uptake and the waves there are more unidirectional.

Two sitings within this area will be taken into consideration. One site will be located about 20 nautical miles from the coast and the other about 300 nautical miles from the coast (outside the territorial zone), lat. 32°S, long. 35.5°E, see Fig. 3.4. The water depths at these sites are about 120 metres and 1 800 metres respectively.

4. SYSTEM ANALYSIS

4.1 Introduction

The preparation of the adsorbent can be carried out at sea or on land. The liquids required for reconditioning can be stored at different places. The possible combinations of preparation and liquid storage locations are shown in Table 4.1. See also Fig. 4.1.

	Location for eluation	Location for storage of liquids		
		Floating unit	Service vessel	Land
A	Floating unit	X	X	
B	Service vessel		X	
C	Land			X

Table 4:1 Possible combinations of preparation and liquid storage locations

The location for eluation and storage of liquids has a direct impact on the overall economic feasibility of the total plant. Below follows a brief description and analysis of the layout of different combinations and the costs connected.

4.2 Basic assumptions

4.2.1 Offshore plant design

The adsorbent beds are located in floating units which are anchored at sea. Each floating unit comprises five cylindrical caissons each one housing one adsorbent bed set.

The total plant is designed for a total annual capacity of about 600 tonnes of uranium. The estimated total number of floating units would then be about 70.

Each adsorbent bed set will be divided into six storeys and each storey into 16 sections. The height of the storey will allow the adsorbent material to expand threefold when fluidized.

The postwash water will be recycled as prewash water, and eluation will be carried out once every fortnight. The floating units are served by service vessels in a way that is suitable for each combination, see Table 4.1. In the combinations B.2 and C.3, the adsorbent material will be pumped as slurry to and from the service vessel.

4.2.2 Pumping of liquids and slurry

In Table 4.2 are shown the storage volumes required per bed set and 14 days production, expressed as multiples of one adsorbent bed set volume V (= 167x0.4=66.8 m^3/m, cf. Clause 2.5). In the cases when a liquid or slurry is circulated, the storage tank is supplemented with one buffer volume dV. This buffer makes it possible to start circulatory pumping without mixing fresh and already used liquids. In the following, it is assumed that the value of dV is equal to one bed set volume, V, per service vessel.

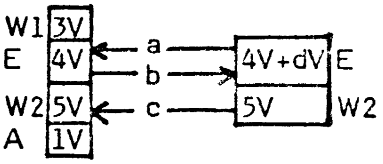
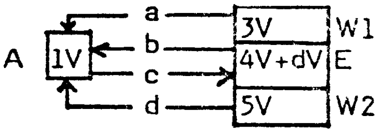
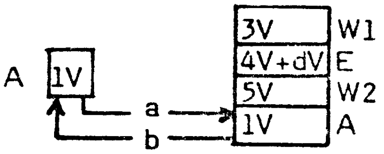
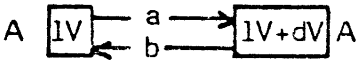
Combination	Pumping scheme		Volumes required	
	Floating unit	Service vessel	Floating unit	Service vessel
A.1			13 V	9V+dV
A.2			1 V	12V+dV
B.2			1 V	13 V+dV
C.3			1 V	1V+dV

Table 4.2 Storage volumes per adsorbent bed set and 14 days. W1 = prewash water, E = eluant, W2 = postwash water, A = adsorbent, V = one adsorbent bed set volume, dV = buffer volume per service vessel.

4.2.3 Time requirements and volumes

4.2.3.1 Elution

The time necessary for prewash, eluation and postwash is determined by the contact times necessary. The contact times for the processes have been fixed at 30 minutes and 4 hours and 30 minutes respectively. With a height of the fluidized bed of 1.2 m, the total time for a complete elution treatment of one adsorbent bed set will, theoretically, be 6.6 h.

It is assumed that the five adsorbent bed sets within one floating unit can be served, as regards pumping of eluant, simultaneously so that the time required for treatment of one floating unit will be about 9 h. However, in the following considerations, the practical time for serving one floating unit has been assumed to be $t_2 = 1d$.

4.2.3.2 Slurry pumping

It is assumed that the adsorbent material in all storeys within one section of one bed set (volume, V/16) can be pumped out in one operation as slurry. With a concentration of about 20% of adsorbent material in the pumped sea water, the theoretical time for emptying the five bed sets within one floating unit is about 3.7 h. The pumping of bed material from a service vessel to the bed sets in the floating unit is assumed to take a longer time. The total time for reconditioning of the five bed sets in one floating unit is estimated to be $t_2 = 1d$.

4.3 Service vessels

4.3.1 Basic assumptions

Two fundamental modes of transport have been investigated. In the first mode, the service vessels will serve one or several floating units until the vessel's loading capacity is reached, thereafter it will return to harbour to unload and load as necessary and then return to the floating units for another service cycle. In the second mode, the service vessels will sail between the floating units and intermediate storage tankers, so that only the latter will return to harbour. The intermediate storage tanker mode is only assumed feasible if the plant is located 300 nautical miles offshore.

For simplicity, all service vessels and intermediate storage tankers are assumed to have a mean speed during the voyages of 15 knots. The total time for one voyage to and from the harbour will then be $t_2 = 1.7$ d and $t_2 = 0.125$ d for the locations 300 and 20 nautical miles offshore. The time at berth in each cycle is set at $t_3 = 1d$.

The volumes which the service vessels will transport are the same as that produced (consumed) by the adsorbent bed sets. These volumes, expressed as multiples of one adsorbent bed set, volume V, are shown in Table 4.2. In the following, it is assumed that each bed set has a length of 52.4 m (cf. Clause 5). The absolute volumes that result are shown in Table 4.3.

Combination	Volume produced by one bed set A(m^3/d)	Buffer volume dV (m^3/vessel)
A.1	2.250	3 500
A.2	3 000	3 500
B.2	3 250	3 500
C.3	250	3 500

Table 4.3 Volumes produced by one adsorbent bed set.

It is assumed that only the adsorbent bed set which is actually being served, is closed for wave powered water intake.

4.3.2 Transport without intermediate storage tankers.

The mathematical model for calculation of the number of floating units, which can be served by the one and the same service vessel is illustrated in Fig. 4.2.

With t_1 = 1d, t_2= 1.7 d and t_2 = 0.125 d and t_3= 1d the results according to Table 4.4 can be derived.

	m	n	(af)	Loading capacity (thousand m^3)				(ss)	(ar)
				A.1	A.2	B.2	C.3		
	1	3	24	159	210	228	21	76	78
	2	2	18	314	418	452	38	120	52
	3	2	12	469	624	676	55	68	52
	4	2	9	624	832	900	72	16	52
300 n.m. off shore	5	1	14	780			90	164	26
	6	1	12				107	138	26
	7	1	10				124	112	26
	8	1	9				142	86	26
	9	1	8				159	60	26
	10	1	7				176	34	26
	11	1	7				193	8	26
	1	6	12					33	156
	2	4	9					39	104
	3	3	8					42	78
	4	2	9					98	52
20 n.m. off shore	5	2	7	as above	as above	as above	as above	46	52
	6	1	12					179	26
	7	1	10					153	26
	8	1	9					127	26
	9	1	8					101	26
	10	1	7					75	26
	11	1	7					49	26
	12	1	6				210	23	26

Table 4.4 Loading capacities of service vessels (thousand m^3) for transport without intermediate storage tankers. m = number of floating units served by one service vessel during one voyage, n = number of groups of m floating units served by the same service vessel during a period of 14 d, (af) = total number of service vessels required for a plant comprising 70 floating units, (ss)= service vessel standstill, (d/vessel, yr), (ar)= number of voyages per service vessel and year.

4.3.3 Transport with intermediate storage tankers

It is assumed that the intermediate storage tankers are on average located 20 nautical miles from the plant and 300 nautical miles offshore when loading takes place.

The total input of volumes to the tankers are those presented in Table 4.3 multiplied by the total number of adsorbent bed sets (=70x5 = 350).

The required intermediate storage tanker capacities are presented in Table 4.5.

t	(ab)	Intermediate storage tanker capacity (thousand m^3 per tanker)				Number of voyages per tanker and yr
(d)		A.1	A.2	B.2	C.3	(ar)
0.2	15	158	210	228	-	126
0.4	8	315	420	445	-	118
0.6	6	472	630	682	-	111
0.8	5	600	-	-	-	104
1	4	-	-	-	88	99
2	3	-	-	-	175	78
3	2	-	-	-	262	64
4	2	-	-	-	350	54
5	2	-	-	-	438	47
6	2	-	-	-	525	42

Table 4.5 Loading capacities of intermediate storage tankers (thousand m^3). t = time for loading one tanker at sea, (ab) = total number of tankers required for a plant comprising 70 floating units.

4.4 Comparison of costs

4.4.1 Introduction

The combinations of location for eluation and location for storage of liquids and the modes of transport can be evaluated primarily by comparison of the costs involved. For such a comparison, costs which are approximately similar in all combinations do not need to be regarded. Thus, the costs of, for example, pumping and harbour fees have been disregarded in the evaluation.

It is mainly the costs relating to transport services, which reflect the overall economic feasibility of the combinations A.1, A.2, B.2 and C.3 as shown in Table 4.1. As regards the floating unit costs, it is obvious that the cost of combination A.1 will be the highest, due to the large storage volumes required. The volumes of the floating units in combinations A.2, B.2 and C.3 are similar.

4.4.2 Costs related to the transport system

It is assumed that the service vessels and intermediate storage tankers will be purpose-built for their tasks.

Today (1980), it is very difficult to predict the development of the contracting prices of newly-built ships. In this project, contracting prices by the end of 1979 have been used in the evaluation.

The capital expenditure has been based on a 15-year vessel lifetime and straight line depreciation. The interest cost has been calculated for the first year, based on a rate of 10%.

Fuel costs have been divided between fuel during voyage, fuel for harbour and fuel at stand by at sea.

Additional operation costs include all other expenses, for example, assurance costs and costs for personnel.

The above costs are shown as functions of the vessel's capacities in Fig. 4.4.

The total annual cost of a vessel is the sum of the partial costs for all voyages during the year.

In order to calculate the transport costs for the combinations A.1, A.2, B.2 and C.3, the total annual cost for each vessel was multiplied by the total numbers of vessels required according to Tables 4.4 and 4.5. The result is illustrated in Fig. 4.5.

4.5 Conclusions

From the graphs presented in Fig. 4.5, the following conclusions can be drawn:

- It is not economically feasible to utilize intermediate storage tankers
- The relative cost difference between the combinations A.1, A.2 and B.2 is small
- The distance from shore to the plant has significant relevance for the cost level
- The combination C.3 is the most economic solution.

On the basis of these results, the combination C.3 (elution on land, storage of liquids on land) was selected for the conceptual design of the floating unit.

5. CONCEPTUAL LAYOUT OF A FLOATING UNIT

5.1 Introduction

A conceptual design for a floating unit for recovery of uranium from seawater has been made. The conceptual design is shown in Figs. 5.2-5.4, 5.8, 5.9 and 5.10.

The floating unit will be built in concrete in order to achieve long lifetime and low maintenance costs. Due to the high outer water pressures, which act on the structure, it is constructed of circular caissons in order to minimize the weight. The caissons will be slip-formed.

The unit will have the space necessary for auxiliary equipment such as pipes, power supply units, pumps, moorings, workshops, living quarters, cranes, heliport and life-saving units.

5.2 Design criteria

Since the exceedance frequency of waves with a significant height of more than 2.5 m is only about 18% and waves with a significant height of 1 to 2 m have the highest absolute frequency at the location selected offshore South Africa, the design seawater inflow has been related to a wave with a significant height of about 2 m. This design inflow is about 1 m^3/s, m.

The design inflow of seawater for slurry transport is 2.0 m^3/s, m.

The design wave crest elevation for survival conditions has been estimated to about 17 metres above the still water level of the sea.

5.3 Design

5.3.1 General description

The principal design of a floating unit is as follows:

- five central circular caissons in a row, each containing adsorbent beds
- 11 circular buoyancy and ballast tanks on each long side of the central row of caissons
- one, buoyancy tank rectangular in plan on each long side of the central row of caissons, which rests on the 11 circular buoyancy and ballast tanks, and with the top designed as the sloping plane for wave energy conversion. Each tank is divided into watertight sections by longitudinal and transverse walls.

- one transverse wall on each short side of the floating unit, which together with the inner longitudinal walls of the rectangular buoyancy tanks, defines a water reservoir in plan
- a horizontal floor submerged between the four walls of the water reservoir, which rests on the five central caissons
- five ring shaped pipe gallery buildings standing on the floor of the water reservoir

5.3.2 Central caissons with adsorbent beds

Each circular, central caisson has an outer diameter of 52.40 m and a height of 17.75 m, the bottom included. An outer shaft runs along the circumference of the inner side of the outer wall of the caisson and reaches vertically unbroken from the upper edge of the caisson to the upper surface of the bottom. An inner shaft, with an inner diameter of 8.00 m, reaches vertically unbroken from the upper edge of the caisson to the lower surface of the bottom. Between the inner and outer shafts of the caisson are 16 evenly spaced, radial walls.

The central caisson is stratified into six horizontal storeys each with an inner, free height of 2.50 m. Each storey within one section between the radial walls is arranged in accordance with the following description.

On the floor there are arranged three, evenly spaced, radial guide walls with a height of 0.80 m. The guide walls are connected to the inner walls of the outer shaft, but do not entirely reach the inner shaft. In the inner wall of the outer shaft there is one opening between each pair of guide walls. Also on the floor there is arranged one wall, circular in plan, with an outer radius of 5.00 m, a height of 0.90 m and the centre coinciding with that of the central caisson.

Between and through this wall and the inner wall of the outer shaft run two plastic pipes, ⌀ 0.71 m, which rest on the floor and each touch one of the radial walls, which transversely limits each section. In the outer shaft, each pipe is connected to a smaller shaft, which is isolated from the outer shaft, with walls. These smaller shafts, the total number of which is 32, are intended for slurry transport, and plastic pipes from six storeys are connected to each pair.

Guide walls are connected to the ceiling, which are arranged in the same way as those on the floor, but with a height of 0.30 m. A circular wall is arranged below the ceiling with a height of 0.90 m, in the same way as on the floor. This circular wall is hung between and connected to the 16 radial walls, so that an opening with a height of 0.30 m is formed between the lower surface of the ceiling and the upper edge of the wall. This wall is, connected at its lower edge to the central shaft by a horizontal ring beam.

On the lower and upper guide walls there are arranged horizontal, perforated corrugated sheet metals. Woven fabrics are placed on the free surfaces of these.

The adsorbent material is stored in the free space between the woven fabrics, with a height of 1.20 m.

The central caisson rests with its bottom on 8 radial walls with a height of 8.50 m. The inner edges of the walls end 8.00 m from the centre axis of the central caisson.

In the free space below the central shaft there is arranged a closed, circular caisson with a diameter of 15.40 m and a height of 4.00 m. Filled with water, the caisson rests on a ring beam connected to the lower edges of the 8 radial walls. The caisson, filled with air, floats and closes the central shaft of the central caisson.

5.3.3 Pipes

To each central caisson there are connected congruous systems of pipes. These systems are connected to two longitudinal and horizontal collecting pipe sets, one set in each of the two rectangular buoyancy tanks. Each collecting pipe set comprises three pipes, one for intake of seawater for mixing of the adsorbent to slurry, one for slurry outlet and one for intake of made up adsorbent material in slurry form. A throttle valve is mounted at each connection before the pipes reach the collecting pipes. The two sets of collecting pipes are connected to each other by three transverse and horizontal pipes. To each end of the transverse pipe system there are connected three vertically mounted pipes, which run up to loading arms, mounted on top of the floating unit. These pipes can be connected to a service vessel by hoists.

Vertical pipes with throttle valves are mounted between the seawater intake openings in the ceilings of the ring-shaped pipe gallery buildings and the outer shafts of the central caissons.

5.3.4 Moorings

The unit will be moored by means of a 14 line system. At the location 120 nautical miles offshore, in a water depth of 120 m, chains with a diameter of 117 mm and 60 tonnes anchors will be utilized. At the location 300 nautical miles offshore, where the water depth is about 1 800 m, wire ropes with a diameter of about 150 mm will be used. In this case, each anchor will comprise 1 500 m chain with a diameter of 150 mm.

5.4 Operation

5.4.1 General description

The principle methods of functioning is as follows:

- seawater rushes up on one of the sloping planes and is accumulated in the water reservoir
- the seawater is forced through openings in the ring-shaped pipe gallery buildings into the adsorbent beds in the central caissons and then to the sea

- the level of the crest of the sloping plane is adjusted by pumping ballast water into or out of the circular buoyancy tanks
- evacuation and filling of the adsorbent material are carried out by slurry pumping, with seawater as carrier, between the floating unit and a service vessel.

5.4.2 Normal operation

During normal operation for extraction of uranium from the seawater, the circular caissons below the central shafts of the central caissons are completely filled with seawater, so that the bottom openings of the shafts are open. The valves on the seawater intake pipes, in the water reservoir, are open. All other valves are closed.

The seawater is forced from the outer shafts in the central caissons into the space under the adsorbent beds, then vertically upwards through the adsorbent material, which will be fluidized, and to the space above the beds under the ceilings. From there the seawater is fed into the central shaft of each central caisson and out to the sea.

5.4.3 Evacuation of adsorbent material

The valves on the seawater intake pipes are closed. The circular caissons below the central shafts are air-filled, so that the central shafts of the central caissons are closed for water flow.

Seawater is pumped from a service vessel in a hoist, connected to one of the loading arms, and into one of the collecting longitudinal pipes. From there the water runs into one section of the outer shaft of one of the central caissons and then enters the six adsorbent beds within this section. Since the normal stream direction is closed by the central sub-bottom caisson, the seawater, mixed with adsorbent material, will run into the two plastic slurry pipes below the adsorbent bed and then into the pair of smaller shafts, which are isolated from the outer shaft of the circular caisson.

The slurry is then transported in another collecting pipe and hoist to the service vessel.

5.4.4 Input of adsorbent material

Made up adsorbent material is slurry mixed on the service vessel and pumped into the floating unit in the third pipe of the collecting pipe set. Six adsorbent beds within one section of one central caisson are fed at the same time.

5.5 Pumps

5.5.1 On board service vessels

In each service vessel, six centrifugal pumps are installed (one stand-by), each with a capacity of about 1.4 m^3/s and a power demand of about 515 kW.

Five pumps are utilized for pumping of seawater into the floating unit and for slurry mixing in the beds. For pumping of made up adsorbent material as slurry into the floating unit, one pump is used for slurry mixing and one for slurry transport. The two pumps are utilized to half their capacity and each one has then a power demand of about 400 kW.

The total energy consumption for the complete reconditioning of one floating unit during one cycle has been calculated to about 23 MWh.

5.5.2 On board floating units

In each floating unit, pumps are installed for level adjustment purposes. Since these pumps can be designed only after simulation of weather conditions, similar to those prevailing on the plant location selected, no estimate has been made of the characteristics of these pumps.

5.6 Plant data

5.6.1 Floating units

A plant comprising 70 floating units has been studied. Each unit has the following basic data:

-	length,	total unit	293.24	m
		sloping plane	261.00	m
-	width,	loading arms incl	126.40	m
		" " excl	96.40	m
-	height,	loading arms incl	74.60	m
		" " excl	40.00	m
-	displacement,	39 m draught	1 065 000	t
-	ballast water,	39 m "	213 000	m^3
		34 m "	87 000	m^3
-	water reservoir volume		120 000	m^3
-	adsorbent material volume		17 500	m^3
-	moorings,	number	14	
		length per each 1 800 m depth	5 250	
		" " 120 m depth	700	
-	concrete volume		180 000	m^3
-	pipes,	HDPE ø 500 mm	4 000	m
		" ø 710 mm	18 250	m
		steel ø 1200 mm	2 900	m
		" ø 1400 mm	1 250	m
		" ø 2000 mm	4 300	m
		" ø 2100 mm	500	m
-	valves, el. throttle	ø 1200 mm	80	
		ø 2000 mm	160	
		ø 2100 mm	80	
-	living quarters		12	persons

5.6.2 Service vessels

The selection of the number of service vessels and their loading capacity is based on the result of the system analysis presented in Fig. 4.5.

If the plant is located 300 nautical miles offshore, nine tankers of about 75 000 dwt each will be selected, whereas for a location 20 nautical miles offshore, eight tankers each of about 55 000 dwt will be selected. Furthermore, for each location one extra service vessel will be required for stand-by redundancy.

6. DYNAMIC RESPONSE OF THE FLOATING UNIT

The wave loads and heave response motions of the floating unit have been computed using program suite NMIWAVE. NMIWAVE has been developed by the National Maritime Institute, England. The programs compute linearised wave loads, added masses, damping coefficients and rigid body response motions for tethered or free structures. By combining diffraction theory for large diameter members with a linearised Morison's equation for smaller members, the programs they compute the fluid forces more efficiently and accurately than either method alone.

Regular waves, with no current, impinge on a stationary structure of general shape. The wave height is assumed small compared with wavelength and water depth. Potential flow is assumed for the diffraction model, and the drag term in Morison's equation is linearised. The floating structure may be free floating or moored by cables which are dragless, weightless and taut.

In this case, the heave response, i.e. the vertical translation, and the oscillating part of the pressure along the center-line of the bottom of the floating unit, have been calculated. The results are shown in the table below.

Under preparation.

7. ACTUAL URANIUM UPTAKE

7.1 Introduction

The annual uranium uptake presented in Clause 3 for the site selected will be reduced primarily as a result of losses, the dynamics of the floating units, directional spreading of the component sea waves and obliquely incoming waves. Secondary reasons for uptake losses are, for example, breakdown due to pollution of the adsorbent and non-optimal level trimming of the floating unit. The secondary reasons for losses are not predictable and will not be discussed. The primary reasons are discussed below.

7.2 Hydraulic losses

The stream channels of the floating unit have been designed in order to keep the flow velocities small and thus to reduce losses. The total loss in the stream channels for seawater intake and outlet has been calculated to 0.14 x q^2, where q is the inflow of seawater per metre.

The adsorbent head loss has been treated in Clause 2.

The losses in the perforated, corrugated sheet metals and the woven fabrics are hard to quantify theoretically. These losses must be determined by hydraulic model tests. For the purpose of reaching an even loading of the adsorbent material within each storey of each section in a central caisson, it is suggested that a loss of about 0.2 m at the design discharge of 1 m^3/s,m is feasible.

7.3 Directional spreading of waves

The uranium uptake loss due to directional spreading of the waves has been calcualted, by assuming that the wave energy distribution is proportional to $(\cos a)^4$, where a is the angle between the directions of the wind and the waves. Of the wave energy available, 90.5 % will reach the floating unit.

7.4 Obliquely incoming waves

If the incoming waves' mean diretion is not perpendicular to the longitudinal axis of the sloping plane, uptake will be reduced.

For the calculation of this loss, it has been assumed that the moorings of the floating unit can be tightened and loosened in such a way that the heading of the unit can be varied to a degree of $\pm 30^\circ$. This directional flexibility implies that wave energy from all directions can be received but this to a lesser extent when waves arrive obliquely.

At a deviation of 30° between the mean wave direction and the perpendicular to the sloping plane, 78.5 % of the incoming wave energy will be received by the unit. The corresponding figure for a 60° deviation is 47.7 %.

7.5 Actual uranium uptake

The theoretical graphs of uranium uptake versus significant wave height, presented in Clause 3, were revised with due consideration given to the hydraulic losses mentioned above. The results are shown in Fig. 7.1.

Taking into account the variations of wave directions and the wave heights concerned it was possible to calculate the actual uranium uptake at the site selected. The true uptake is estimated to be about 3.4 tonnes/yr, 100 m.

7.6 Number of floating units required

As mentioned in Clause 4 the total plant will produce about 600 t of uranium per annum.

The design presented in Clause 5 suggests a length of the sloping plane of 261 m and thus each floating unit has a production potential av 2.61 x 3.4 = 8.9 tonnes/yr. The total number of floating units required will then be 600/8.9 = 67.4 or about 70.

8. COSTS

8.1 Investment costs

The cost estimates refer to the price level at the end of 1979 in Sweden and do not include the processing plant on land and the harbour facilities.

The costs of the floating units have been based on bills of quantities and manpower requirements. The costs relating to moorings and vessels have been estimated by manufacturers and shipping companies.

The cost of the titanium oxide required, 1.225×10^6 m^3 or about 1.35×10^6 tonnes for the total plant, has a significant influence on the economic feasibility of the total concept. In this report, this cost will be expressed as multiples of the titanium cost per kilogram, Ti. Thus the investment cost in titanium oxide for the complete plant is 314xTi million USD.

The total investment costs for the complete plant, with processing plant and harbour structures excluded, are shown in Table 8.1.

	Cost ($USD\times10^6$)	
	Distance from coast	
	20 n.m.	300 n.m.
Floating units	7 895	7 895
Moorings	325	1 495
Winches etc.	815	815
Service vessels	240	300
Titanium oxide	314xTi	314xTi
Total	9 275+314xTi	10 505+314xTi

Table 8.1 Total investment costs, with processing plant and harbour excluded, Ti = titanium oxide cost (USD/kg)

The cost of the construction yard has been estimated, and is based on area and excavation requirements. This was estimated to about USD 23 million. The possible construction of a municipality is not included in this cost.

It has been assumed that 10 floating units will be produced per year, during a total time span of seven years. The manpower requirement is about 10 000 employees.

8.2 Operation and maintenance costs

8.2.1 Labour costs for operation and administration.

The manpower requirements have been estimated at 560 for service on the floating units, 400 for service on the service vessels and 25 for administration. The total labour cost will be about USD 95 million per annum.

8.2.2 Inspection, maintenance and repair

Underwater inspection of the concrete structures of the plant will be carried out once every two years by three teams of divers. The annual cost for long-term hire of three diving vessels with divers has been estimated to about USD 50 million.

The moorings will be inspected once every two years with the aid of remote-controlled underwater inspection equipment. The estimated annual costs for this service are USD 4 and 6 million for the sitings 20 and 300 nautical miles offshore, respectively.

The need for supply vessels for the transport of, for example, spare parts, has been estimated to three vessels, which will be hired for a total annual cost of about USD 6 million.

The annual cost for maintenance and repair of the concrete structures and the pipe installations will be about USD 4 million.

The sum totals of the annual costs for inspection, maintenance and repair are thus about USD 64 and 66 million for the locations 20 and 300 nautical miles offshore, respectively.

8.2.3 Energy costs

With reference to Clause 4, the total fuel costs related to the service vessels will be about USD 6 and 14 million per year at the locations 20 and 300 nautical miles offshore, respectively.

The annual cost of energy for the pumping of slurry, based on the energy demand mentioned in Clause 5, will be about USD 5 million for the total plant.

The cost of operating the pumps for ballast water adjustments, has been estimated to be of the same order as that for the slurry pumps, or about USD 4 million per year and total plant.

The cost relating to all remaining energy supply on board the floating units has been estimated to about USD 1 million per year.

Thus, the annual total energy costs for the plant operation will be about USD 16 and 24 million per year for the locations 20 and 300 nautical miles offshore, respectively. In the cost for electric energy is included maintenance and repair of the power stations and the distribution networks.

8.2.4 Insurance costs and harbour fees

With reference to Clause 4, the total annual costs for insurance of the service vessels will be about USD 13 and 15 million, stand-by vessels included, for the locations, 20 and 300 nautical miles offshore, respectively.

The insurance cost of the floating units will be about USD 195 million per year and total plant.

Harbour fees are not included in this report.

8.2.5 Transport

Annual cost for the transportation of personel by helicopter will amount to about USD 5 million.

8.2.6 Adsorbent loss

During each elution process, a loss of about 0.3% in volume is expected. The annual loss of adsorbent material for the complete plant will then be about 8%, which figure corresponds to a cost of about 25xTi million USD (Ti= titanium oxide cost, USD/kg).

8.2.8 Total operation and maintenance costs

The total operation and maintenance costs for the complete plant, with processing plant and harbour structures excluded, are shown in Table 8.2.

	Cost (USDx10^6)	
	Distance from coast	
	20 n.m.	300 n.m.
Labour costs	95	95
Inspection, maintenance and repair	64	66
Energy	16	24
Insurance	208	210
Transports	5	5
Adsorbent loss	25xTi	25xTi
Total	388+25Ti	400+25Ti

Table 8.2 Total annual operation and maintenance costs, with processing plant and harbour excluded. Ti = titanium oxide cost (USD/kg).

9. CONCLUSIONS AND RECOMMENDATIONS

9.1 Plant design

The design of a floating unit and an offshore plant service system, which have been presented in this report, are to be regarded as a solution in principle of an integrated plant. The plant proposed, comprises all the functions required for the extraction of uranium from seawater. However, the limited time in which the project was carried out did not permit any extensive optimization of the concept. Anyhow, the system will serve as a basis for a conceptual calculation of the costs connected with uranium uptake from the sea, by using wave power and floating offshore units.

The proposed mooring systems are of a conventional catenary type. Alternatively, dynamic positioning systems can be utilized, especially if the water depth is considerable. Furthermore, such a system can be advantageous if the speed of the ocean currents is low.

9.2 Further investigations required

Below are listed some important aspects which should be investigated before a more refined and detailed design can be made of an offshore plant:

- the composition and capacity of the adsorbent material
- the design of adsorbent beds and the hydraulic characteristics involved
- water inflow over a sloping plane of irregular, multidirectional and obliquely incoming wave systems.

9.3 Conceptual cost calculation

In order to make an estimate of the costs associated with the offshore plant proposed, a conceptual cost calculation has been made. The result will not be the final, future cost but will be an indication of magnitude.

The estimate is based on the costs presented in Clause 8 and the following assumptions:

- the depreciation time is 50 years for the floating units; 15 years for the mechanical equipment including the service vessels and the mooring winches; 10 years for the adsorbent material and 5 years for the mooring lines and the anchors
- the price of titanium oxide is USD 1.10 per kg
- the facilities are written off on a straight line to zero value and must then be replaced with new equipment

- the processing plant on land and the harbour facilities are not included
- the annual uranium uptake is 600 tonnes
- the rate of interest is 10%.

The annual costs are shown in fig 9.1.

The costs of the uranium produced are shown in Fig. 9.2. To these costs should be added the costs of the processing plant and the harbour. Indicated by the graphs is a cost dependence on the water depth and the distance from the coast. Thus, a location 300 nautical miles offshore, in a water depth of 1 800 m will increase the cost by about 200-300 USD/lb, compared to a location in a water depth of 120 m and 20 nautical miles offshore.

Approximate calculations of the cost of a floating unit, which will be constructed as a box, indicate that the costs will be reduced compared to the presentation in Fig. 9.2. Estimates of these costs are presented in Table 9.1.

	Cost of uranium (USD/lb) Distance from coast	
Year	20 n.m.	300 n.m.
1	1 280	1 560
50	750	960

Table 9.1 Estimates of costs of uranium produced by an offshore plant. Box-type floating unit. Basic assumptions acording to Clause 9.3.

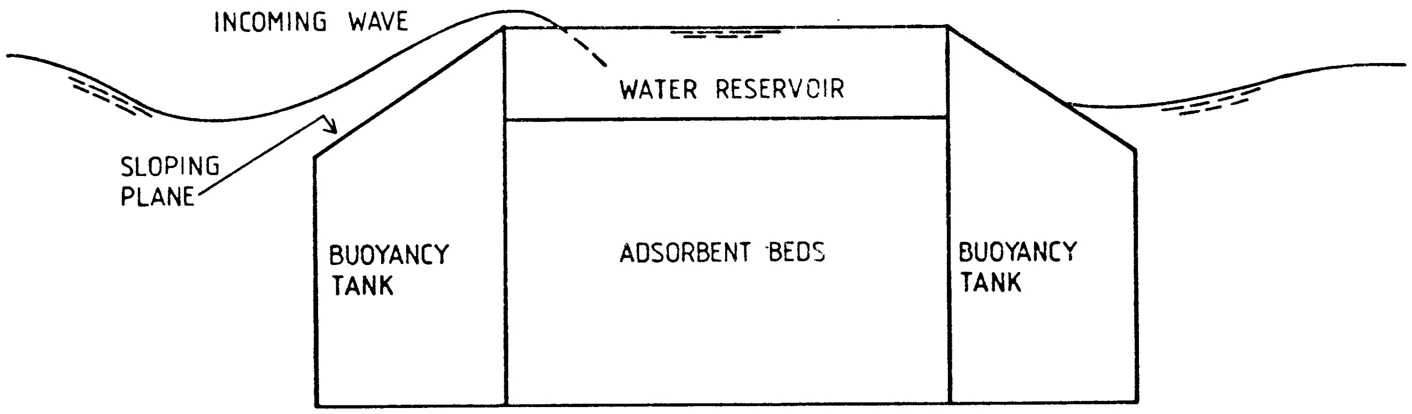
REFERENCES

Exxon Nuclear Company Inc,. Extraction of Uranium from Seawater, Reports XN-RT-14 and XN-RT-15, 1979.

Coastal Engineering Research Center, U.S. Army, Shore Protection Manual, Washington D.C. 1977

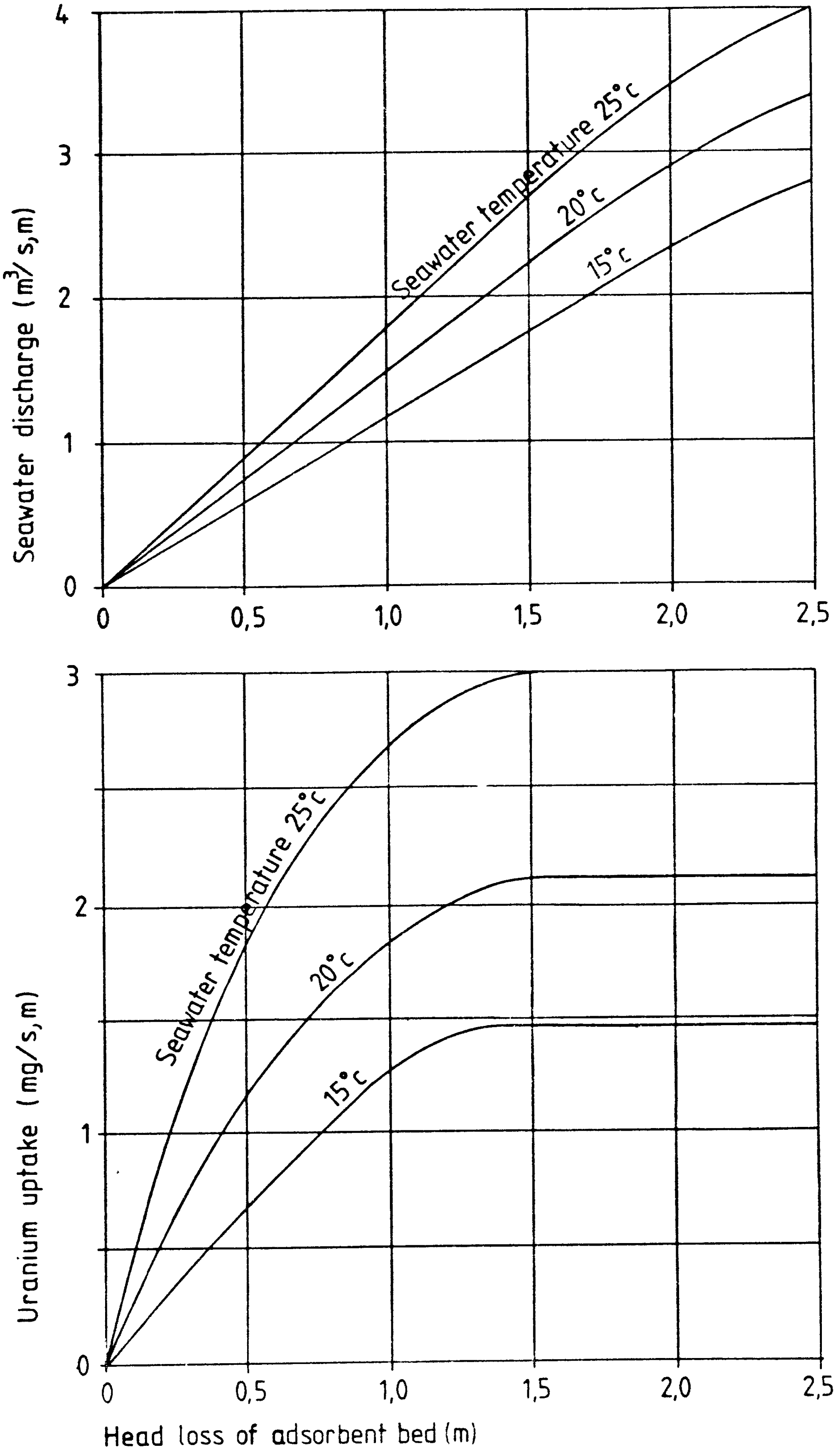
SCHEMATIC LAYOUT
OF FLOATING UNIT
FOR RECOVERY OF
URANIUM

FIG. 1.1



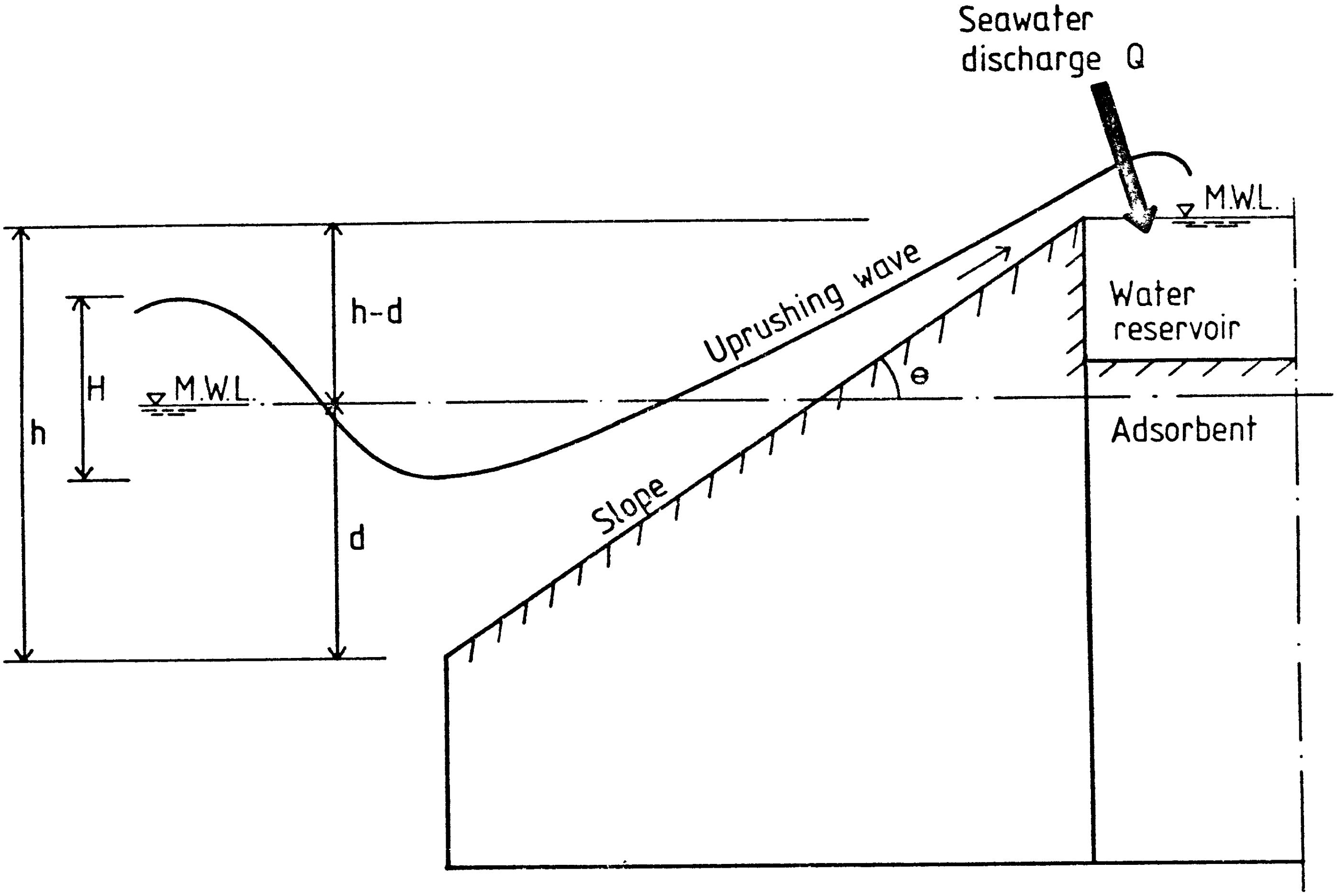
URANIUM UPTAKE VERSUS SEAWATER DISCHARGE AND HEAD LOSS

FIG. 2.3



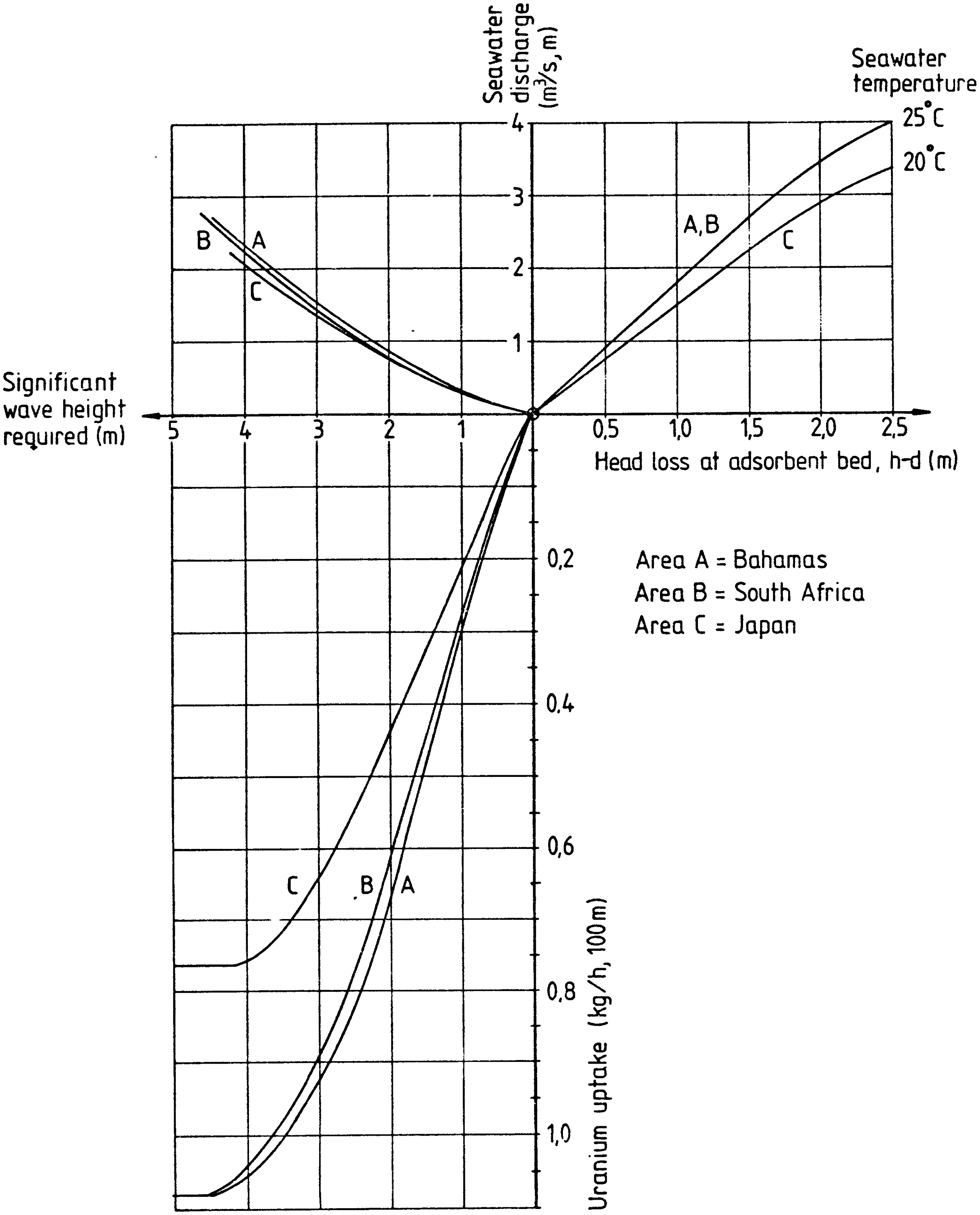
UNIT FOR RECOVERY OF URANIUM.
FUNDAMENTAL MODE OF ACTION,
NOTATION

FIG. 3.2



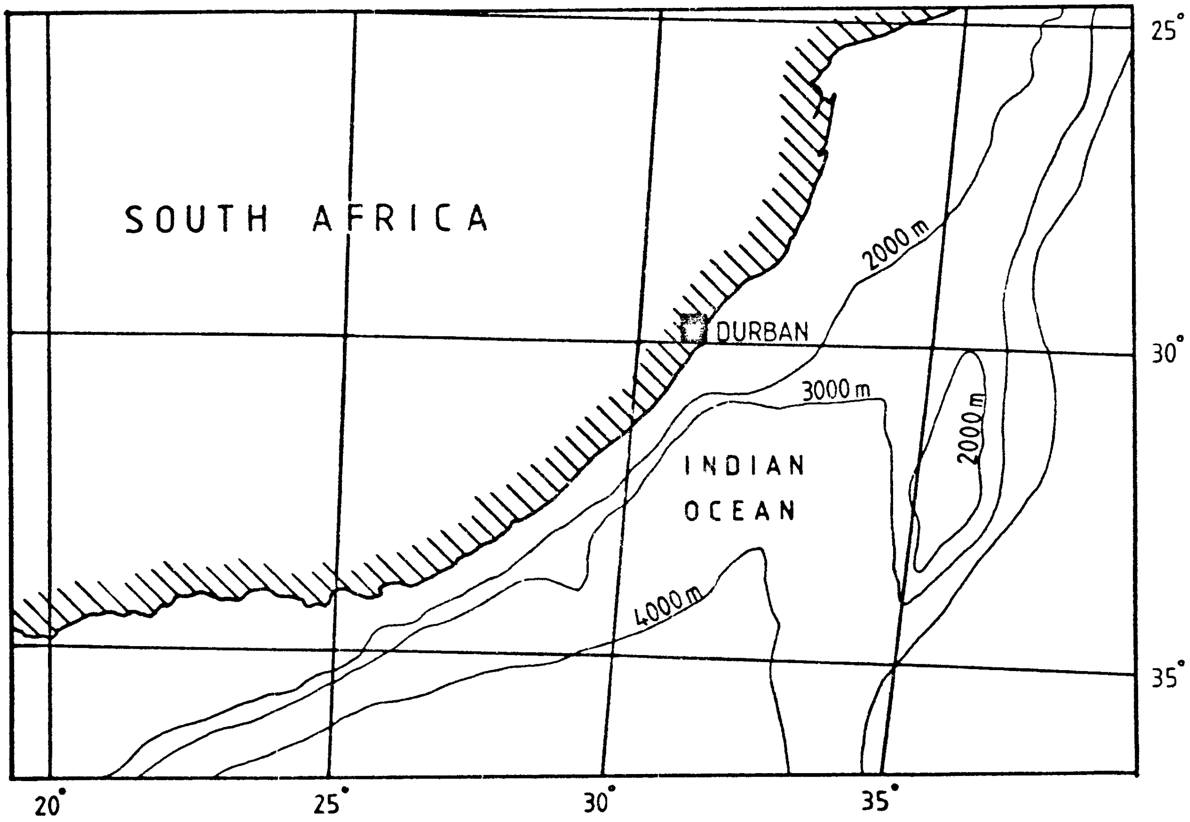
THEORETICAL URANIUM UPTAKE VERSUS SIGNIFICANT WAVE HEIGHT

FIG. 3.3



MAP

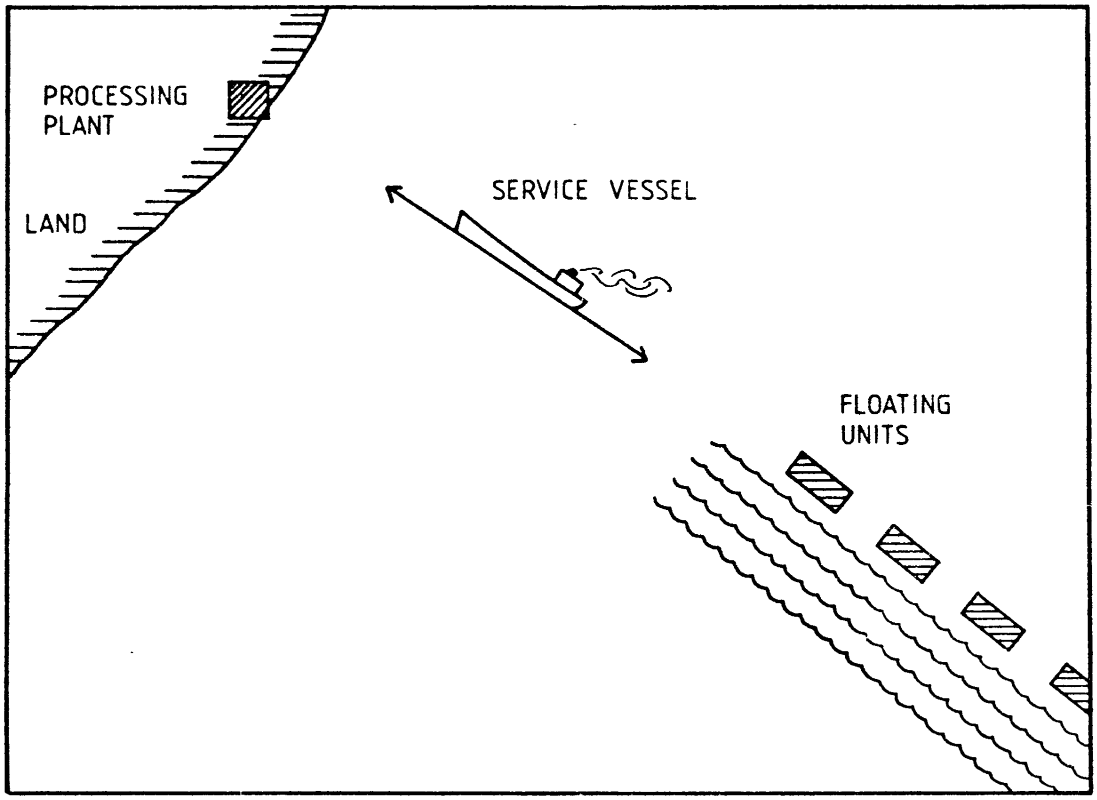
FIG. 3.4



SOUTH AFRICA
DURBAN
INDIAN OCEAN
2000 m
3000 m
4000 m
2000 m
25°
30°
35°
20°
25°
30°
35°

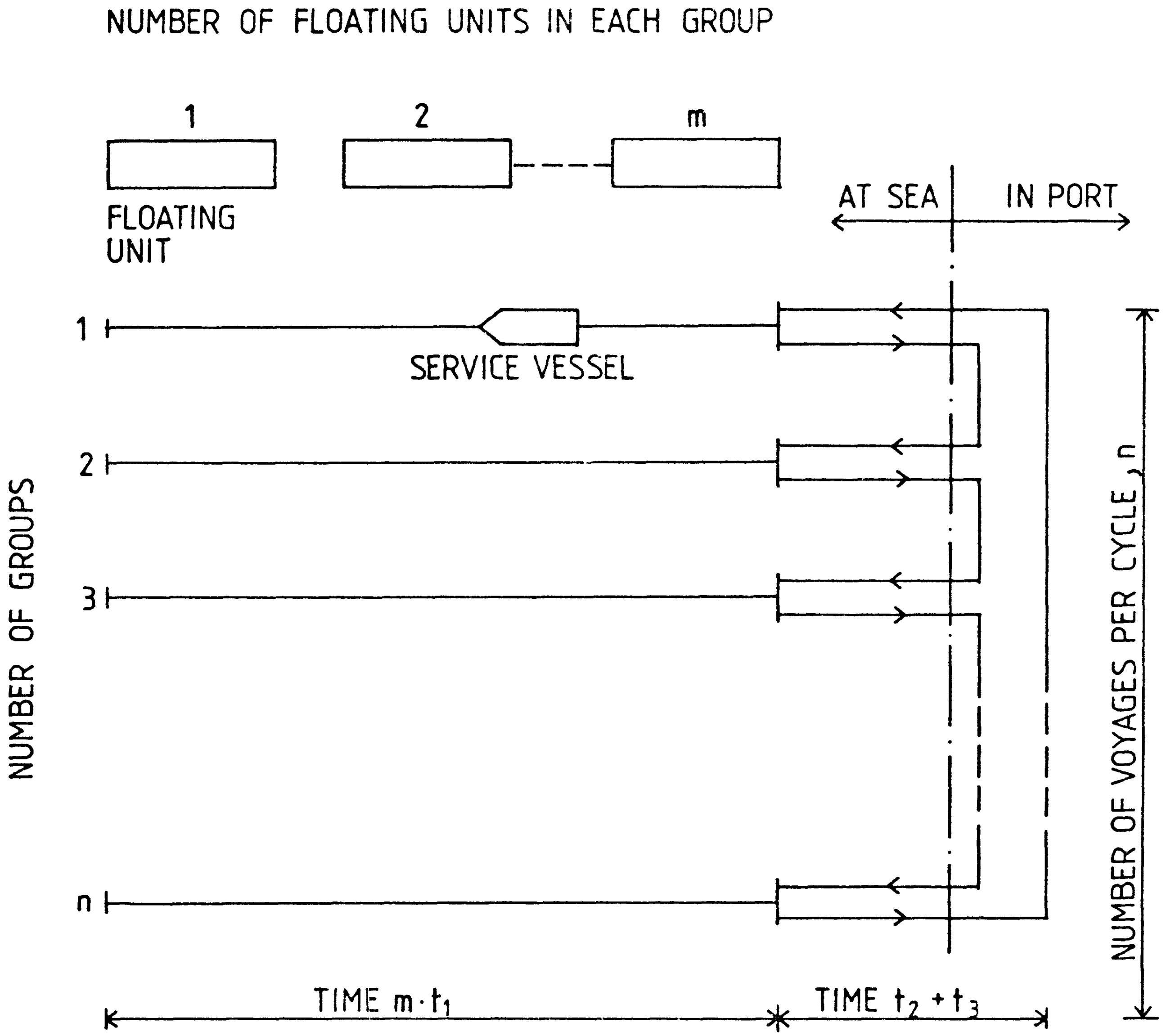
BASIC ELEMENTS
IN SYSTEM ANALYSIS

FIG. 4.1



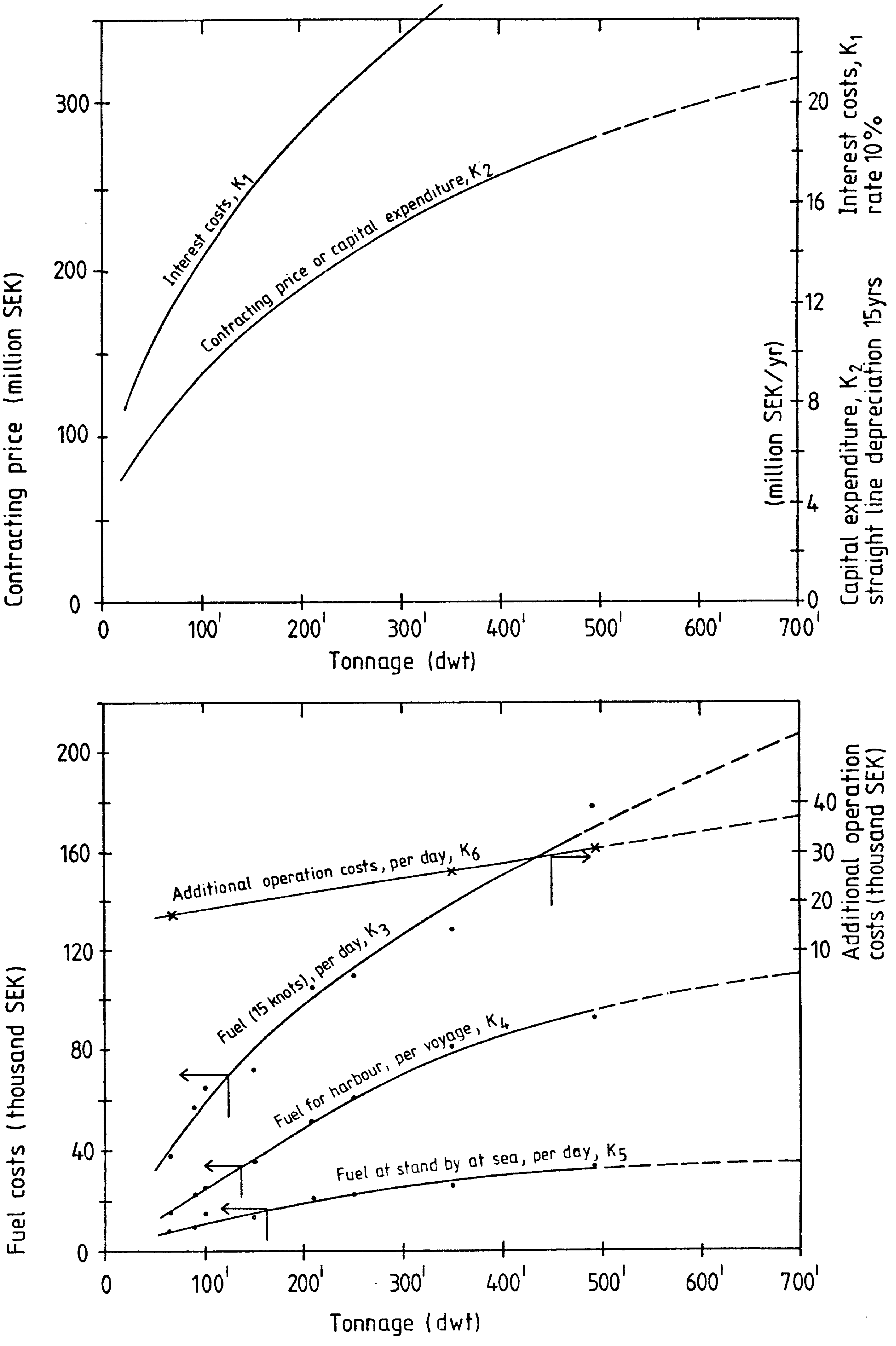
SERVICE VESSELS
FUNDAMENTAL MODE
OF SERVICE, NOTATION

FIG. 4.2



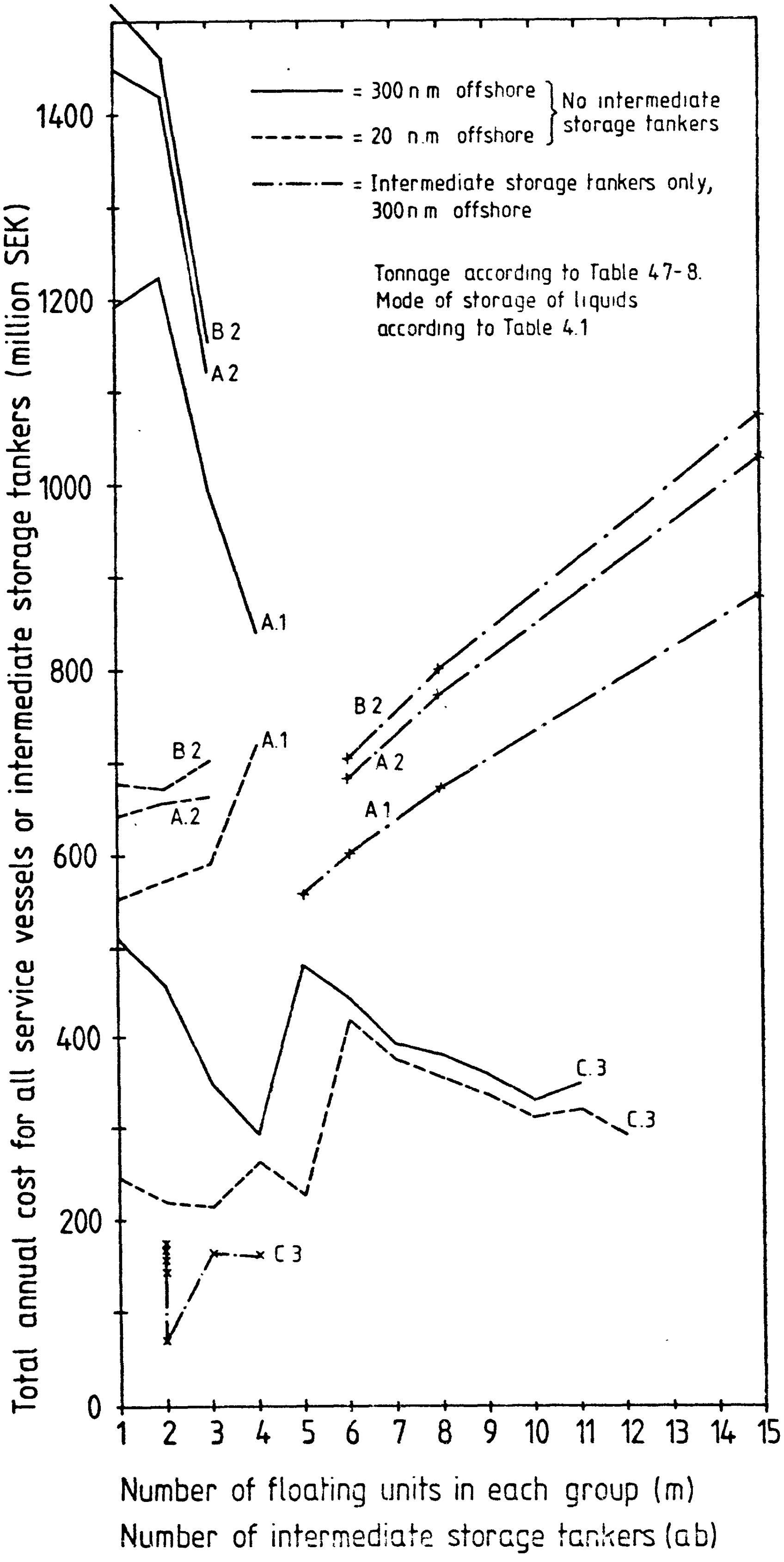
COSTS FOR SERVICE VESSELS
(END OF 1979)

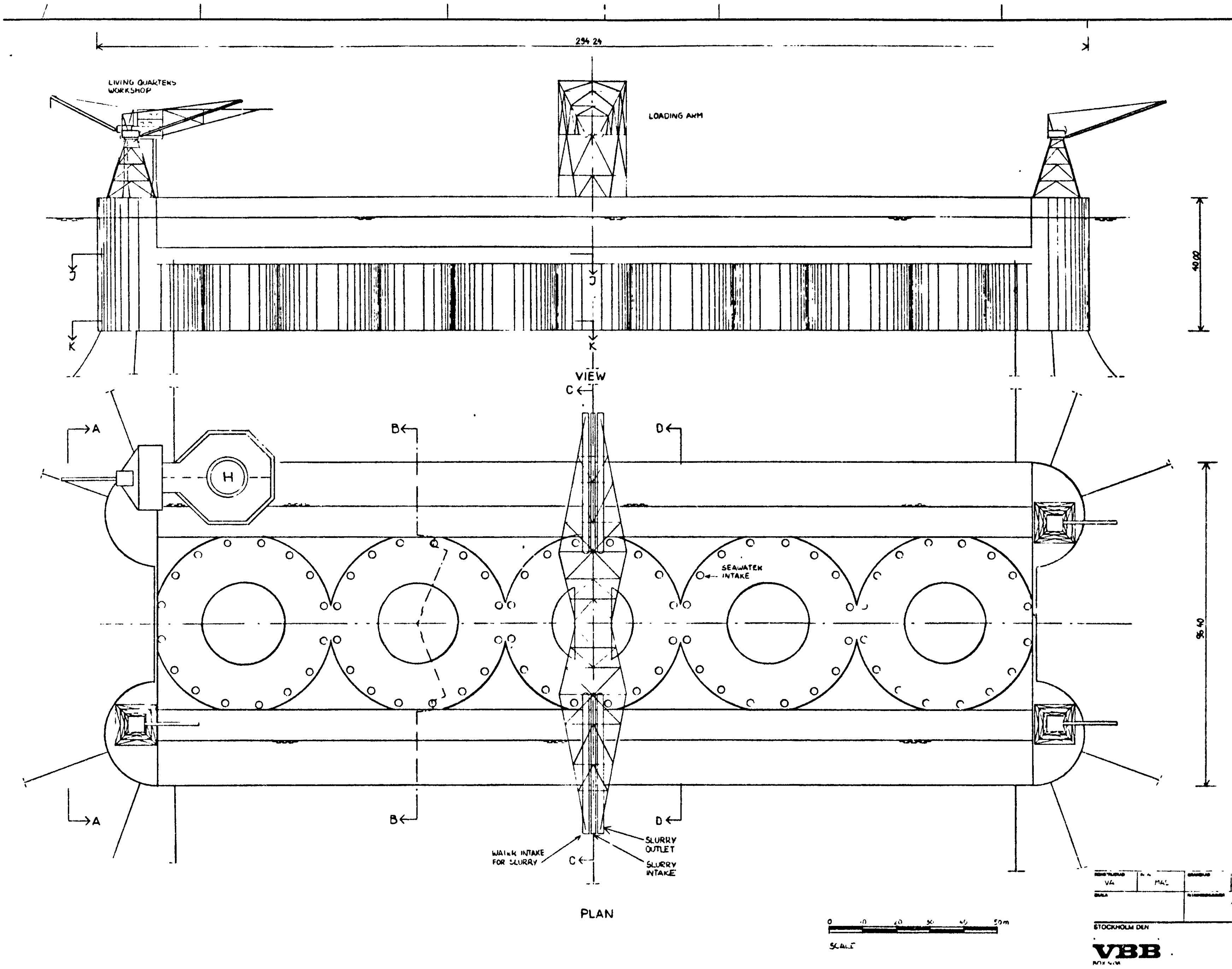
FIG. 4.4



TOTAL ANNUAL COST FOR
ALL SERVICE VESSELS OR
INTERMEDIATE STORAGE TANKERS

FIG. 4.5



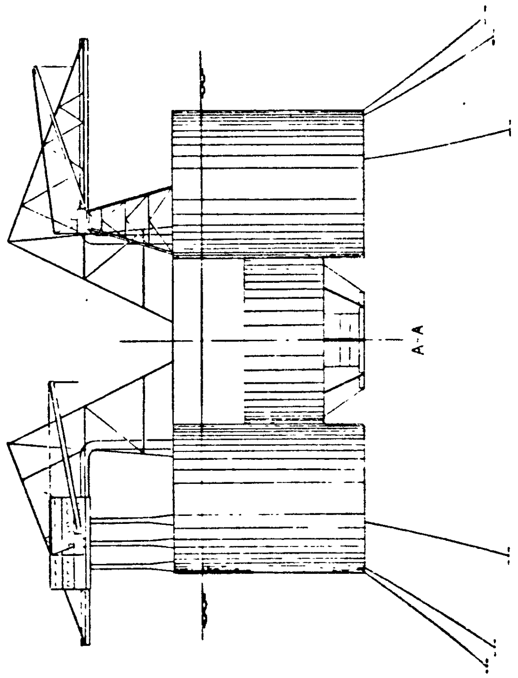


FLOATING UNIT

FIG. 5.2

FLOATING UNIT

FIG. 5.3



JA

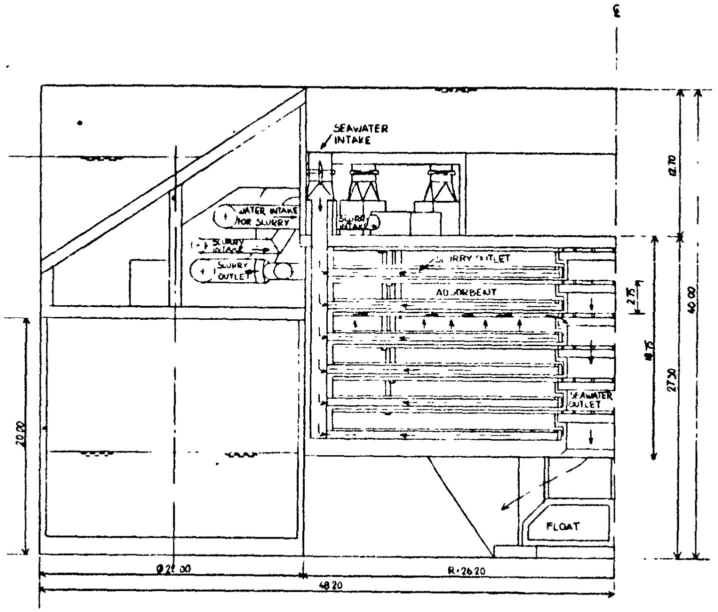
MAS

2

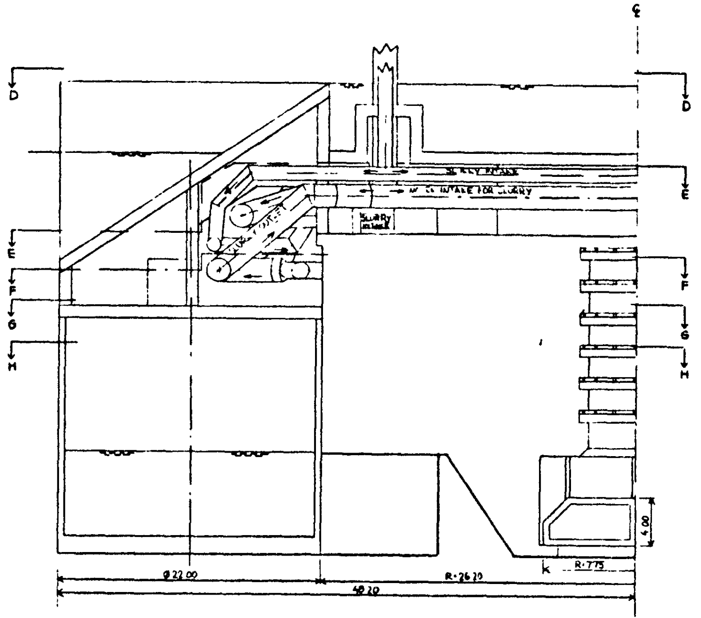
STOCKHOLM DEN

VBB

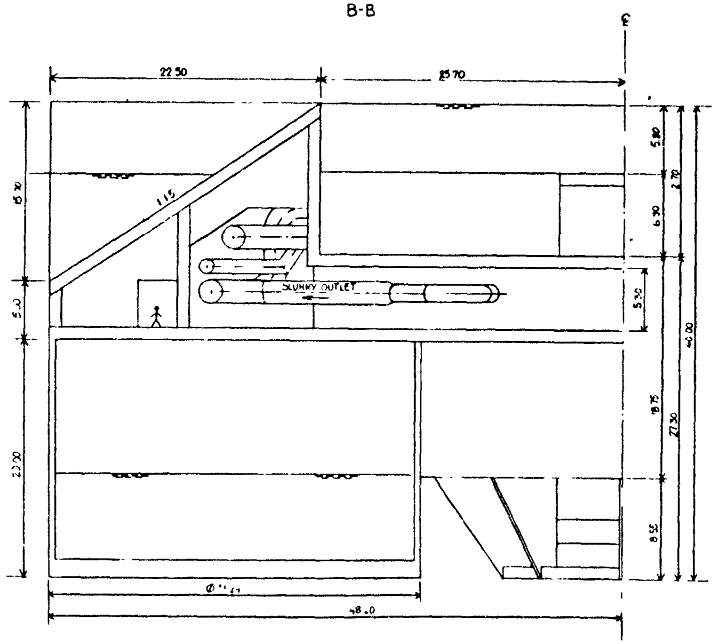
FLOATING UNIT



B-B



C-C



D-D

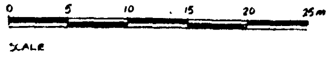


FIG. 5.4

14	MAS		A77.3
		3	

STOCKHOLM DLN

VBB

FLOATING UNIT

FIG. 5.8

VA

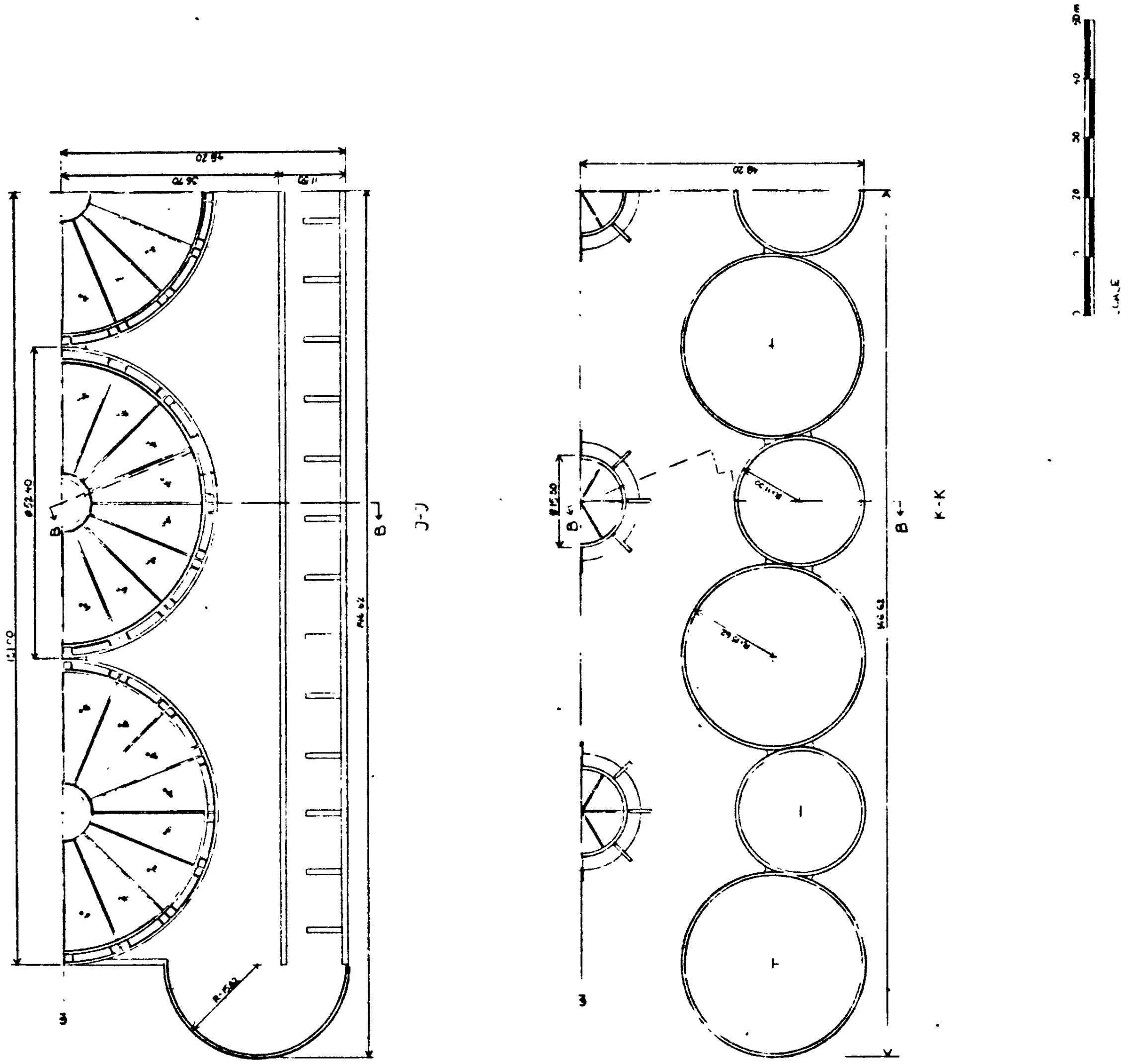
MAS

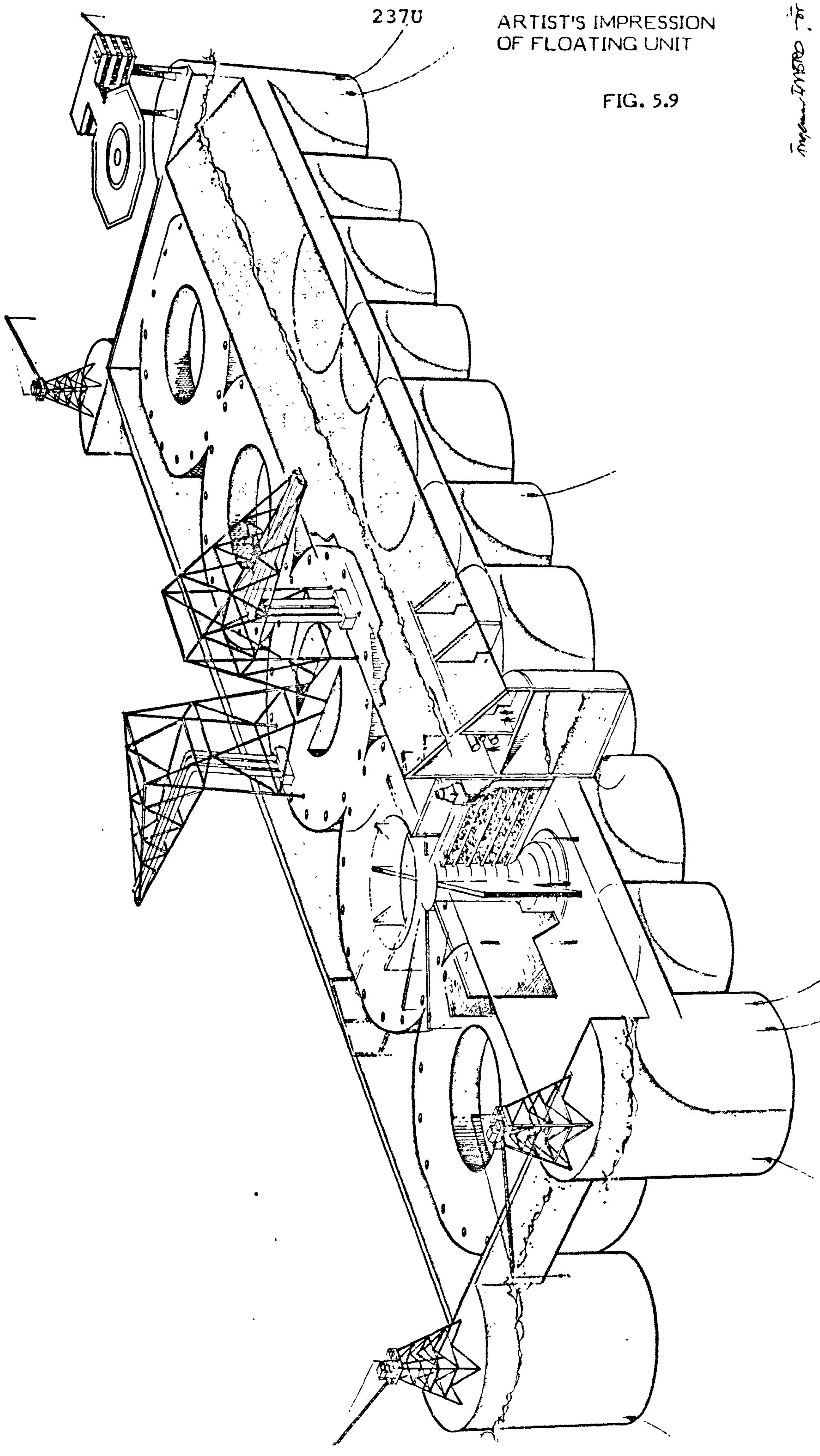
A7723

7

STOCKHOLM DEN

VBB

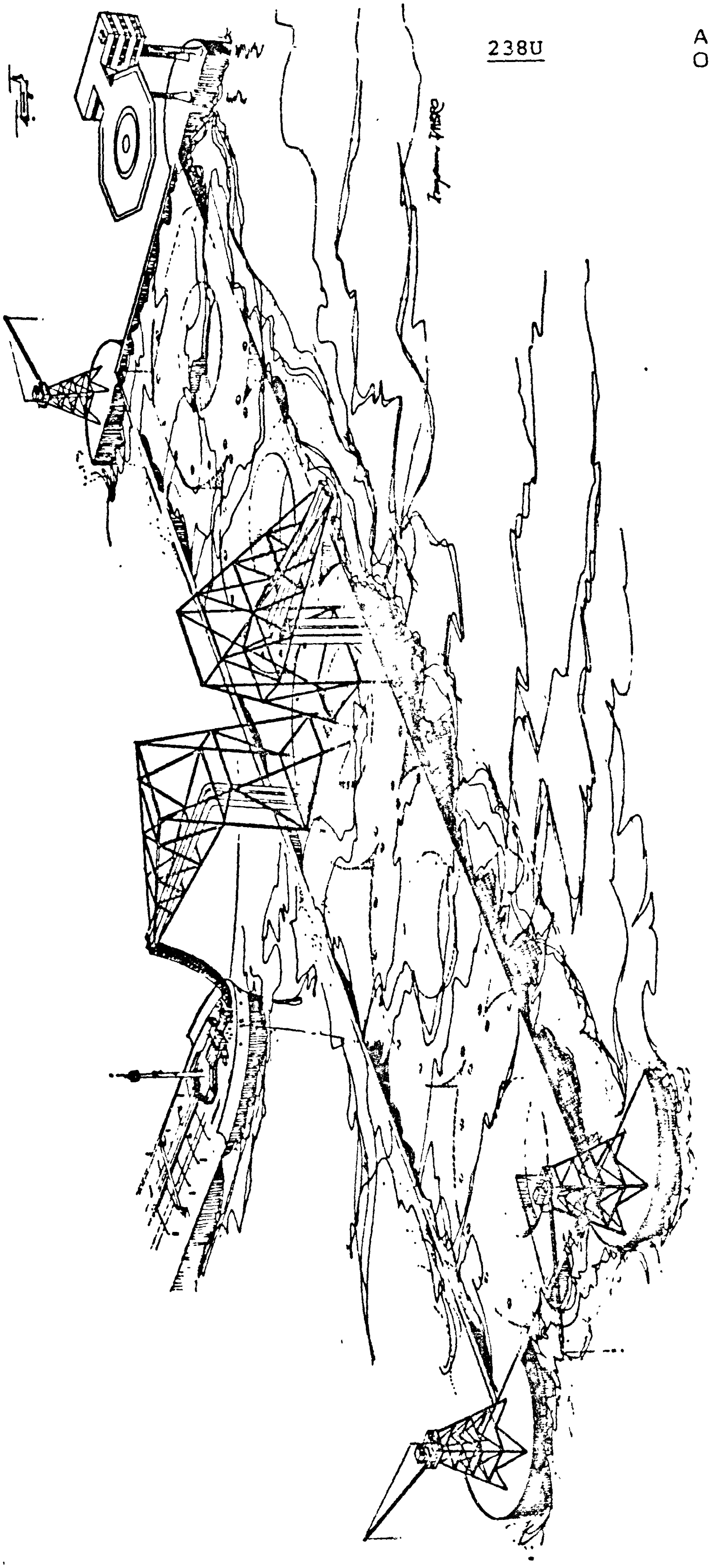




ARTIST'S IMPRESSION
OF FLOATING UNIT

FIG. 5.9

VBB

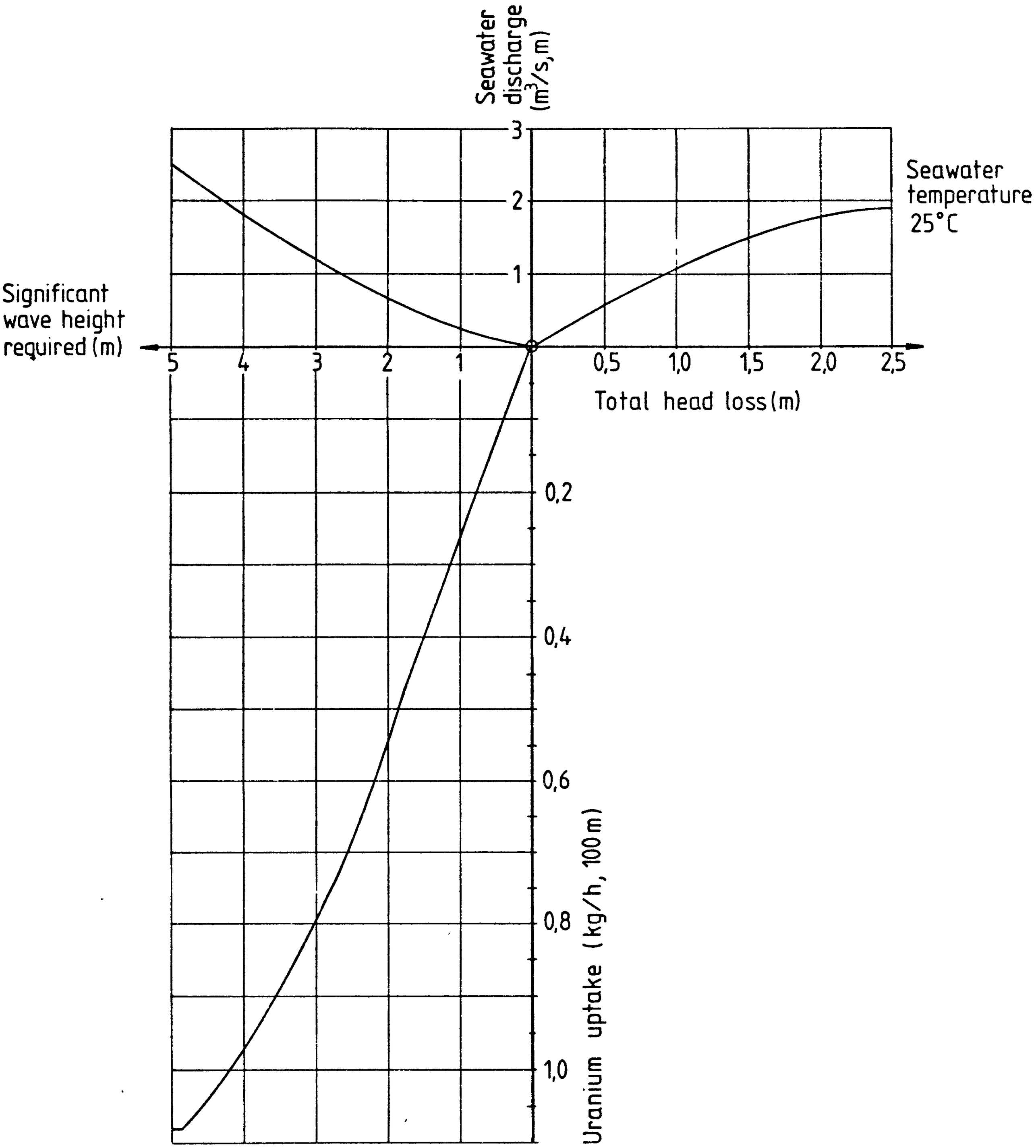


ARTIST'S IMPRESSION
OF FLOATING UNIT

FIG. 5.10

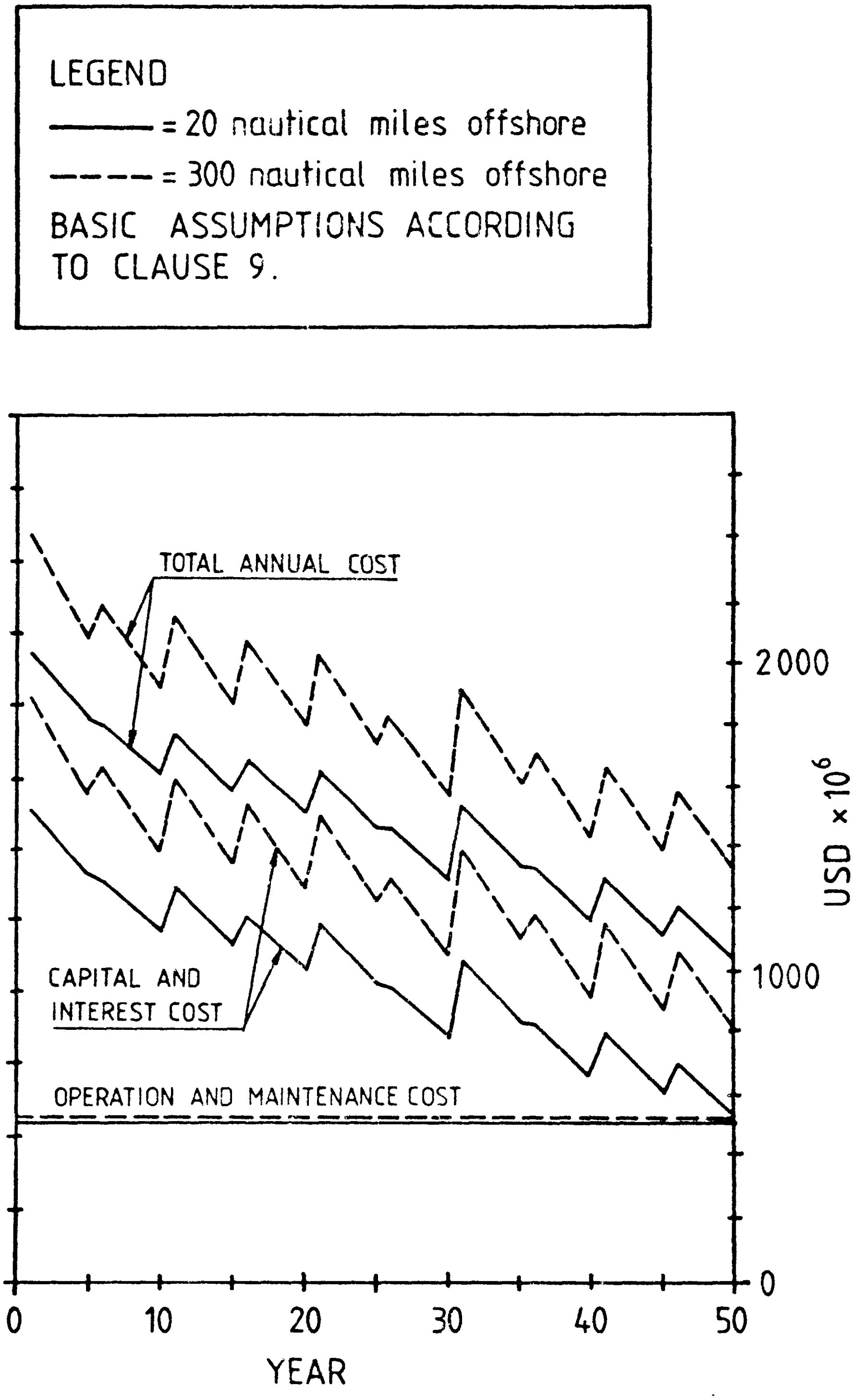
URANIUM UPTAKE VERSUS SIGNIFICANT WAVE HEIGHT AND TOTAL HEAD LOSS AT A LOCATION OFFSHORE SOUTH AFRICA

FIG. 7.1



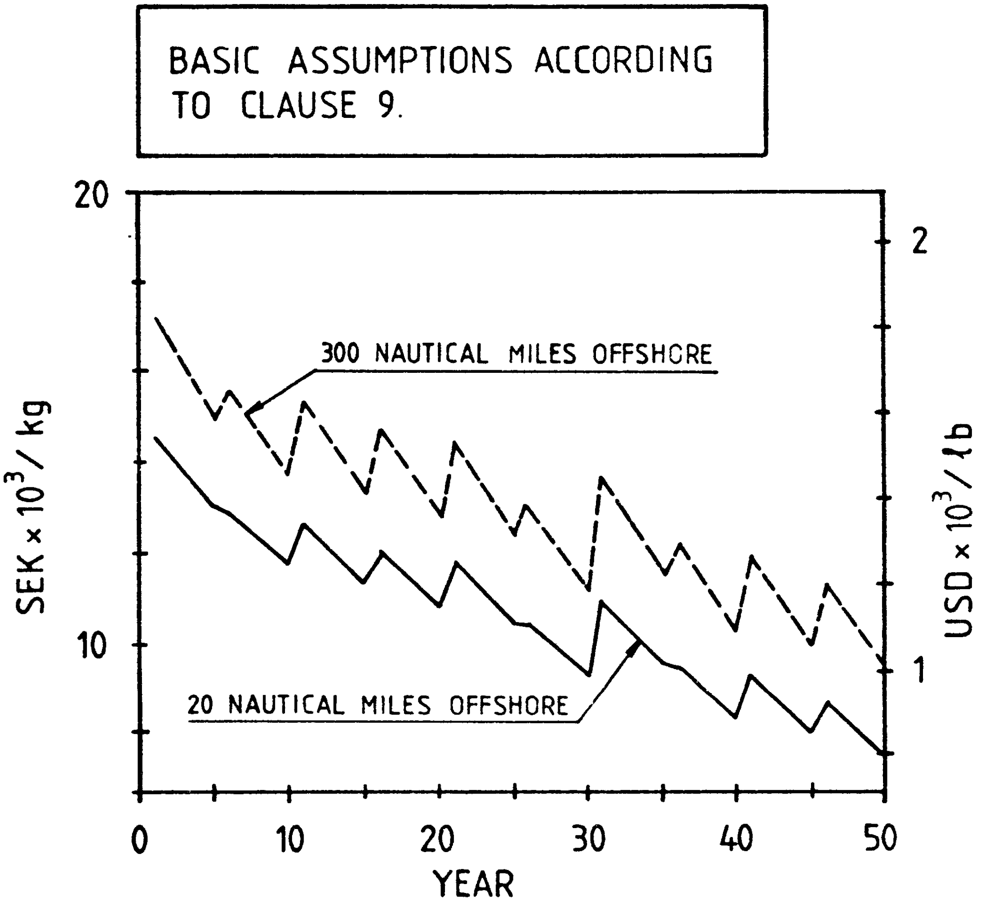
ANNUAL COST
OF OFFSHORE PLANT

FIG. 9.1



COST OF URANIUM
PRODUCED BY OFFSHORE PLANT

FIG. 9.2



Discussion on Dr. Vallander's Paper

In response to a question on parametric studies, Dr. Vallander stated that while an optimization had not yet been carried out, the capital cost of the floating units, and of the moorings, particularly with respect to their lifetime, were areas deserving attention.

It was indicated that the bed was an upflow bed in a slightly fluidized state. The particles are 0.5-1mm in diameter. In general parameters from the EXXON study were used in a very conservative manner.

In response to a question from Dr. Best, it was explained that the study was based on the average over an ambient spectrum of waves ranging from 0.5 to 2.5 meters in height.

With respect to economics it was indicated that the combination of price increases for terrestrial yellowcake and anticipated improvements in sorber properties should lead to a breakeven situation in 10-15 years. Hence an early start on unit construction was indicated: ultimately some 70 units would be built over a period of 30 years using a workforce of 10,000 men.

Lawrence Livermore Laboratory Concept for Uranium Recovery from Seawater

by

Dr. D. Gregg and Dr. F. Wang

(The following summary was reconstructed by the editors from the tape recording of the presentation; it is heavily edited and is not a verbatim transcription. The figures which are appended, however, are unaltered copies of the viewgraphs used by Dr. Gregg in his talk.)

The work reported here is preliminary in nature, reflecting an effort of 1-1/2 months duration. Hence the focus will be on the conceptual thinking underlying this work, which may well be subject to change during the coming year.

Our initial step was to review the comprehensive EXXON report to analyze the fundamental problems involved in recovering uranium from seawater. The central process step is the loading of hydrous titanium oxide (the sorber of consensus choice) with uranium, followed by a fresh water wash, elution with an ammonium carbonate solution, and then steam stripping of the latter.

Evaluation of the overall system shows that high capital investment is the dominant cost contribution, responsible for on the order of 70% of the projected cost of the uranium. Variations in this cost alone, depending on parameters such as the interest rate, would be sufficiently large to obscure the effect of many other factors. Thus we concluded that reducing capital cost is the primary target for cost reduction if a successful uranium from seawater process is to be developed.

Another major requirement is the large amount of fresh water needed to wash the titanium hydroxide. It is unlikely that many sites can be found having large amounts of fresh water next to a suitable oceanic environment for a recovery plant.

A troublesome fundamental problem is that while the titanium hydroxide sorber concentrates the uranium from seawater by a factor of 10^4 to 10^5 - an enormous separation step - the ammonium carbonate elution reduces this by a factor of a hundred or so. In effect, one is merely dealing with the ratio of carbonate concentrations in the elutant and in seawater - the sorber material is, from this point of view, irrelevant. A sorber having less capacity could be used and the concentration in the eluant stream could still be the same. In fact, if a less soluble material than titanium hydroxide were used, one could use more concentrated ammonium carbonate solutions and get a higher concentration of uranium. Furthermore, using this approach one has to steam strip a massive stream of eluant which is only a factor of a thousand or so smaller than the seawater stream - obviously a very energy intensive operation. This all leads to a product cost which is a factor of ten higher than acceptable in terms of 1990 market conditions, and a situation where the existence of a favorable overall energy balance must be questioned.

Thus we concluded that a process is needed which is the ultimate in simplicity.

In the EXXON report it was noted that activated carbon of some types might be capable of absorbing uranium at a level of 500 micrograms per gram. In addition, there was reference to Japanese work in which the carbon was loaded with titanium hydroxide to yield capacities as high as 800 micrograms per gram of carbon. The subject concept, then, is to <u>take the activated carbon approach and obtain the activated carbon from coal gasification.</u>

In the United States a synfuels economy is in prospect, particularly if gas and oil finds continue to decline. The production of activated carbon is a step in goal gasification, since the coal is pyrolyzed and then steam-activated, or partly gasified with steam. Hence there is the capability of producing activated carbon far less expensively than customary by making it as part of a synfuels economy.

The next step is to attain the lowest possible investment. Ocean-sited platforms are subjected to tremendous forces, because in the present application they will have to intercept ocean currents. Hence they will be expensive and hard to move. Thus our approach is to essentially avoid the need for any structure by scattering the activated carbon on the surface of the ocean, allowing it to settle to the bottom, and then "vacuuming it up" from the ocean floor. This avoids the need for both fresh water and eluant. The carbon can be taken back to the coal gasification plant and gasified to make more synfuels gas, or burned in a power plant. The uranium will be recovered from the ash. Instead of losing a factor of a hundred in concentration during elution, a factor of ten to a hundred is gained in the conversion to ash, for a net improvement by a factor of 10^3 to 10^4 - a very important difference. The ash becomes a uranium-rich ore which can be processed by conventional means.

A major advantage to this process is that seawater pumping is eliminated, which is not just an energy expenditure, but also involves an enormous capital investment. One also eliminates the need for an elaborate structure (which involves major capital investments), eliminates the need for elution (which requires a large chemical plant and additional investment), and also eliminates the need for fresh water. All of these developments are in the direction of elegant simplicity, which should result in a much lower capital investment. While we are not prepared to quote a firm estimate, initial back-of-the-envelope calculations indicate a factor of ten to a hundred reduction in capital investment.

The first step in evaluation of this process is to determine the capabilities of activated carbon. Although other materials may be suitable (as Dr. Heitkamp's data on peat suggest), or the carbon can be modified by treating it with phosphoric acid or chelating agents, the initial effort is on carbon alone.

A primary concern is with particle size and setting characteristics. Eventually we will have to worry about things such as storm losses and the like, but the initial focus is on the basic system concept, which involves using a ship to scatter activated carbon on the surface of the sea, from which it settles to the bottom. There may or may not have to be bottom preparation. This would represent an undesirable capital expenditure, but, if needed, a honeycomb grid can be envisioned which would prevent ocean bottom currents from sweeping the carbon sediment away.

The basic part of the process lies in the sorption of uranium by the carbon particles as they settle. Once on the bottom the carbon can just be sucked up to effect recovery. Contamination by bottom sediment need not be a problem since a layer many feet thick of activated carbon could be created. Even several square miles of material ten feet thick wouldn't begin to tie up as much of a capital investment as the large processing plants envisioned in other concepts. The suction-type recovery process uses standard ocean mining technology. Nothing new or unproven is involved. Technology also exists (eg. ultrasonic probes) to measure sediment thickness.

Without going into detail, one should note that an alternative concept could also be built around particles that float instead of sink.

Regardless of whether the particle sinks or floats, the limiting step is probably going to be diffusion through the layer around the pellet as the particle undergoes settling at low velocity. Using the conventional diffusion equation and Stoke's Law for settling, an equation can be derived for the uranium concentration in the pellet as a function of the diffusion coefficient (D), the settling depth (L), the density of the pellet and the diameter of the pellet to the fourth power. Note that the pellet is not saturated, and the extreme sensitivity to diameter. This functional dependence will apply to other processes as well: close attention must be paid to pellet diameter when it comes to enhancement of the uranium concentration in the pellet.

If one begins with literature-reported values of 300 milligrams per kilogram as the uranium concentration, and calculates the depth required as a function of pellet diameter and the time it will take to traverse that depth, the practical range of such parameters leads to pellet diameters of something like 50 microns. In other words one is not looking at particles as large as 0.1 mm diameter - much smaller diameters are needed to exploit attainable particle capacities.

Another way to look at the process is to focus on the transit time involved. This is basically the time to reach pellet saturation. Again the pellet diameter is a strong factor. Low velocities are involved - but this would also be the case in a fixed bed. The inescapable conclusion therefore, is that small diameter particles are essential to reaching high concentrations.

Variations on the basic concept are possible to deal with problems which may arise. For example, if the unconfined particles would be swept away by strong currents prior to collection, contactor containers could be fastened to a chain and moved in the current. The amount of structure would still be small. If this scheme proves to be attractive, strong currents exist off the coast of California which would useful for this purpose.

In the last few days prior to this meeting a laboratory setup was devised to contact activated carbon with uranium-bearing seawater. A neutron activation analysis capability was established to measure uranium content.

Activated carbons tested to date have not shown significant ability to concentrate uranium to levels above their initial uranium content, which has been found to be appreciable. However, the program has just started so that the results can not yet be viewed as discouraging.

Contacting and settling tests have been conducted in real seawater. One micron activated carbon particles have been stirred in seawater to form a dilute suspension in which the visual presence of the absorber is hardly detectable. Nevertheless the tests have confirmed that settling-out does occur, and with a high recovery.

Thus an experimental capability has been established, a technique for analysis has been devised, candidate active carbons, and a number of additions thereto, have been identified, and initial experiments are underway.

This, then, constitutes the state of the Lawrence Livermore program is this area.

EXXON URANIUM-FROM-SEAWATER PROCESS

PROCESS STEPS

1. LOAD TITANIUM HYDROXIDE SORBANT WIH URANIUM BY SEAWATER CONTACT IN FLUIDIZED BEDS (PUMPED SEAWATER SYSTEM)
2. WASH TITANIUM HYDROXIDE WITH FRESH WATER
3. ELUTE URANIUM FROM TITANIUM HYDROXIDE WITH AMMONIUM CARBONATE
4. STEAM STRIP AMMONIUM CARBONATE

EXXON URANIUM-FROM-SEAWATER PROCESS

MAJOR PROCESS PROBLEMS

1. VERY LARGE CAPITAL INVESTIMENT IN SEAWATER PUMPING SYSTEM, ADSORPTION BEDS, AMMONIUM CARBONATE FACILITIES, AND FRESH WATER FACILITIES; REPRESENTING 70% OF THE PROJECTED PRODUCT COST = \$2,100 TO \$2,600 PER LB U_3O_8 IN 1995 \$
2. LARGE AMOUNTS OF FRESH WATER ARE REQUIRED FOR WASHING TITANIUM HYDROXIDE WHICH SEVERLY LIMITS THE NUMBER OF POSSIBLE LOCATIONS
3. THE ELUTION STEP LOOSES A FACTOR OF 100 IN CONCENTRATION OVER WHAT IS ACHIEVED WITH THE TITANIUM HYDROXIDE, WHICH RESULTS IN A LARGE AMMONIUM CARBONATE STREAM AND PROCESS PLANT
4. STEAM STRIPPING OF THE AMMONIUM CARBONATE IS ENERGY INTENSIVE
5. THE RESULTANT COST OF THE URANIUM IS A FACTOR OF 10 HIGHER THAN WHAT IS PROJECTED TO BE ECONOMICAL

LLNL URANIUM-FROM-SEAWATER PROCESS

1. SORPTION MATERIAL = ACTIVATED CARBON OR MODIFIED ACTIVATED CARBON DERIVED FROM COAL (GASIFICATION)

2. EXXON STUDY REPORTED 500 ug U/g C AND 800 ug U/g C (LOADED WITH TITANIUM HYDROXIDE

LLNL URANIUM-FROM-SEAWATER PROCESS

PROCESS STEPS

1. PRODUCE ACTIVATED CARBON VIA A COAL GASIFICATION PLANT
2. CONTACT ACTIVATED CARBON SORBANT WITH SEAWATER USING A SETTLING PROCESS (NO PUMPING OF SEAWATER)
3. VACUUM ACTIVATED CARBON OFF OF SEA FLOOR
4. GASIFY OR BURN ACTIVATED CARBON (FURTHER CONCENTRATING THE URANIUM IN THE ASH)
5. EXTRACT THE URANIUM FROM THE RICH ASH ORE BY CONVENTIONAL TECHNIQUES

LLNL URANIUM-FROM-SEAWATER PROCESS

PROCESS ADVANTAGES

1. ELIMINATES SEAWATER PUMPING, THE NEED FOR AN ILLUENT, AND THE NEED FOR A FRESH WATER WASH
2. SHOULD RESULT IN MUCH LOWER CAPITAL INVESTMENT AND REQUIRED PROCESS ENERGY

MAJOR PROCESS ISSUES

1. URANIUM LOADING ON ACTIVATED CARBON
2. ACTIVATED CARBON MODIFICATIONS REQUIRED TO IMPROVE ITS SORBTION PERFORMANCE
3. ACTIVATED CARBON PARTICLE SIZE NEEDED TO MEET SYSTEM REQUIREMENTS
4. MINIMIZATION OF SORBANT LOSSES WHEN CONTACTED WITH SEAWATER

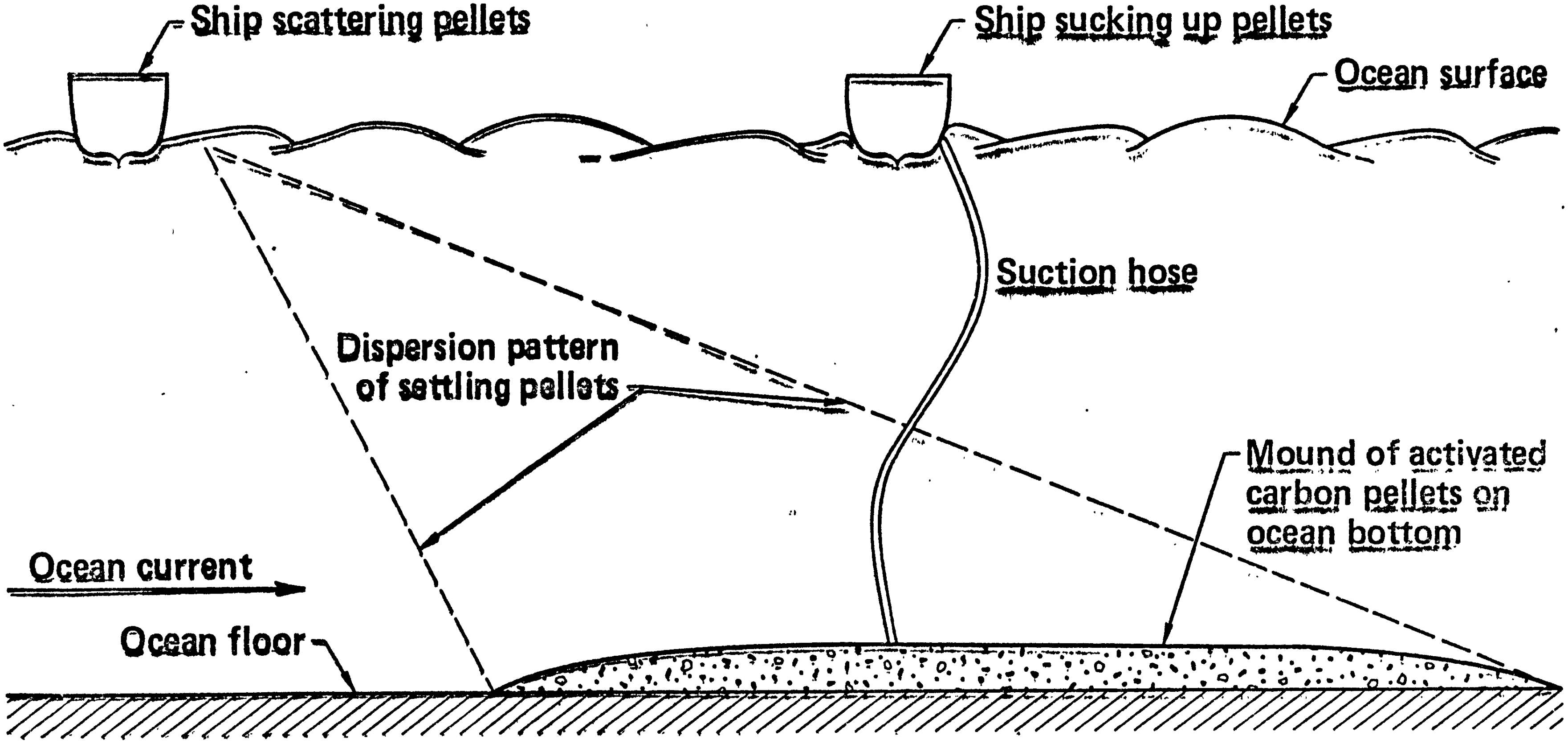
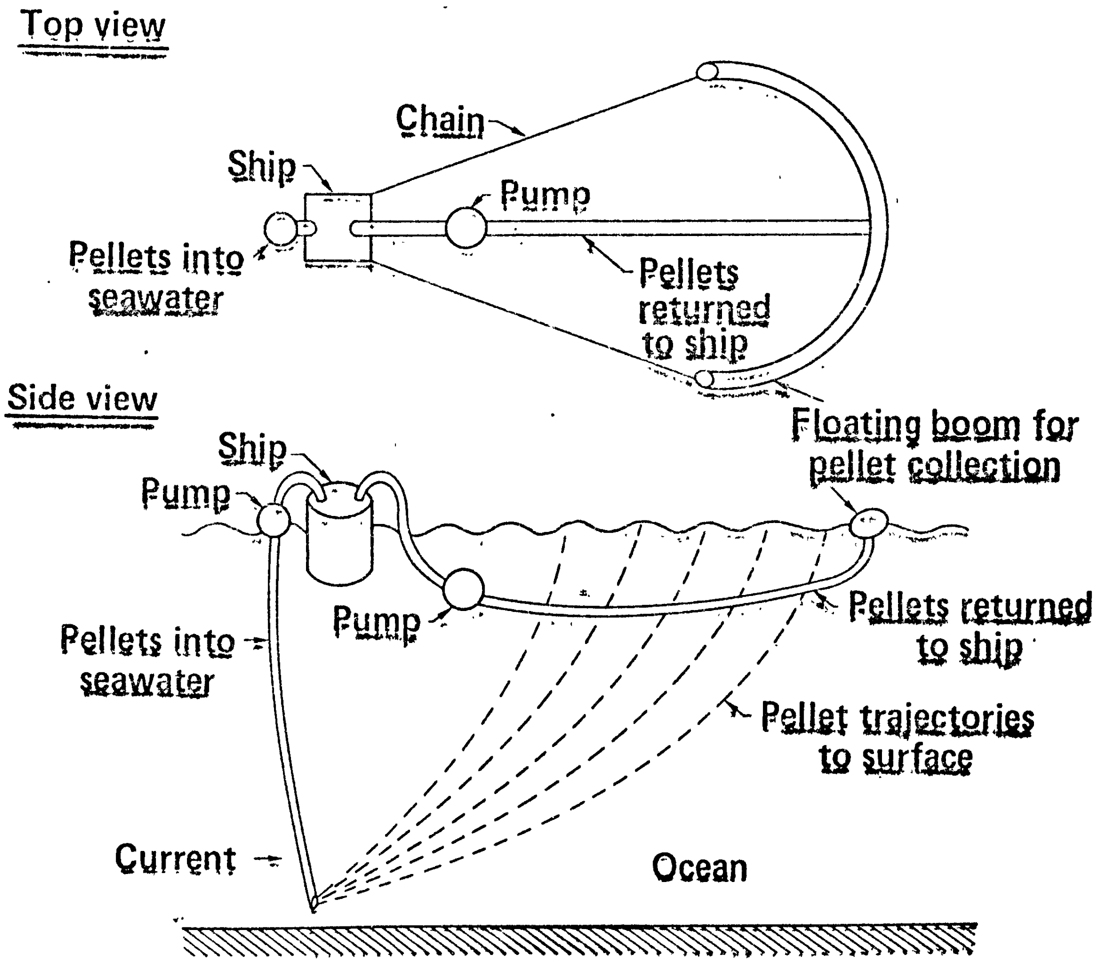


Figure 2. Uranium from Seawater Recovery Process using Settling Activated Carbon Adsorption Pellets.

A CONCEPTUAL DESIGN, SHOWING TOP AND SIDE VIEW, OF A PROCESS FOR RECOVERING URANIUM FROM SEAWATER WHERE BOYANT ION EXCHANGE PELLETS ARE RELEASED DEEP IN SEAWATER AND COLLECTED AT THE SURFACE



CHARACTERISTICS OF SETTLING ACTIVATED CARBON

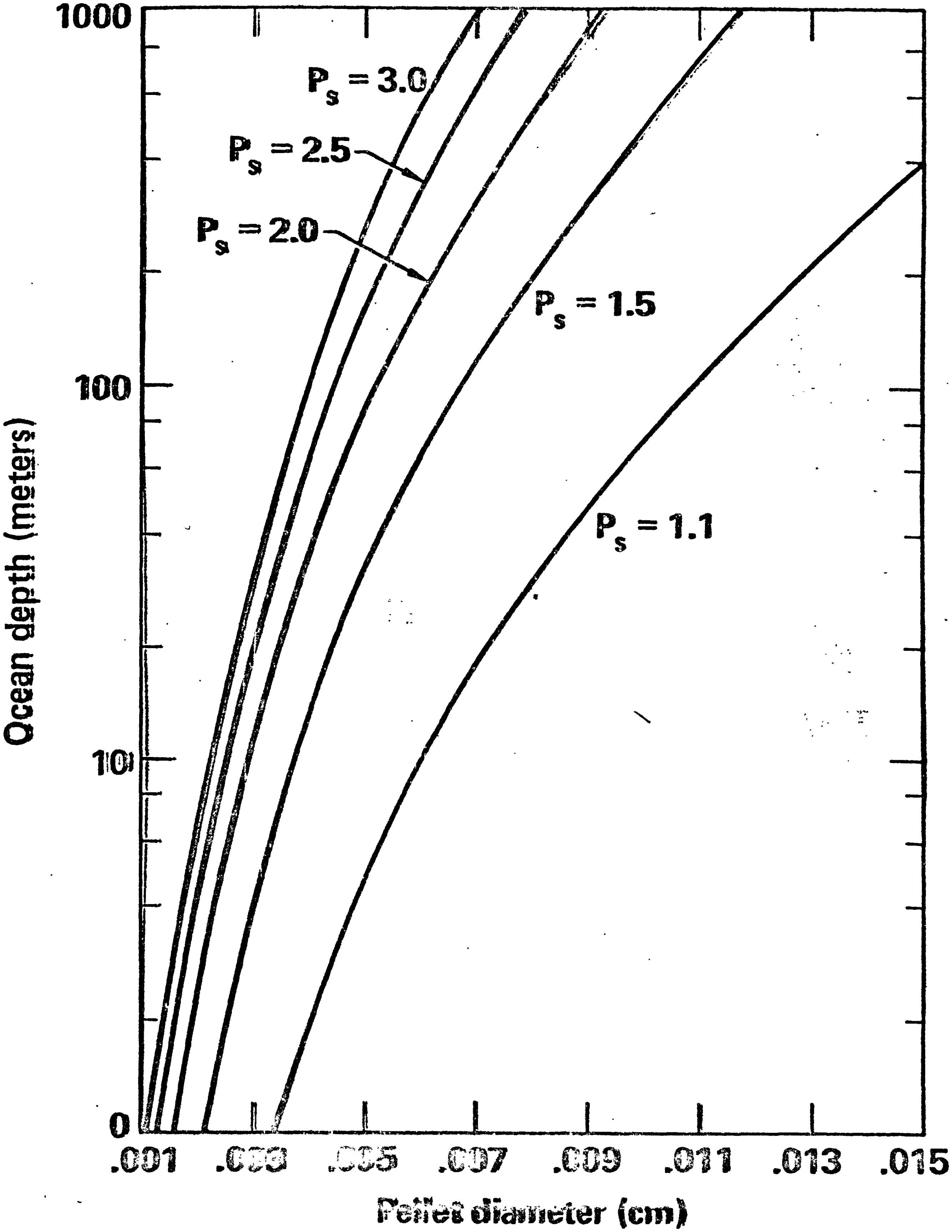
1. CONCENTRATION OF URANIUM ON THE SETTLING ACTIVATED CARBON PELLETS ASSUMING STOKES FORMULA FOR SEDIMENTATION AND SEAWATER DIFFUSION LIMITED MASS TRANSPORT OF URANIUM TO THE PELLET SURFACE

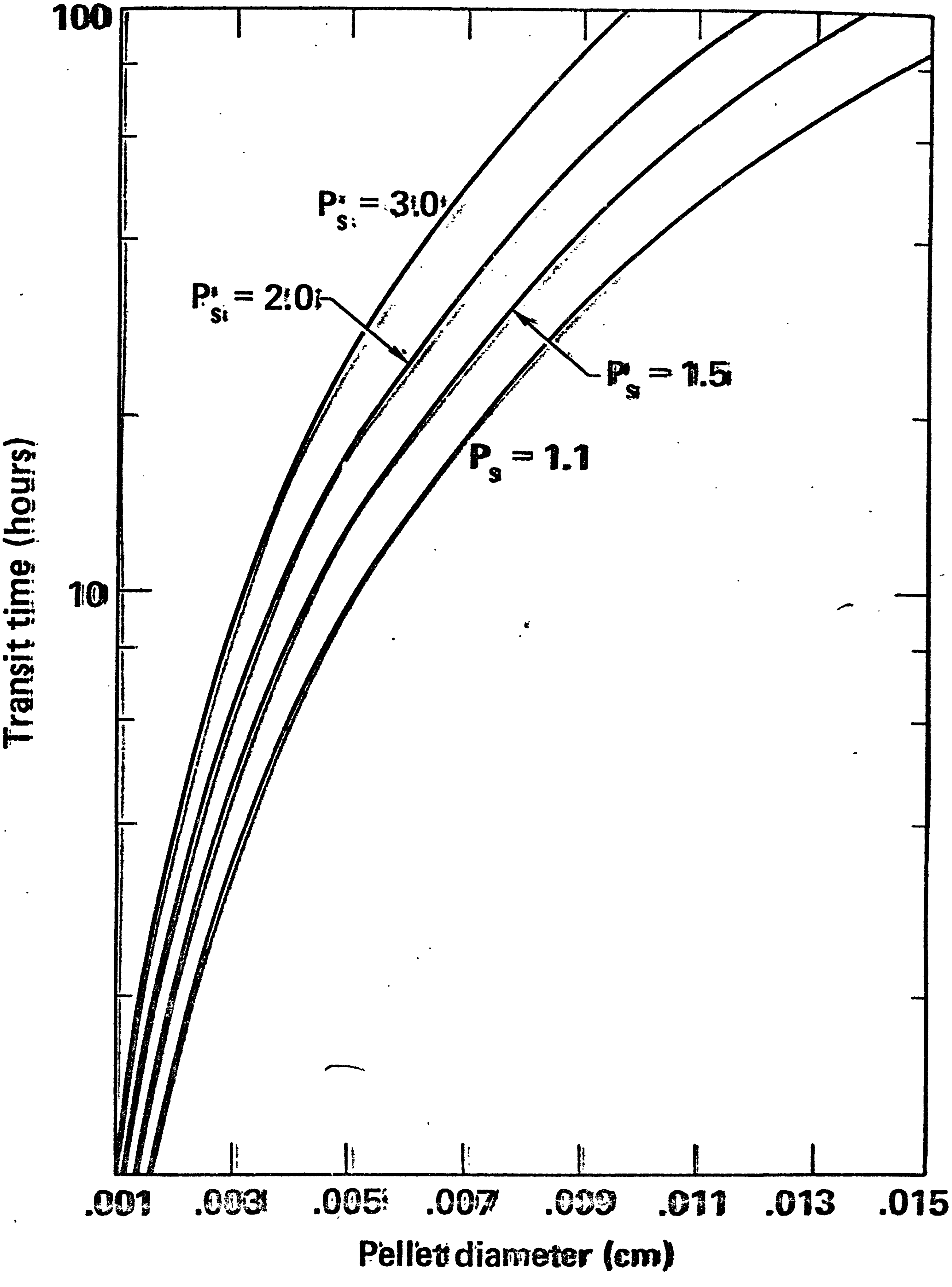
$$C = 2.2 \times 10^{-3} \frac{cDL}{p_s (p_s - 1) d^4}$$

2. REQUIRED SETTLING DEPTH AND TIME ASSUMING REPORTED CONCENTRATION OF 500 mg U/Kg C

$$L = 6.9 \times 10^{12} p_s (p_s - 1) d^4 \qquad \text{cm}$$

$$t = 1.27 \times 10^{9} p_s d^2 \qquad \text{sec}$$


Ocean depth (meters)
1000
100
10
0
Pellet diameter (cm)
.001
.003
.005
.007
.009
.011
.013
.015
Ps = 3.0
Ps = 2.5
Ps = 2.0
Ps = 1.5
Ps = 1.1


100
10
Transit time (hours)
P_s = 3.0
P_s = 2.0
P_s = 1.5
P_s = 1.1
.001
.003
.005
.007
.009
.011
.013
.015
Pellet diameter (cm)

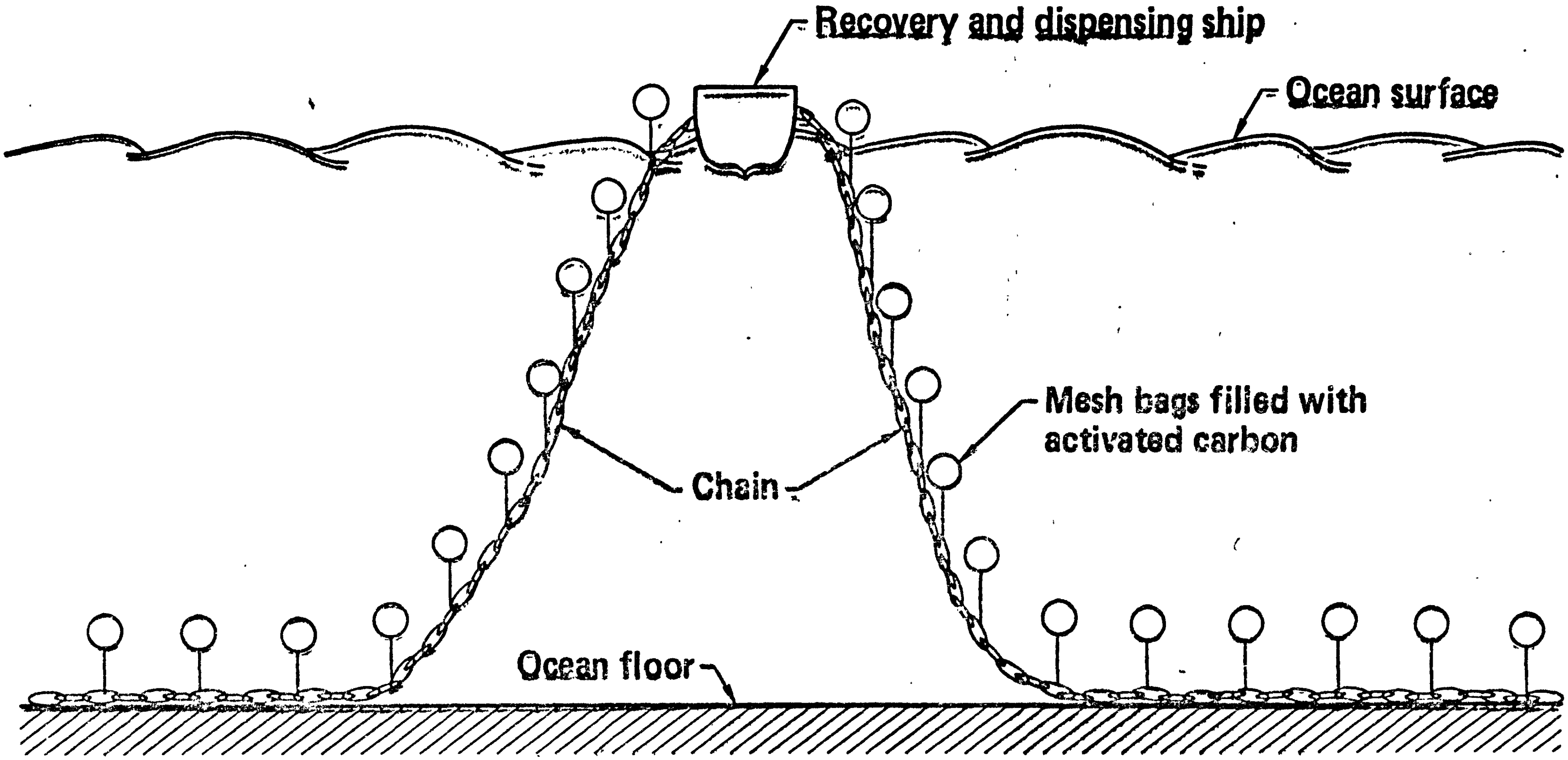


Figure 5. Uranium from Seawater Recovery Process using Activated Carbon Pellets Contained in Mesh Bags.

PRELIMINARY RESULTS ON URANIUM UPTAKE BY THREE ACTIVATED CARBON SAMPLES

SAMPLE	URANIUM CONC. BEFORE SEAWATER EXPOSURE (ug/g)	URANIUM CONC. AFTER SEAWATER EXPOSURE (ug/g)
1	0.07	0.16
2	0.10	0.25
3	0.97	0.68

LLNL URANIUM-FROM-SEAWATER PROGRAM

PROGRAM STATUS

1. PROGRAM IN PROGRESS FOR 1.5 MONTHS
2. SEAWATER TESTING AREA SET UP
3. INITIAL SEAWATER CONTACTING PROCEDURE DEMONSTRATED
4. SETTLING OF ACTIVATED CARBON POWDER DEMONSTRATED IN SEAWATER
5. CHEMICAL ANALYSIS USING NEUTRON ACTIVATION INITIATED
6. 10-20 SAMPLES OF COMMERCIAL ACTIVATED CARBON OBTAINED
7. NUMEROUS (20-30) POTENTIAL ACTIVATED CARBON ADDITIVES HAVE BEEN IDENTIFIED AND OBTAINED
8. THE FIRST EXPERIMENTAL RESULTS HAVE BEEN OBTAINED

Discussion on Dr. Gregg's Paper

Mr. Hooper and Dr. Lewellen commented on a question raised by Dr. Gregg with respect to the energy cost of hydrous titanium oxide. Their estimates were: an initial cost of 1000 units of energy (gigawatt hrs thermal), and a replacement cost of 0.08 out of a total of 14000 for the entire system.

Dr. Muzzarelli and others raised several questions regarding the thickness and horizontal extent of the carbon deposit on the ocean bottom. Dr. Gregg responded that the strong (fourth power) dependence of settling rate on particle diameter would permit one to select a favorable overall set of performance parameters. The ambient ocean depth, for example, could be reduced to as little as several meters.

In response to a question regarding the practicality of burning the wet carbon after recovery, it was noted that the coal used in gasification was already somewhat wet, containing around 30% water, and that in any event some drying could be carried out. Dr. Kelmers noted that the Australians are currently burning coal having as much as 60 to 80% water.

Kelmers and Campbell both pointed out that dumping large amounts of carbon into the sea might be considered to have an adverse environmental impact.

Dr. Fremery mentioned the problems experienced at UEB of removing uranium from ash formed in high temperature combustion. Dr. Gregg mentioned a solar gasification process which did not produce molten ash particles.

In response to a question on settling rate, Dr. Gregg mentioned their experiments on 1-10 micron particles which settled out in a 1 meter tank in less than 24 hours. He reiterated, however, that the rate was readily adjustable for a given application by exploiting the diameter to the fourth power dependence.

A member of the audience asked whether one would have to process 10^6 tons of carbon to recover a ton of uranium. Dr. Gregg replied that one should not base such calculations on their very preliminary results to date, but that the eventual goal is to reduce the processing requirement to 10,000 tons/ton or less.

Practical Constraints on Systems for the Extraction of Uranium from Seawater

by

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MIT

1. Introduction

The application of elementary mass, energy and cost balances can define the useful range of key design features for uranium recovery stystems. Although workers in this field have undoubtedly computed such limiting cases during their research, very little information of this genre has been published.

Both actively-pumped systems, in which seawater is passed through a bed of absorber or ion exchange resin particles, and passive current-interceptor systems (1), are considered. Because of our current research interests, parameter values which might be appropriate for advanced ion exchange materials are used in the illustrative examples. However, the results can also be applied, with minor changes, to the more conventional titanium hydroxide base absorbers.

2. Limitations imposed by Bed Costs

A first, and obvious, restriction is that the annualized cost of the adsorber bed be less (by some appropriate factor) than the value of the recovered uranium. This translates into the requirement:

$$1 \geqslant R_1 = \frac{\phi\, \beta\, \gamma\, t_o}{5.26 \times 10^5\, XW\, f\, G\, U} \qquad (1)$$

where (representative values in parentheses):

X = concentration of uranium in seawater,
lb U/lb water (3.3×10^{-9})
W = density of seawater, lb/gal (8.55)
f = fraction of uranium recovered (≤ 1.0)
G = filter bed flow loading, gpm/ft^2 ($\sim$1.0)
U = market value of uranium, \$/lb ($\sim$30)
ϕ = annual carrying charge rate, yr^{-1} (≥ 0.10)
β = (installed) cost of bed material, \$/lb (1.0)
γ = density of bed material, lb/ft^3
t_o = (extrapolated) void-free thickness of bed, ft
= actual thickness, $t \div (1-\varepsilon)$, where ε = volume fraction voids

Using the quoted numerical values and $R_1 = 1/2$, one finds that $t_o \leq 0.02$ ft = 0.25 in. Hence the compacted bed thickness must be less than 1/4 inch (the expanded thickness might be as much as an order of magnitude larger). Note that the cost per unit area of the filter bed, $S = \beta\,\gamma\, t_o$, would be $\sim$ 2 \$/ft^2, which must include the cost of superstructure and bed support, as well as the cost of the medium itself. Also note that the annual carrying charge rate for an industrially funded venture would be 2 to 2.5 times as large as the value used here, which is more appropriate for government sponsorship. The value of ϕ also depends on the useful system and filter medium life: if less than ten or so years, higher ϕ values would again be appropriate. The value of β used was based on the current cost of ion exchange resin ($\sim$1 \$/lb) -- but note the optimism implicit here, in that this does not account for the bed support structure. On the other hand, the recent NASAP and INFCE studies indicate that LWR units could remain competitive for uranium prices ranging up to five times the value used here.

Thus, while the above considerations can only be used to establish order of magnitude limits, it is clear that one is constrained to use thin beds and motivated to keep costs low by using active coatings on inexpensive substrates, etc.

The total bed surface area is also a parameter of interest. If our goal is to collect F lbs U/yr ($\approx$400,000 for a 1Gwe LWR)

$$A = \frac{F}{5.26 \times 10^5 \ XW f G} \qquad (2)$$

Again, for the values quoted --

$$A \geq 3 \times 10^7 \ \text{ft}^2$$

Thus extremely large frontal areas are called for. We can now compute the bed volume, hence absorber mass:

$$M = \gamma A t_o \approx 60 \times 10^6 \ \text{lbs},$$

which, incidentally, is roughly comparable to the total annual US consumption of ion exchange resins (but only about 1% of the yearly US styrene production)

3. Constraints Imposed by an Energy Balance (5)

The extraction of uranium from seawater will be attractive only if the energy expended to recover it is less (by some appropriate factor) than the energy which can be generated per unit mass of uranium in a representative nuclear reactor.

This restriction takes the form

$$1 \geq R_2 = \frac{5000\ (F/P)\ \Delta p}{\eta_1\ \eta_2\ (10^9 X)\ f\ B\ \rho} \qquad (3)$$

where terms not previously defined are:

(F/P) = lbs natural U per lb slightly enriched U charged to the reactor (6)

Δp = pressure drop across entire filter apparatus, psi

B = reactor fuel burnup, MWD/MT (30,000)

η_1 = thermodynamic efficiency of heat engine driving the pump (0.35)

η_2 = overall mechanical efficiency of the pump (0.8)

ρ = density of seawater, lb/ft^3 (64)

For $R_2 = 1/10$ and the values shown above, $\Delta p \leq 6$ psi.

This restriction is again quite sobering, and motivates the thought that a seaborne unit might be preferred, if not essential, to keep parasitic losses sufficiently low.

In passing we may also note the impressive volume of water handled: GA ≈ 30 x 10^6 gpm, which is approximately 60 times the flow rate of condenser cooling water in a 1 Gwe LWR, and 3/4 the flow rate of the Nile River! The sheer size of the overall venture may favor the use of several smaller units per reactor served.

As a consistency check, the recovery system (shaft) pumping power is:

$$S = 3.25 \times 10^{-6} \frac{W}{\rho} \Delta p, \text{ Mw}$$

or for $\Delta p = 6$ psi, $S = 78$ Mw

4. Elementary Mass Transfer Limitations

Uranium must not only be transported to the bed, but once there it must be transferred to and into the particles.

For an inexhaustible filter bed the fractional removal is given by:

$$f = 1 - e^{-NTU} \qquad (4)$$

where NTU = number of transfer units

For a bed of spherical particles of diameter d

$$NTU = \frac{6 K \rho t_o}{60 W G d} \qquad (5)$$

where K = mass transfer coefficient, lb/hr ft^2 (lb/ft^3)

For laminar flow around an isolated sphere:

$$K = \frac{2 D}{d} \qquad (6)$$

where D = diffusivity of uranyl carbonate complex in seawater (7.75×10^{-6} ft^2/hr) (2)

Combining Eqs (4), (5) and (6):

$$f = 1 - e^{-\frac{12 D \rho t_o}{60 W G d^2}} \qquad (7)$$

From Eq (7) it can be shown that the uranium collection rate, the product of f and G, increases monotonically with G -- but while fG is directly proportional to G at low G, it approaches an asymptotic limit at high G. Hence attempting to go beyond $f \approx 2/3$ will be wasteful in terms of bed thickness (hence bed cost) and pressure drop (hence pumping power). The large incentive to use small particle diameter is also evident: for t_o = 0.02 ft and NTU = 1 (f = 63.2%), Eq (7) indicates that :

$d \leq 5 \times 10^{-4}$ ft = 0.15 mm.

There are both optimistic and pessimistic assumptions built into Eq (7). The increase in mass transfer coefficient with flow rate has not been allowed for. On the other hand only fluid side resistance has been accounted for: resistances contributed by interior pores and the solid phase has been ignored. Over the range of interest the net effect should be to overestimate the fractional recovery.

5. Pressure Drop Relation

A complementary, if somewhat redundant, constraint can be obtained by considering the pressure drop correlation for laminar flow through a packed particle bed:

$$\Delta p = \frac{150\ WG\mu\ (1-\varepsilon)\ t_o}{144(60) g\ d^2\ \rho\ \varepsilon^3}, \text{psi} \qquad (8)$$

where

μ = viscosity of seawater ($5 \times 10^{-4}\ \frac{\text{lb}}{\text{ft sec}}$)

g = 32.2 lb mass ft/lb force sec^2

ε = volume fraction voids ($\approx$0.4)

For $\Delta p \leq 6$ psi, t_o = 0.02 ft, and the previously quoted values of other parameters, Eq (8) gives $d \geq 3.35 \times 10^{-5}$ ft =

0.01 mm, which is compatible with the mass transfer target value of $d \leq 0.15$ mm.

Equation (8) shows that the otherwise beneficial small diameter has a detrimental effect on pressure drop. This can be offset by using an expanded bed (larger ε), more transparent configurations (stacked/corrugated mesh, steel wool, etc); o even perhaps a fluidized bed, although the latter option would appear to involve some serious problems, such as particle attrition and the difficulty of avoiding channeling in thin beds. It may be necessary to go to beds having high porosity, in any event, to mitigate plugging by particulate matter.

6. Other Configurations

The cost and complexity of actively pumped systems strongly suggests that consideration be given to passive, current-driven systems. Free-stream mass fluxes can be quite high, i.e.

$$G = 658\ m,\ \text{gpm/ft}^2 \qquad (9)$$

where m = current velocity, mph

Hence for a 3 mph current G would be quite large, $\sim$2000 gpm/ft^2, which in turn would provide mass transfer coefficients an order of magnitude larger than in the creep-flow conditions through packed beds previously discussed. The catch is that the filter would have to be very transparent (eg a coated wire mesh or net, as in Ref (2)) so as not to impede flow. The combined effect of an open weave and a thin bed reduces the effective volume by more than an order of magnitude -- negating the increase in K. Use of a less porous bed is counterproductive since stagnation pressures are quite low:

$$\Delta p_s = \frac{0.015 \quad \rho}{2\ g} \; m^2, \text{ psi}$$

Thus for our 3 mph current a maximum head of 0.13 psi could be provided.

In spite of these limitations the sheer simplicity of this approach justifies further attention.

7. Fluidized Beds

Use of a fluidized bed in lieu of a packed bed is another option which has many points in its favor, not the least of which is resistance to fouling.

Stoke's law gives an optimistic upper limit on the flow loading sustainable without carryover for a fluidized bed:

$$G \leq \frac{60\ d^2 g\ \rho^2\ (SG-1.0)}{18\ \mu\ W}, \text{ gpm/ft}^2 \qquad (11)$$

where SG is the specific gravity of the absorber particles relative to seawater.

The pressure drop through a fluidized bed is given by:

$$\Delta p = \frac{\rho\ t_o\ (SG-1.0)}{144}, \text{ psi} \qquad (12)$$

For an ion exchange resin having SG = 1.1, d = 0.1 mm, and t_o = 0.02 ft, the above equations give Δp = 0.0009 psi, and $G \leq$ 1.1 gpm/ft^2. Hence, while the flow loading has not been increased, the pressure drop is trivial, and well within the range of ocean current stagnation pressures.

It is tempting to contemplate increasing the bed thickness, but the limit of Eq (1) still applies, which makes this unattractive unless G can be increased proportionally. Use of a coated particle having a dense core (to increase SG) would be of benefit here, but less than a factor of ten improvement could be contemplated.

The concern over filter material losses (by carryover, attrition and dissolution), which is particularly strong for fluidized beds, is readily appreciated if one ratios the cost of losses to the value of the product:

$$1 \geq R_3 = \frac{\beta \; Z}{U \; X \; f} \qquad (13)$$

where Z = weight fraction of absorber material in effluent seawater.

For the representative parameter values already quoted and $R_3 = 1/5$, one finds that $Z \leq 20$ ppb.

8. Comments and Conclusions

As of now there is no generally agreed upon overall conceptual system design for a practical uranium-from-the-sea facility. Elementary considerations, some of which were recapitulated here, suggest that the design envelope of acceptable parameters severely restricts the available options. More work is clearly in order, but it would appear that a viable system must employ absorber particles of small dimensions, in thin beds of high void fraction, most likely sited at sea.

It would also appear that considerable useful input in the formulation of a design approach could be gained by closer attention to research in progress on other energy options. For example, the high-capacity, low-head axial flow pumps under consideration for OTEC units are also ideal for sea-borne uranium facilities; and, in the area of passive systems, one should note that the kelp farm biomass concept shares many similar problems, including current-driven nutrient transport.

Figures 1 and 2 illustrate preliminary conceptual designs of active and passive units for the recovery of uranium from seawater which may have the potential of meeting the requirements established here. They will be used as the starting point for further work on system design in the DOE-sponsored project on uranium extraction from seawater at MIT.

References

(1) F. R. Best and M. J. Driscoll,
"Prospects for the Recovery of Uranium from Seawater"
MITNE-231, Jan. 1980.

(2) C. Bettinali and F. Pantanetti,
"Uranium from Seawater: Possibilities of Recovery Exploiting Slow Coastal Currents"
Uranium Ore Processing, IAEA, Nov. 1975.

Appendix

A number of assumptions were made in the developments presented in the body of the text which require support. Several are connected with flow regime, which we assumed to be laminar. This is readily verified. The particle Reynolds number is:

$$N_{Re} = \frac{d\ WG}{60\,\mu} \qquad (A.1)$$

where μ is the viscosity of seawater. For G in gpm/ft^2 and d in mm:

$$N_{Re} = 0.935\ dG \qquad (A.2)$$

Thus for d = 1 mm, G = 1 gpm/ft^2, $N_{Re} \approx 0.9$, which is far below the laminar/turbulent transition point of ∿10. Hence we are assuredly laminar; moreover N_{Re} is sufficiently low to justify use of the low-flow limit in computing the mass transfer coefficient (mass transfer Nusselt number = 2.0).

In the mass transfer calculations we also ignored bed exhaustion. This may be considered an optimistic asymptotic case for low-capacity absorbers. However, we really had in mind advanced ion exchange media which might have a capacity, C, of as high as 0.1 lb U per lb resin. The cycle time (time between regeneration of the saturated bed) is:

$$T = \frac{C\gamma\ \ t_o}{5.26 \times 10^5\ \ XW\ f\ G}\ \text{yr} \qquad (A.3)$$

For the previously quoted representative values of these parameters one finds that

$T \geq 13$ years.

Clearly, one would not find it practical to operate an advanced absorber to near-saturation. On the other hand, one might well be satisfied with materials having capacities a factor of 10 to 100 lower.

Although uranium recovery from seawater is formidable engineering endeavor, it is comforting to know that the thermodynamic mimimum work of separation is quite modest:

$$W_s \simeq \frac{1}{M_u}\left[\Delta H_s - RT\ \ln\left(\frac{X}{10^9}\ \frac{M_s}{M_u}\right)\right]\ \frac{\text{Kwhr}}{\text{lb U}}$$

where ΔH_s = heat of solution, Kwhr/lb mole

(∼±3, varies with chemical species)

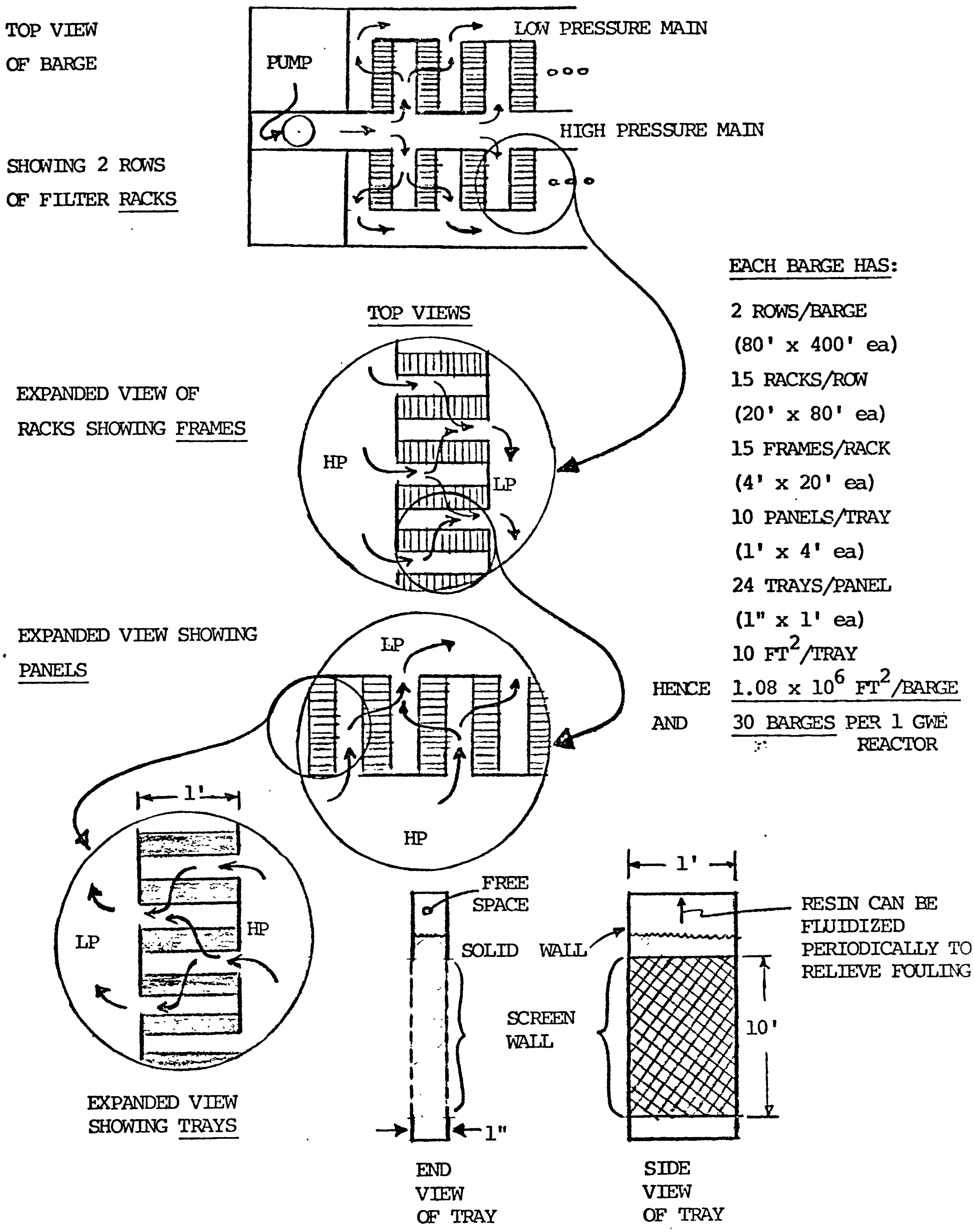
$RT \simeq 0.3$ Kwhr/lb mole

M_s, M_u = lbs per mole seawater and uranium, respectively

(∼18, 238)

Hence for the parameters cited, $W_s \simeq 0.04$ Kwhr/lb; and even if energy costs a dollar per Kwhr, the minimum cost of separation would only be a few cents a pound!

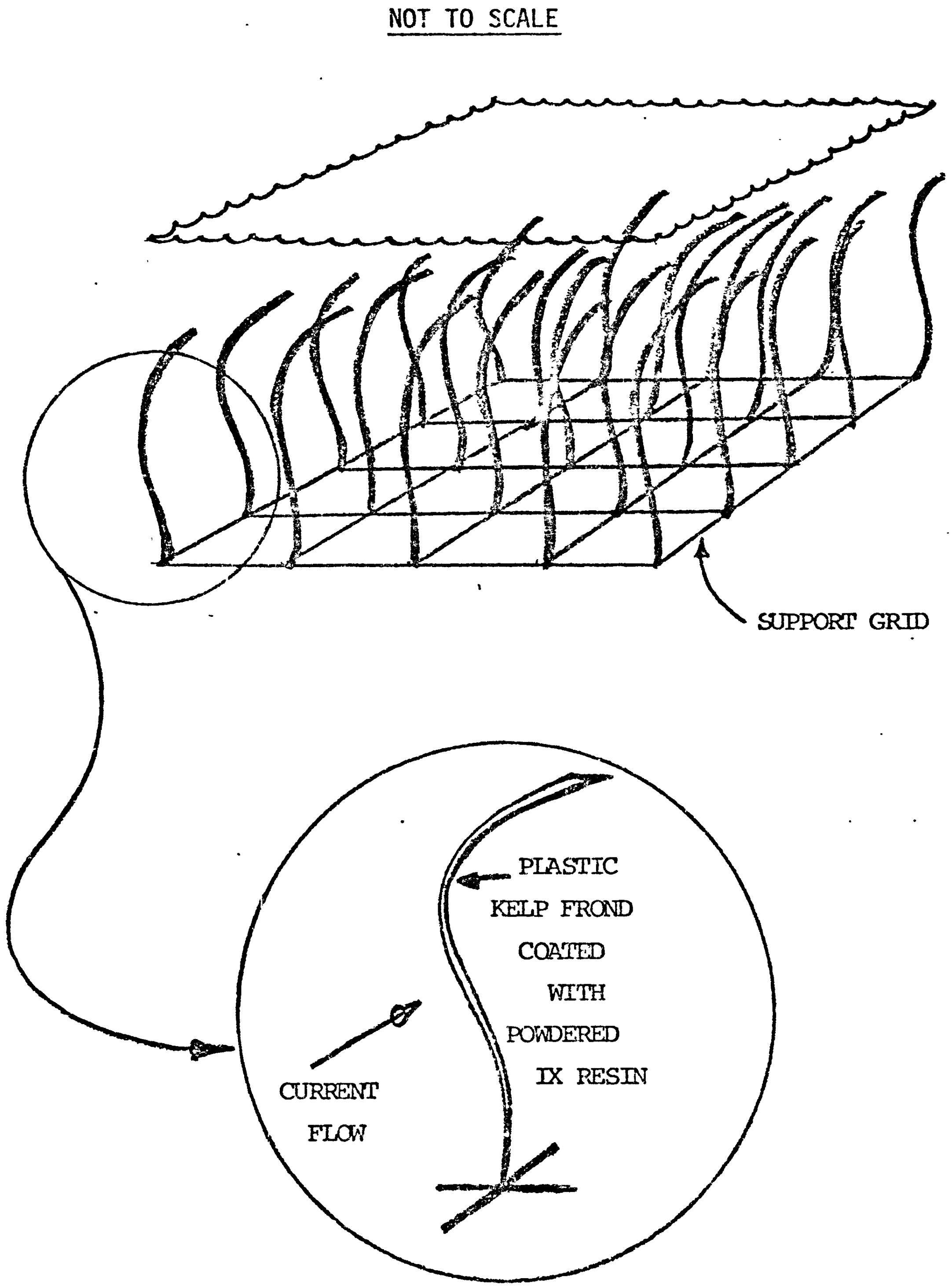
NOT TO SCALE



EACH BARGE HAS:

2 ROWS/BARGE
(80' x 400' ea)
15 RACKS/ROW
(20' x 80' ea)
15 FRAMES/RACK
(4' x 20' ea)
10 PANELS/TRAY
(1' x 4' ea)
24 TRAYS/PANEL
(1" x 1' ea)
10 FT^2/TRAY
HENCE 1.08 x 10^6 FT^2/BARGE
AND 30 BARGES PER 1 GWE REACTOR

FIG. 1 ACTIVE CONCEPT BASED ON OTEC BARGE ANALOGY



FOR EACH 1 GWE REACTOR ONE NEEDS A 1000 ACRE FARM OF KELP FRONDS ON A 1 FT x 1 FT GRID, EACH FROND 1 FT WIDE x 100 FT LONG

FIG. 2 PASSIVE CONCEPT BASED ON KELP FARM ANALOGY

Discussion on Prof. Driscoll's Paper

Dr. Morgan noted that it would be of some interest to compare the energy which could be extracted from the uranium collected by "plastic kelp" to the amount of energy which could be extracted from an equal acreage of biomass kelp.

The Effect of System Improvements on Uranium Recovery From Seawater

by

F. R. Best (MIT) and M. J. Driscoll (MIT)

The reason for interest in the recovery of uranium from the world's oceans is clear: they contain on the order of 4000 million tons of U_3O_8 -- enough to sustain thousands of LWRs for thousands of years without resort to plutonium recycle or the introduction of breeder reactors. The reasons for skepticism as to the prospects of this undertaking are also obvious: the low concentration of uranium in seawater (∿3.3 ppb) necessitates large flow rates and sorber bed areas--to sustain one large LWR the ocean water throughput must be about half the volumetric flow rate of the Mississippi river. To help resolve key points at issue, work has been carried out to:

(a) develop a model describing the engineering and economic performance characteristics of a generic system

(b) employ the model to predict U_3O_8 production costs using state-of-the art technology

(c) carry out sensitivity analyses, parametric studies and process optimizations to identify targets for R&D efforts which could lead to a competitive system.

A computer program, URPE, was developed incorporating analytic models for adsorption and pressure drop in packed beds (or in stacked tubes), the use of actively-pumped or passive current-interception flow induction, and a multi-purpose plant to generate electricty to drive the seawater pumps, distill water and produce chemicals for use in bed elution. Unlike previous studies, which have been centered about the use of large terrestrial civil works (2), the present conceptual design assumes a modular sea-borne system. The adsorber used in the studies was hydrous titanium dioxide (HTO), the consensus choice of the various researchers worldwide who are pursuing the goal of uranium-from-seawater. In addition to calculating the kinetic behavior of the adsorption process, the program executes a complete mass and energy balance around the overall system, sizes all components and estimates all associated costs to arrive at a unit price of product, \$/lb U_3O_8.

The program was benchmarked against previous studies by ORNL and EXXON by inputting their system's characteristics to URPE. The cost breakdown for each subsystem generated by URPE was either in good agreement with the corresponding ORNL and EXXON values, or the reason for the observed difference was apparent (e.g. the more sophisticated bed kinetics treatment in URPE and the large interest during construction term in the EXXON study). The results (in 1979\$) were, for ORNL: 627 \$/lb U_3O_8; for EXXON (without interest during construction): 740 \$/lb U_3O_8 and for MIT: 650-1322 \$/lb U_3O_8. These values correspond to a terrestrially-sited unit using proven technology, and not subjected to any substantial design optimization. They are clearly uncompetitive compared to the current price of U_3O_8 (30 $/lb) or even the projected breakeven price of U_3O_8 used in LWRs in competition with breeder reactors or coal-fired fossil units (∿150 $/lb).

In the next stage of the evaluation a sea-borne recovery system was iteratively optimized to deliver minimum cost U_3O_8. Table 1 summarizes both key input data and selected items from the computer output. As can be seen, the total price of U_3O_8. 316 $/lb, is considerably lower than for the benchmark comparisons, but still not competitive. By tracking the variation of key parameters in the optimization process it was possible to establish a number of important generalizations:

(a) Actively pumped systems outperform passive current interceptor systems

(b) Packed beds are superior to stacked tubes as a substrate for the adsorber film

(c) Optimum systems have thin beds (on the order of inches thick), small particles (on the order of 0.1 mm dia.) and thin adsorber coatings (∿5 μm)

(d) The high cost of desalinated water in pre- and post-elution bed washing operations is sufficiently large to warrant close attention to refinement of this step.

In the final phase of the work. parameteric and sensitivity studies were carried out to identify targets of opportunity for future R&D efforts, and to establish ultimate bounds on potential system performance.

Table 1

Characteristics of an Optimized State-of-the-Art Packed Bed System

Parameter	Value
I. Input Specifications	
Adsorber Properties:	
Adsorber Capacity	210 mg U/kg Ti
Uranyl-HTO Equilibrium Constant	2.28
Diffusivity of Uranyl Species in HTO	4.39×10^{-16} m^2/s
Economic Conditions:	
Fixed Charge Rate	25%/yr
Plant Capacity Factor	80%
Lang Factor (System cost/component cost)	4.46
Annual Production Rate	200 tons U_3O_8/yr
II. Optimized Output	
Superficial Velocity in the Bed	1.08×10^{-3} m/sec
Particle Diameter	64.6 μm
Bed Thickness	1.18×10^{-2} m(0.5 in)
Loading Time	32 hrs
Coating Thickness	5.3 μm
Bed Area	3.10×10^{6} m^2
III. Costs	
Adsorbent Losses	12
Chemical Make-up	39
Water	63
Pumping Power	46
Annualized Capital, Maintenance and Labor	156
Total (1979 $)/lb U_3O_8	316

Adsorption capacity and pumping power requirements are two of the most important and contested parameters in the analysis of uranium-from-seawater systems. Adsorption capacity is important for obvious reasons. That the capacity of HTO for uranium is a contested property is clear from the wide range of values reported for capacity. Although the pumping power required for any given system design is not disputed, the choice of system conceptual design to minimize pumping power requirements does depend on how important pumping power is considered to be by the designer.

A study of the effect of increasing adsorption capacity and pumping power was performed in order to assess the impact of these items on optimized uranium production cost. The study was performed by starting from the optimized base case, increasing the item of interest, and re-optimizing the entire uranium recovery system design.

The adsorption capacity was varied, starting with the base case value of 8.68 x 10^{-5} lb U/lb HTO (210 mg U/kg Ti), and increasing the capacity to a maximum value of 3 x 10^{-2} lb U/lb HTO (72,380 mg U/kg Ti). This range includes all of the reported values of HTO capacity, including experiments in spiked seawater, and concludes with a capacity which might be typical of an ion exchange resin. Figure 1 shows the data plotted from the URPE output.

The data show the maximum improvement which might be expected as sorber capacity increases. Very large (but not phys-

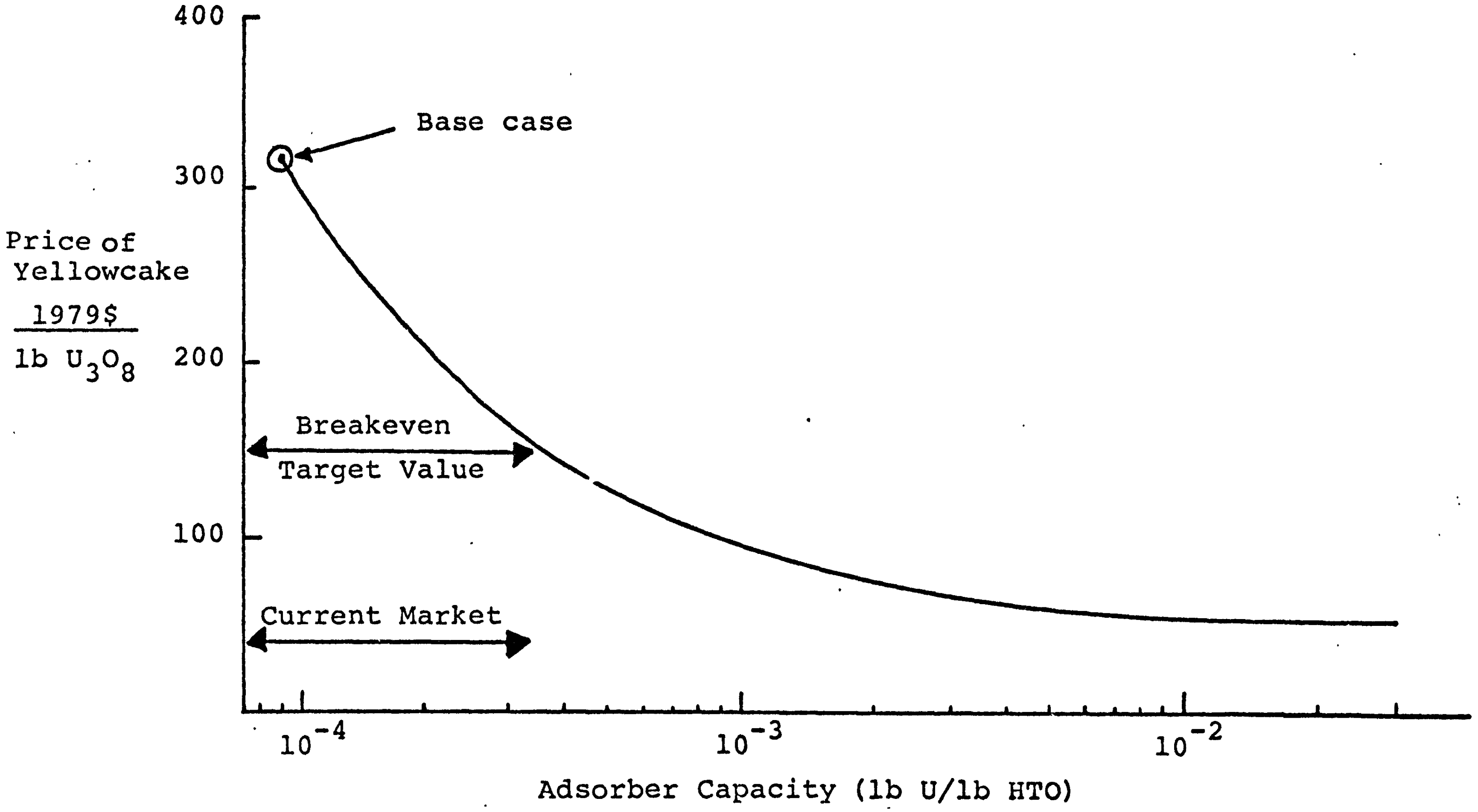


Fig. 1 Optimized U_3O_8 Cost as a Function of Adsorber Capacity

ically impossible) increases in sorber capacity would be required to bring production price down to the range of the 1980 spot market price for U_3O_8, 30 $/lb. However, the capacity need only be increased to 3.5 x 10^{-4} lb U/lb HTO (847 mg U/kg Ti) in order to produce uranium at a price of 150 $/lb U_3O_8, the breakeven price. It is recognized that it is unlikely that a single recovery system model could accurately predict production costs over such a wide range of sorber capacity. However, the trend of decreasing cost with increasing capacity is so strong that work to improve sorber capacity, or identify alternate adsorbers having a high capacity, should clearly be carried out.

The pumping power was varied from the base case value, to ten times the base case value. The results are plotted in Figure 2. This figure shows that the cost of uranium production increases much less than one-to-one with increasing pumping power requirements (due, for example, to the need for augmented prefiltering or excessive bed fouling) and could be offset by relatively smaller increases in adsorber capacity.

Summary and Conclusions

As a result of running the URPE code over a wide range of bed operating conditions, it was found that U_3O_8 produced from seawater using state-of-the-art materials could not cost less than about 316 $/lb U_3O_8 (1979 $). This result is also supported by a comparison of URPE performance and economics models with ORNL and EXXON analyses. Inclusion of interest on capital during

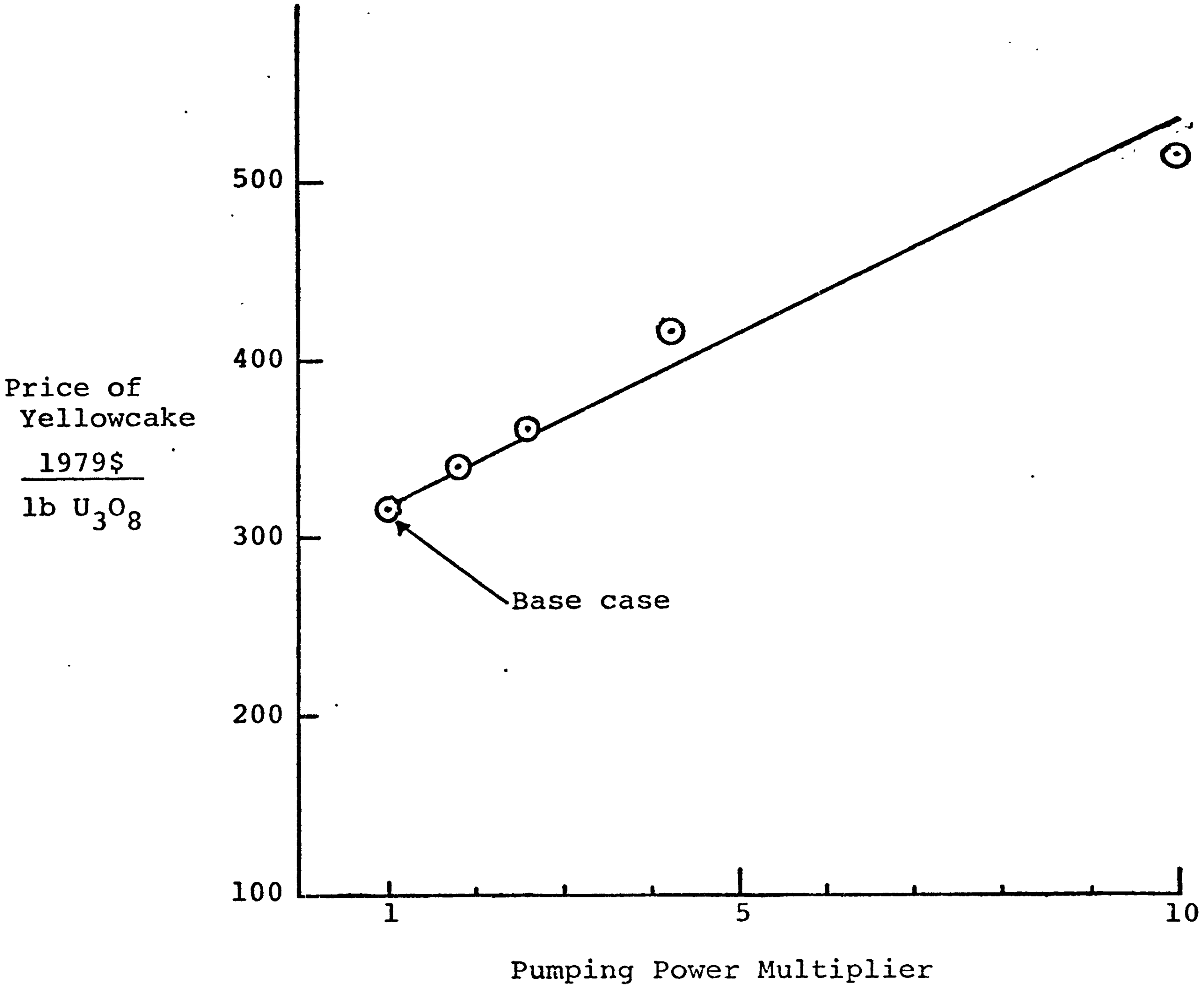


Fig. 2 Optimized U_3O_8 Price as a Function of the Increase in Pumping Power Requirements

construction would increase this value, but increases in sorber capacity would lead to offsetting cost reductions. The potential of higher capacity adsorbers for reducing costs, together with development of an effective method of reducing the costs of chemicals expended during elution could bring the ultimate production price below 150 \$/lb U_3O_8. Indeed, this goal would appear assured if capacities typical of ion exchange resins could be demonstrated for uranium in seawater.

References

1. F.R. Best, M. J. Driscoll, "The Recovery of Uranium From Seawater," MIT-EL 80-001, January 1980.
2. "Extraction of Uranium from Seawater," EXXON Nuclear Company, Reports XN-RT-14 and XN-RT-15, February 1979.

Discussion on Dr. Best's Paper

Dr. Wang asked for the definition of the equilibrium constant used; Dr. Best indicated that his definition corresponded to the form required for the mathematical treatment used, and had been determined by fitting Japanese data.

Mr. Campbell concurred that differences between the MIT and EXXON results were in large part due to the interest during construction term. The EXXON system involved a large on-shore construction project, requiring 15 years, whereas the MIT rig was a modular unit constructed in a shipyard over a 2 year period. Both the MIT and Swedish concepts, for example, adopted this approach, in part to reduce the large capital costs otherwise incurred.

Dr. Denzinger asked if the computer model could be applied to other concepts and adsorbers; Dr. Best replied that this was possible given that one expressed the bed rate constant in the form required by the computer program, or replaced that module in the code.

A general discussion then arose as to why the capacity proved to be so important a varable. Dr. Best indicated that this was due to the fact that the program re-optimized important parameters such as loading time and bed thickness whenever capacity was changed, and that cost reduction often corresponded to reductions in system size because of the strong influence of plant capital costs.

Chapter 5

Discussion Sessions

This chapter contains summaries of the two major open discussion sessions held at the conference: the "First Day Panel Discussion," and the "Concluding Discussion" at the completion of the conference.

As is the case throughout this report, the discussions have been summarized from a tape recording, and are not verbatim, having been edited to improve continuity, coherence, and grammar.

First Day Panel Discussion

At the end of the first day Dr. Best chaired a panel of all first-day speakers (see the agenda in Appendix A to this report for a list of speakers, co-authors, and their topics). The following discussion was reconstructed in summary form by the editors from a tape recording.

The first major topic was that of particle attrition. Prof. Kanno noted that such measurements were difficult because the bed typically exhibited a weight increase due to buildup of calcium and magnesium carbonates. He indicated that chemical analyses permitted estimation of a 0.1-0.2 percent loss by weight of sorber per cycle. He stated that losses were due to mechanical attrition rather than chemical attack. Hooper then related UK experience, describing tests in which particles were agitated in water and then screened to measure volumetric losses as fines. Again losses were found to be due to particle breakdown and not dissolution. Particles showed rounding over time, and losses were greater in fluidized beds. He pointed out that particle strength could be improved by variations in the production process. They have in the past quoted losses amounting to 10% of the bed per year (which he felt should be cited as closer to 5%); and this is a large loss - up to 20 tons of sorber per ton or uranium recovered. Dr. Fremery underlined the fact that the mode of particle preparation is of great importance. The type of base used to induce precipitation from the titanium salt solution, the temperature and time of precipitation, and several other parameters influenced the type of gel formed. In this manner it is possible to control abrasion resistance, and to obtain acceptable particles in this regard.

The leading role of hydrous titanium oxide (HTO) was acknowledged, in large part because sufficient information already exists to evaluate a complete system design. Advances are still being made, however, such as the use of ilmenite as a starting material, acceptance of a higher impurity content, and a better definition of methods for preparation of material having reproducible, uniform properties. The question as to whether higher strength always meant lower effective capacity was raised, and while some felt that this was a valid generalization, others felt that this overstated the facts.

Drs. Best and Wang raised the issue of coated particles. Although earlier system designs were based on the use of such particles, the conferees all agreed that there had not been a successful demonstration of the capability for making such particles. Furthermore, several of the participants questioned the desirability of moving in this direction, for the following reasons:

a. the coating process used would most likely increase costs over that of an all-HTO particle, which was already fairly inexpensive. Specific processes critiqued were metal vapor deposition followed by subsequent chemical treatment (Wang) and the UO_2-type sol/gel process for fuel developed at ORNL (Campbell)

b. if particles did undergo attrition, solid particles had the advantage of always exposing a freshly active surface

c. The use of heat or bonding agents in the coating process would invariably reduce particle capacity (Kanno)

d. quality control would become more difficult.

Countervailing opinions were not strongly voiced. However, Mr. Hooper recalled a Japanese mining company patent for coating fibers using a thin vinyl alcohol layer containing HTO precipitate, followed by polymerization. Several speakers later addressed whether ion exchange resin was more suitable for coated-particle applications. Here FRG and Rohm and Haas representatives indicated that it could most likely be done. However, Mr. Jones again raised the question as to the effect of exfoliation, and the need to use the whole bead if possible.

The discussion then focussed on the fact that uranium was really sorbed only in a thin surface layer on HTO. This has many implications:

a. capacities reported as weight of U per unit weight of HTO are rather uninformative unless particle size is also specified - which is not always done in the literature (Morgan)

b. Prof. Kanno made the point that it is really the exposed porous surface area which counts, which is harder to specify, and variable

c. internal porosity has not proved especially advantageous due to the slowness of internal diffusion

d. similar comments apply to IX resins, but here macroreticular resins may be advantageous; although it was pointed out that on a theoretical basis nearly 50% of the IX mass could be loaded with uranium, this won't be reached in practice, due again (in part) to the impracticality of complete exposure

e. hence HTO was at its performance limit only in a geometric or systems sense - no one has determined how to load a particle to its chemical limit

f. small particle size is an obvious way to obtain large surface/volume ratios

g. FRG representatives reported some conceptual ideas on moulding "cylinders" having a star-shaped cross section to create a larger, protected exposed surface

h. losses due to surface attrition would be especially onerous in that they would lose considerable uranium-disproportionate to sorber losses, and ecological consequences would have to be considered.

The discussion next turned to the subject of elution: using hydrochloric or sulfuric acids for IX resins or sodium or ammonium carbonates for HTO. Several points were made:

a. recycling of chemicals is imperative from both the cost and environmental aspects. Some ventured the thought that HCl could be recycled whereas H_2SO_4 might not - although it might be inexpensive enough to use nonetheless, if PH and sulfate effects could be tolerated in the environment

b. Mr. Campbell made the point that the eluate was still a fairly dilute solution, requiring considerable additional concentration, which could be combined with the process for chemical recovery

c. sodium carbonate appears to be replacing ammonium carbonate as the eluant of choice for HTO

d. washing the bed pre and post elution remains an expensive proposition. It is necessary for HTO carbonate elution, however, to avoid blinding the bed with calcium and magnesium carbonate precipitates.

Dr. Gregg asked whether significant energy was required to produce HTO. Someone recalled a value of 80 kwhr/kg. Hence if one lost 100 kgHTO/kgU and obtained 5000 KwD/kgU_{NAT} (≃30,000 MWD/MT of 3 wt % U), then the HTO losses would amount to 80(100)/24(5000), or perhaps 6% of the energy obtained from the uranium. (Ed. note: see additional comment following Dr. Gregg's paper.)

A protracted discussion of the elution process followed centering on how the concentration of uranium in the eluant stream varied with the sorber loading - whether at one extreme it was nearly independent, or on the other directly proportional; also discussed was the effect of elutant concentration - again whether high concentrations led to high uranium concentration. It became clear that a better modeling of the elution process (paralleling existing analyses of the loading process) was in order.

Prof. Driscoll raised the point that one could probably not exploit capacities higher than somewhere in the range 1-10 mgU/gm sorber because of the need to transport the uranium to the sorber: loading times would become prohibitively long.

Relevant experience was cited in the area of secondary concentration:

a. IX methods in use at uranium ore processing mills,

b. solvent extraction of 40ppm solutions in South Africa,

c. 5ppm U in copper waste solutions using IX resins and sulfuric acid elution (Kelmers)

d. some 17 years of experience on 7ppm minewater (Jones)

e. commercial operations in Texas at the 20-25ppm level using ammonium carbonate leaching (Jones).

As a final topic for the session, the question as to whether ion exchange resins might eventually surpass HTO was raised. Dr. Schwochau ventured that both the rate of uptake and the capacity could be anticipated to be superior in the long run.

Concluding Discussion

At the end of the conference following the presentation of the final paper and Dr. Fujii's remarks, a concluding open discussion was held.

In his capacity as co-host/co-chairman Prof. Driscoll shared some of his personal reactions with the conferees.

He first noted his impressions that hydrous titanium oxide could now be considered as a fully proven sorber material, one on which considerable data exists and one which could now be used to create suitable particles in a reproducible manner. Ion exchange resin, on the basis of early information, appears to be even more promising, but its performance has not yet been demonstrated in all particulars. Finally, it was also encouraging that new concepts were still arising: peat/humic acid, activated carbon, chitosan.

It was also striking that all materials appear to be effective only in a thin surface layer. No one has yet devised a particle configuration which permits the entire bulk to be affective. Whether this is an attainable goal, particularly in a cost affective manner remains an intriguing unanswered question.

In the area of system design and analysis there appeared to be a number of competitive ideas still contending for acceptance, including both fixed multilayer beds and fluidized beds; either supplied by seawater which is pumped, or where the needed head is provided by currents or waves. Perhaps the only general trend is toward siting of the contactor in the sea, whether it is free floating, moored, or fixed to the bottom. This is clearly motivated by the necessity of keeping non-productive head losses to a minimum.

As a final observation, the benefits of continued information exchange are obvious, if only to avoid duplication of effort. In this regard the hope was expressed that more attention would be given to the reporting of details when it comes to sorber performance: particle size, suface area, pore size, density, composition (wet or dry basis, water and especially titanium masses). While it may be too early to attempt to negotiate a standard terminology and practice in this regard, with enough information the various researchers can translate data into their own preferred frame of reference.

A final point was the observation that several groups of workers were speculating about eventual target prices as low as 200 \$/lb U_3O_8, which is beginning to approach breakeven economics versus other advanced energy sources.

Dr. Kelmers made a number of salient points regarding the lack of sufficient attention to modeling of the uranium distribution in sorber particles. Experimental evidence clearly indicates that the center of the particles is relatively uranium free, that the uranium is restricted to a thin layer on the surface, and that the gradient across this layer is steep. Thus reported particle "capacities" of 200ppm really correspond to something like 2000ppm in the surface layer and perhaps even 20,000ppm at the solid/seawater interface. Thus true equilibrium distribution coefficients may be quite large, ie

$$K_D \sim \frac{20,000}{0.0033} \sim 10^7$$

This has many important implications:

a. most distribution coefficient data reported for finite-size particles is not really "equilibrium" data in the true chemical sense

b. HTO performance could be enhanced appreciably if more of the bulk material could be effectively contacted with fresh seawater

c. surface attrition is a potentially large source of product loss.

Professor Driscoll noted that surface concentrations approaching 20,000ppm (2wt%) were approaching the range where a non-chemical "elution" process might become of interest: slurry honing, in which a thin surface layer is shaved off using an abrasive grit suspended in water. It was also noted that surface concentrations could be measured accurately using fission track methods.

Prof. Kanno and others n6ted the potential benefits of creating accessible pores on the particle surface. UK researchers noted, however, the propensity of pores to become clogged with calcium and magnesium deposits FRG experimenters reported some conflicting evidence in this regard. The distinction was made between carbonate deposits and blockage by sorption on active sites in competition with uranium. It was suggested that HTO had only one type of active site, that uranium could compete affectively with calcium or magnesium for these sites, but that transition metal ions could irreversibility deactivate such sites, evidence being quoted for the ability of copper and nickel to do so.

A discussion then ensued of the controlling parameters governing the production and sustenance of viable HTO. Water content was identified as the dominant parameter: starting the drying/polymerization process at 80% H_2O and not going below 35-45 net % H_2O - otherwise the HTO cracks, powders and loses adsorptive capacity. Maintenance in a wet state from that point on is also crucial. It was noted that HTO prepared in this manner was amorphous in nature. FRG researchers indicated that one could produce material which underwent less than 4% attrition losses per cycle, when used in 30-day cycles.

Prof. Kanno raised the question of apparent inconsistencies among various sensitivity and parametric studies: for example some show product costs are a weak function of sorber capacity, while others exhibit a strong dependence on this parameter. Some reasons for this dissonance were noted:

a. Mr. Campbell noted that in the EXXON studies capital costs and the costs of money were so important that other variations were in the "noise level."

b. Prof. Driscoll noted that two generic types of studies should be contrasted: sensitivity and sub-optimization - in the former one parameter is varied at a time; in the latter several parameters are varied simultaneously. Hence, while sensitivity studies might show a small effect, a key parameter, such as capacity, might allow several other parameters to reach (sub) optimum levels in a more comprehensive optimization scheme.

c. It was noted that there was no general agreement on which and how many parameters should be fixed a priori, as compared to those which would be allowed to vary freely or within some envelope of constraints.

John Patterson of the USDOE led a discussion in response to Dr. Fujii's request on behalf of the IAEA for increased international cooperation in the area of uranium from seawater, indicating that his office was supportive of such initiatives. It was suggested that researchers in this field begin by providing imput on the national level to the Working Party on Uranium Extraction. This in turn might lead to a subgroup of the working party composed of representatives of those member states interested in pursuing research in this area.

Prof. Driscoll suggested that a minimum goal in the short term might be to endorse some entity as a repository to which we could all send research reports, and which would periodically prepare and circulate a bibliography in this area.

Prof. Driscoll then declared the meeting as officially closed, and expressed the hope that the conferees might convene again in several years to report upon the successful completion of the many interesting and promising avenues of research described at the meeting.

Appendix A

Topical Meeting
on
The Recovery of Uranium from Seawater

sponsored by

U.S. Department of Energy and
Massachusetts Institute of Technology Energy Laboratory
December 1-2, 1980
Cambridge, Massachusetts

Agenda

Monday, December 1

All sessions will be held in the West Lounge of the Student Center.

Time	Activity	Speaker
8:30-9:00	Check in, coffee and doughnuts in the West Lounge	
9:00-9:10	Welcoming address	Prof. M. Driscoll (MIT)
9:10-9:20	Opening statement - U.S.DOE Perspective on Uranium from Seawater	Mr. J. Patterson (DOE)
9:20-9:50	Uranium Recovery from Seawater - Status of Technology and Needed Future Research and Development	Dr. A. Kelmers (ORNL)
9:50-10:20	Feasibility Study of Uranium Extraction from Seawater; Prof. S. Binney - University of Oregon (co-author)	Mr. M. Campbell (Exxon Nuclear)
10:20-10:30	Break	
	<u>Sorber Preparation and Performance</u>	
10:30-11:00	Macrocyclic Ligand to Bind Uranyl Ion Specifically from Seawater; Dr. Y. Kobuke (co-author)	Dr. I. Tabushi (Kyoto University)
11:00-11:30	The Advantage of Fast Reacting Adsorbents Such As Humic Acids for the Recovery of Uranium from Seawater - Part I	Dr. D. Heitkamp (KFA)
11:30-12:00	The Advantage of Fast Reacting Adsorbents Such as Humic Acids for the Recovery of Uranium from Seawater - Part II; Prof. K. Weagerner, Technical University Aachen, Drs. Ch. Schnell, D. Heitkamp, Dornier Systems (co-authors)	Dr. H. Denzinger (Dornier Systems)

Time	Activity	Speaker
12:00-1:30	Lunch-participants are free to arrange their own lunch; the Student Center Cafeteria is located on the same floor as the West Lounge	
	Process Design Studies	
1:30-2:00	Practical Constraints on Systems for the Extraction of Uranium from Seawater; Dr. F. Best, Ms. C. Nitta, Mr. J. Whaley (co-authors)	Prof. M. Driscoll (MIT)
2:00-2:30	United Kingdom Research Program; Dr. G. Llewelyn (co-author)	Mr. E. Hooper (AERE-Harwell)
	Sorber Preparation and Performance	
2:30-3:00	Uranium Recovery from Seawater by Ion Exchange; Dr. G. Beasley, Rohm and Haas (co-author)	Dr. S. Maroldo (Rohm and Haas)
3:00-3:15	Break	
3:15-3:45	Studies on Complexing Resins Accumulating Uranium from Seawater; Drs. L. Astheimer, H.-J. Schenk, E. G. Witte;	Prof. K. Schwochau (Instut. fur Chemie Julich)
3:45- 4:15	Recovery of Uranium From Seawater	Prof. M. Kanno (University of Tokyo)
4:15-5:00	Panel Discussion and Question and Answer Period	Dr. F. Best (Moderator)
5:45	Welcoming Dinner - MIT Faculty Club, 6th floor, 50 Memorial Drive	

Tuesday, December 2

All sessions will be held in the West Lounge of the Student Center

9:00-9:30	Coffee and doughnuts	

Process Design Studies

9:30-10:00	On the UEB Concept of Uranium Extraction from Seawater; Drs. H. G. Bals, M. Fremery (co-authors)	Dr. J. Bitte (Uranerzbergbau)
10:00-10:30	Lawrence Livermore Laboratory Concept for Uranium Recovery from Seawater; Dr. F. Wang (co-author)	Dr. D. Gregg (Lawrence Livermore Laboratory)
10:30-10:45	Break	

Sorber Preparation and Performance

10:45-11:15	The Interaction of Uranium with Chitin and Chitosan and Its Recovery from Seawater	Prof. R. Muzzarelli (U. of Ancona)
11:15-11:45	The Recovery of Uranium by Chelation with Chitosan	Prof. B. Averbach (MIT)
11:45-1:30	Lunch-participants are free to arrange their own lunch; the Student Center Cafeteria is located on the same floor as the West Lounge.	

Process Design Studies

1:30-2:00	Recovery of Uranium from Seawater by Using Wave Power and Floating Offshore Units; Drs. S. Forberg, G. Lagstrom, Royal Institute of Technology (co-authors)	Dr. P. Vallander (National Swedish Board for Technical Development)
2:00-2:30	Adsorption and Elution of Uranium in Seawater	Prof. M. Kanno (University of Tokyo)
2:30-3:00	The Effect of System Improvements on Uranium Recovery from Seawater, Prof. M. Driscoll (co-author)	Dr. F. Best (MIT)
3:00-3:30	On The UEB Concept of Uranium Extraction From Seawater	Dr. M.I. Fremery (Uranerzbergbau-GMBH)
3:30-3:45	IAEA Perspective on Recovery of Uranium from Seawater	Dr. Fujii (IAEA)

Tuesday, December 2

3:45-4:00	General Question and Answer Period; Panel Discussion on the Future of Uranium Recovery from Seawater	Prof. M. Driscoll (MIT)
4:30	Concluding comments; end meeting	Prof. M. Driscoll

Appendix B

LIST OF ATTENDEES

Prof. Benjamin Averbach
13-5082
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Mr. Hein De Baar
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Dr. Glen Beasley
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