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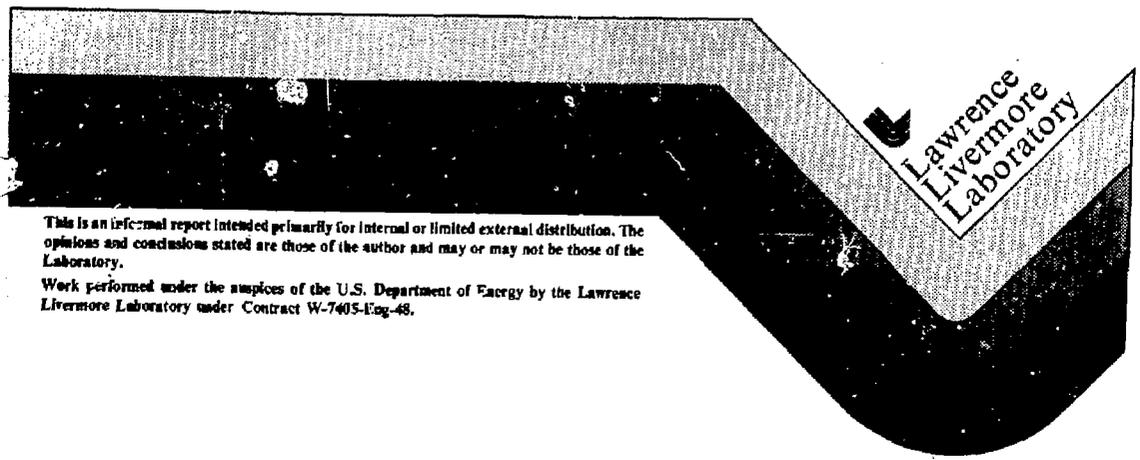
UCID-19569

URANIUM FROM SEAWATER

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September 21, 1982



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Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract W-7405-Eng-48.

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ABSTRACT

A novel process for recovering uranium from seawater is proposed and some of the critical technical parameters are evaluated. The process, in summary, consists of two different options for contacting adsorbant pellets with seawater without pumping the seawater. It is expected that this will reduce the mass handling requirements, compared to pumped seawater systems, by a factor of approximately 10^5 , which should also result in a large reduction in initial capital investment. Activated carbon, possibly in combination with a small amount of dissolved titanium hydroxide, is expected to be the preferred adsorbant material instead of the commonly assumed titanium hydroxide alone. The activated carbon, after exposure to seawater, can be stripped of uranium with an appropriate eluant (probably an acid) or can be burned for its heating value (possible in a power plant) leaving the uranium further enriched in its ash. The uranium, representing about 1% of the ash, is then a rich ore and would be recovered in a conventional manner. Experimental results have indicated that activated carbon, acting alone, is not adequately effective in adsorbing the uranium from seawater. We measured partition coefficients (concentration ratios) of approximately 10^3 in seawater instead of the reported values of 10^5 .⁽¹⁾ However, preliminary tests carried out in fresh water show considerable promise for an extraction system that uses a combination of dissolved titanium hydroxide (in minute amounts) which forms an insoluble compound with the uranyl ion, and the insoluble compound then being sorbed out on activated carbon. Such a system showed partition coefficients in excess of 10^5 in fresh water. However, the system was not tested in seawater.

INTRODUCTION

Both the high and the low projections for annual world uranium demands made by INFCE (see fig. 1)⁽²⁾, indicate that we can anticipate a shortage in the world uranium supply in about 15 to 20 years, with the production shortfall growing very rapidly with time thereafter. This projection is based on the maximum attainable production capability from all known high grade uranium resources and includes the by-product uranium from phosphoric acid plants. The current by-product uranium production from phosphoric acid plants in the United States is 3300 tonnes of uranium oxide annually (1978).⁽³⁾ Although significant, this is less than a quarter of the uranium presently required annually by nuclear power plants. The growth of uranium production from phosphates is dictated by the rate of use of phosphates as fertilizers and thus will not be expandable to meet our projected requirements.

It is essential that research be initiated on methods for obtaining uranium from low grade resources. Seawater represents the largest single resource of uranium in the world (four billion tons at a concentration of 3.3 ppb). *This is to be compared with estimates for other low grade resources available to the United States: Chattanooga shale (five million tons), phosphate deposits (three million tons), and Conway granites (two million tons).* Uranium from the Chattanooga shales, the Conway granites, and seawater have been the subject of a number of studies, but no commercially feasible process has been identified to date.

The primary technical and economic problems with recovering uranium from seawater are due to its very low concentration. On this basis, one might reject research on recovery from seawater in favor of the Chattanooga shale or

the Conway granites which have uranium concentrations a few thousand times greater (20 to 60 ppm). However, it is not difficult to imagine that the strip mining, grinding, retorting and chemical processing of the Chattanooga shale or the Conway granites will also be a monumental task and could result in unacceptable environmental consequences. In contrast, it is envisioned that the environmental consequences of a process for recovering uranium from seawater will be much less severe, and this might be the determining factor in making it a more attractive low-grade resource than either the Chattanooga shale or the Conway granites. This assumes the development of a successful process, which is the ultimate goal of this research effort.

Commercialization of uranium from low grade uranium resources will, in the final analysis, depend on economic factors. The projected requirement for additional uranium and the break-even cost will depend on which breeder/conventional reactor strategy (assuming that a strong nuclear industry will survive its present political problems) is adopted. It is estimated that the breeder reactor will cost considerably more to build than the conventional non-breeder, reactors. The break-even fuel cost is estimated to be approximately \$500 per pound of yellow cake, i.e., the price at which conventional reactors will no longer be able to economically compete with breeder reactors. These cost figures are subject to change as the world gains more experience with commercial breeder reactors. However, we believe both conventional and breeder reactors will be used for years to come. Therefore, there will be a continuing need for uranium and if it can be recovered from seawater within the competitive price range, we can provide an essentially unlimited supply of uranium. Even though there may be some very formidable technical problems, the potential payoff for recovering uranium from seawater is sufficiently large to warrant a research effort directed at evaluating

processes that have potential for recovering such uranium economically and with an acceptable energy efficiency.

PRIOR PROPOSED AND EVALUATED APPROACHES FOR URANIUM RECOVERY FROM SEAWATER:

The most comprehensive analysis of a uranium from seawater system for the United States was performed by the Exxon Nuclear Company and Oregon State University under DOE contract. A four volume report was issued on their work in 1979.⁽⁴⁾ A more recent publication, a PhD thesis by Best from MIT,⁽⁵⁾ also supported by DOE through the MIT Energy Research Laboratory, addressed some of the major problem areas revealed by the Exxon report. The Exxon report presents a review of the numerous options considered for uranium recovery from seawater found in the literature, supplemented with information obtained from visits to various laboratories around the world which are active in this area. One of the most significant assessments they made was that the amount of potential uranium recovery from pumped seawater already used to cool power plants or from tidal basins would be too small to be worthy of consideration for the United States. This left seawater pumped systems or systems that utilized ocean currents to pump seawater. Since the Exxon study contract was to provide a cost analysis of uranium from seawater, they made some necessary but fatal decisions. It was decided that the basic design criteria for the plant would have to utilize the best understood engineering and chemical technology. This led them to a seawater pumped system and titanium hydroxide as the adsorbent material. The plant was to be located on a land based site in Puerto Rico and the titanium hydroxide would be loaded into large fluidized beds supplied with pumped seawater. This approach allowed them to make a fairly reliable estimation of the cost of the produced

uranium (\$2100/#U₃O₈ in 1995 dollars), but also clearly showed that the uranium would be too expensive if produced in this manner and that a novel, radically different, approach would be required if one were to hope to produce the uranium economically.

The process evaluated by Exxon is extremely useful in that it provides a well done reference against which to compare an alternative approach. The process required the construction of a large, capital intensive, land based plant which used pumped seawater through fluidized beds of hydrous titanium oxide. The chemical processing required five operational steps:

1. Loading the titanium hydroxide adsorbent with uranium by direct contact with seawater.
2. Washing the titanium hydroxide with fresh water.
3. Eluting the uranium from the hydrous titanium oxide with ammonium carbonate.
4. Steam stripping to recover the ammonium carbonate from the eluant.
5. Preparing a solid uranium product.

A plant design in the manner described by the Exxon report has the following major problem areas:

1. The construction of a large, land-based plant dominated by massive seawater pumping requirements, large and expensive adsorption beds, large ammonium carbonate handling facilities, as well as fresh water handling facilities. The capital investment required to construct the plant represented approximately 70% of the final projected cost of the produced uranium.
2. Large amounts of fresh water are required for washing the titanium hydroxide, which severely limits the number of possible locations for such a plant.

3. The elution step results in a stream which has a uranium concentration which is only approximately 10^3 greater than that in the initial seawater. Even though the initial adsorption step on titanium hydroxide results in an impressive amount of concentration of the uranium (a concentration increase of approximately 10^5), a factor of 10^2 in concentration is lost when the titanium hydroxide is eluted with ammonium carbonate. This is a critical point to understand since the resultant concentration improvement of the uranium in the ammonium carbonate solution is due solely to the ratio of the carbonate ion concentration in the eluant vs. that in seawater, and is independent of the adsorbent material used. One would thus conclude that it would be desirable to use more concentrated ammonium carbonate, and thus get higher concentrations of uranium in the eluant. However, the Exxon report presents data that shows when the ammonium carbonate concentration is increased much above 0.1 M, the titanium hydroxide is strongly dissolved, resulting in an unacceptable loss rate. Thus, it appears that this approach unavoidably results in an elution step that loses the very attractive concentrating effect that is achieved when the titanium hydroxide first adsorbs the uranium out of the seawater.

4. Steam stripping of the massive eluant stream will be very energy intensive, and when combined with the power required to pump the seawater, places the feasibility of achieving net energy gain with the plant in serious question. A net energy analysis of the system, which would have been very interesting, was not performed by Exxon.

5. The resultant projected cost of uranium, which varied from \$2100 to \$2600 per pound of U_3O_8 in 1995 dollars, is approximately a factor of ten higher than what is expected to be economical.

The approach by Best from MIT deals with some of these problems by moving the plant to a sea based platform. However, the seawater is still pumped (with a current assist), the uranium is still adsorbed on beds of titanium hydroxide, and all the following chemical processing is the same. He calculates a lower uranium cost, but the analysis is not as detailed or complete as the Exxon analysis. Thus the number is probably less reliable. It is our opinion that the changes invoked by Best are not likely to reduce costs significantly, and could, instead, increase them. The cost of making the all weather, sea based plant and supplying it with large quantities of fresh water could be far more expensive than the land based plant evaluated by Exxon. We thus believe that a radical departure from these fairly standard approaches is required, and the departure we believe will be the most likely to be successful is presented in the next section.

THE LLNL OCEAN CURRENT URANIUM RECOVERY SYSTEM:

As was clearly demonstrated by the Exxon-Oregon State report, the primary goal of an improved uranium from seawater system has to be a dramatic reduction in initial capital investment for the plant. Secondary goals should be to reduce the cost of the chemical processing and minimize the requirement for fresh water in the process. It is proposed that all of these goals will be accomplished in the process presented herein. The first goal is accomplished by invoking a fundamental principal that only adsorbent material will be pumped or otherwise manipulated, and not seawater. This will reduce the pumping or materials handling requirement for the first extraction step by a factor of approximately 10^5 . This dramatic reduction in materials handling (eliminating seawater pumping) is expected to result in a very large reduction in required initial capital investment. We plan to substitute activated carbon for titanium hydroxide as the adsorbent material. This

results in one very attractive potential advantage. The activated carbon, after it is loaded with uranium, can be burned (extracting its energy to produce power) or gasified, leaving an ash which is a highly concentrated uranium ore. This eliminates the requirement for the massive ammonium carbonate elution system with its energy intensive steam stripping operation, and it eliminates the need for the large amounts of fresh water required to wash the adsorbent before the elution step. Thus, both the plant construction and the chemical processing are greatly reduced in size and simplified. The product, which is a uranium rich ash, is then processed in a conventional manner. Also, the highly concentrating first adsorbing step which is achieved both by activated carbon, and titanium hydroxide, is not then lost by a sequential elution step, but rather the following combustion step further concentrates the uranium.

The potential economic success of this system depends crucially on two items: 1) the feasibility of producing a sufficiently low cost activated carbon with adequate uranium adsorption characteristics, and 2) the feasibility of thoroughly contacting this activated carbon with seawater currents and recovering it without large capital investment and with acceptably low losses of the activated carbon. The proposed methods of accomplishing these requirements are described in more detail below.

1. Activated Carbon for Uranium Recovery from Seawater: Activated carbon has been reported to be very effective in adsorbing uranium from seawater, in that it has been shown to be capable of adsorbing 500 mg U/Kg carbon.^[1] This makes it as effective as most preparations of titanium hydroxide which ranges from 200 to 1500 mg U/Kg titanium hydroxide. However, the Exxon report has only this one reference where the effectiveness of activated carbon in extracting uranium from seawater was quantitatively measured.^[1,4] It is

also well understood that the adsorbitivity of a particular activated carbon can vary dramatically, depending upon the original carbon source material used, the method of pyrolysis, and the method of activation.⁽⁶⁾ Therefore, there is a clear need to gather more data on the specific performance of different activated carbons for recovering uranium from sea water.

There are a variety of sources of carbonaceous materials which have been used to make commercial grade activated carbon. They include a variety of biowastes such as walnut shells, coconut shells, paper mill wastes, wood chips and bark, etc., as well as a variety of coals which produce some of the most effective activated carbons.⁽⁶⁾ It is anticipated that for a uranium from seawater plant the requirements for activated carbon will be so large that the primary feedstock will have to be the more plentifully available coal. The plant designed to produce the activated carbon should establish its economics not only on the production of the needed activated carbon, but will also collect and sell the liquid and gaseous products resulting from the coal processing. In other words, the proposed activated carbon plant should be an integral part of a coal liquifaction and gasification plant. The process steps required to produce the activated carbon, which are first to pyrolyze the coal, and then to partially react the remaining char with steam to activate it, naturally produce valuable liquid and gaseous products. We estimate that the plant could be operated at a profit by selling only the gas and liquid "byproducts", and deriving no value from the activated carbon produced. This would make it possible to produce the activated carbon at a very affordable price, which would make burning of the activated carbon in the seawater extraction process economically feasible.

If it becomes necessary to elute the uranium off of the activated carbon so that it can be reused, it is still possible that an advantage over titanium

hydroxide will be retained since the activated carbon will not be dissolved even in very concentrated eluents. The preferred elution procedure would probably be an acid leach, since this would remove the uranium and reactivate the carbon in a single step. This type of extraction method is not feasible with titanium hydroxide since it would be strongly dissolved in the acid. Also, the need for the fresh water wash of the adsorbent is eliminated. The wash is essential for the titanium hydroxide system to remove minerals and thus reactivate it.

2. Basic Plant Design Options: There are two basic plant design options which we are considering: 1) A design where the activated carbon is contacted with seawater by scattering appropriately sized carbon particles on or near the top of the ocean, allow them to sink to the bottom adsorbing uranium, and then suck them off the bottom and into a barge. They are then taken to the process plant which further processes the particles to extract the uranium (and burn them to produce power at the same time). 2) The second design concept consists of packing activated carbon in appropriately shaped mesh bags, placing the bags into the ocean attached to and spaced along a long chain anchor, allowing the natural ocean currents to force flow through the activated carbon. They are then picked up and sent to the uranium extraction plant.

Both of these plant design options adhere to our guiding fundamental decision that one must not attempt to pump the seawater. Only the adsorbent material is manipulated.

The first of these plant options allows one to minimize the amount of physical structure that is in contact with the seawater and thus minimize capital investment and maintenance costs. However, it suffers from a great deal of uncertainty as to the ability to recover a large enough fraction of

the activated carbon which was scattered at the surface. The second plant option gives one positive control over the activated carbon by placing it in bags, but increases the capital and maintenance costs. A more detailed evaluation is needed to better evaluate the tradeoffs between the systems.

Some of the unique characteristics of the two processes are presented below.

A. The Activated Carbon Surface Spreading Process Design: The conceptual design of this approach is presented in Fig. 2. In this design the adsorbent is dispersed on or near the surface and settles to the bottom, extracting the uranium. Ocean water is replenished by an ocean current. The activated carbon, which eventually forms a thick mound on the bottom, is then pumped up with a suction device. The parameters that need to be evaluated for this system include the scatter of the particles as they settle to the bottom. This will depend on a complex interaction between the ocean current velocity, the turbulence associated with that current, and the characteristics of the activated carbon particles.

Some preliminary estimates have been made to interrelate the adsorbent particle diameter and its density to the required minimum ocean depth to achieve a particular uranium concentration on the adsorbent. Particle dispersion effects and interaction effects between particles are neglected. The relationships are presented as follows:

It is first necessary to estimate the traversal velocity of the adsorbent pellets. This is done by using Stokes' formula for sedimentation for spherical grains:

$$u = \frac{gd^2 (P_s - P_l)}{18\eta} \quad (1)$$

where u is the terminal velocity of the particle, d is the diameter of the particle, g is acceleration due to gravity (981 cm/sec^2), p_s is the density of the sphere, $p_1 = 1$, $n = 0.01$, and $g \approx 981$, then equation 1 can be simplified to:

$$u = 5450(p_s - 1)d^2 \quad \text{cm/sec} \quad (2)$$

where p_s is in g/cm^3 and d is in cm .

The mass transfer rate to the sorption pellets can be estimated by using the equation for mass transfer to a sphere in a moving fluid, assuming the concentration on the sphere to be zero. This, in essence, assumes that the concentration on the sphere is always far lower than its equilibrium concentration.

An equation for calculating this mass transfer rate is as follows: (7)

$$\frac{Kd}{cD_{ab}} = 2.0 + 0.60 \left[\frac{du p_1}{n} \right]^{1/2} \left[\frac{n}{p_1 D_{ab}} \right]^{1/3} \quad (3)$$

where K is the mass transfer rate, d is the diameter of the sphere, c is the concentration of uranium in the seawater, D_{ab} is the diffusion coefficient, p_1 is the density of the seawater, n is the viscosity of the seawater, and u is the velocity of the pellet in the seawater.

Let us first assume that the velocity of the pellets is small and thus the second term on the right of equation 3 is small compared to 2.

Thus:

$$K = \frac{2cD_{ab}}{d} \quad (4)$$

It is also assumed that the time over which the mass transfer takes place is the transit time of the sphere settling through the ocean. Thus, using equations 2, 4, and the equations for the volume and area of a sphere, and assuming that the adsorption pellet does not approach equilibrium concentration, the concentration of uranium on the spherical pellet can be expressed as follows:

$$C = 2.2 \times 10^{-3} \frac{cD_{ab}L}{\rho_s (\rho_s - 1) d^4} \quad (5)$$

where ρ_s is the density of the sphere, L is the depth of ocean that the pellet traverses, and C is the concentration of uranium on the pellet.

One of the most important features which equation five points out is that the concentration of uranium on the pellet, after it has traversed a particular depth of ocean, is inversely proportional to the fourth power of the pellet diameter. Therefore, changes in pellet diameter can compensate for large changes in other parameters.

It is useful to use equation five to estimate ranges of particle diameters, densities, and ocean depths which should be considered. To do this, it is assumed that the uranium concentration on the pellet can reach 500

mg U/Kg C (the reported value in the literature) without pellet saturation effects playing a significant role. It is also assumed that the concentration of uranium in seawater is the commonly reported value of 3.3×10^{-9} g/g. Since we have no measurements for the diffusivity of the uranyl carbonate complex in seawater, a typical diffusivity for molecules in water is assumed, $10^{-5} \text{ cm}^2 \text{ sec}^{-1}$. [8] With these assumptions, the depth of ocean that the pellets must traverse to reach the stated uranium concentration is:

$$L_w = 6.9 \times 10^{12} p_s (p_s - 1) d^4 \text{ cm} \quad (6)$$

and the time required to reach this depth and thus uranium concentration is

$$t_s = 1.27 \times 10^9 p_s d^2 \text{ sec} \quad (7)$$

Parameterized plots of these two equations are presented in Fig. 3 and 4, with depth and time changed to meters and hours to give a better physical feeling to the reader. It can be seen from these figures that the most desirable particle size will range slightly around a diameter of 0.005 cm (50 microns), and large deviations from this diameter will probably not be acceptable.

It should be pointed out that the above calculations assume no flow through an adsorption pellet. If the pellets are manufactured in a manner where they have a sufficiently open structure so that seawater will flow through them as they settle, much larger particles could be used. The times required for the adsorbent pellets to settle also unfold into potential dispersion problems. We have concluded that high velocity ocean currents will be undesirable in that they are likely to cause the pellets to be spread over too large an area at the bottom. Moderate to slow currents (0.1 mph or less) will probably be required to keep dispersion effects manageable.

A similar process using buoyant adsorption pellets, with a surface collection system, would have a different set of interesting features and

could be designed also, if suitable sorption pellets could be fabricated.

B. The Activated Carbon Contained in Mesh Bags Process Design: For this design option, the activated carbon is loaded into mesh bags which are made slightly buoyant and anchored in the ocean by spacing them along a heavy chain. A conceptual design of this process is presented in Fig. 5. The chain serves not only as a means of anchoring the bags, but also as a means of placing the bags into the ocean and retrieving them. It is anticipated that the bags might be fabricated in the shape of small parachutes to maximize the effect of the ocean current in causing seawater to flow through the activated carbon. It is conceived that there will be a very long continuous chain placed in the ocean in a circle, which will allow a ship to operate continuously along the chain removing uranium saturated activated carbon and refilling the bags with fresh activated carbon. The activated carbon would then be processed in the same manner as described above.

This design allows us to retain positive control over the activated carbon pellets. However, the pellets will have a different set of physical requirements than for the spreading and settling system described in the previous section. They must be compatible with the mesh bag in terms of low losses through the holes in the mesh, and have a sufficiently high permeability so that a loaded bag will easily allow seawater to flow through it. These requirements will probably dictate carbon pellets which are considerably larger than those calculated for the settling system. However, in this case the larger pellets are acceptable since longer contact times are available and saturation of the larger pellets is not expected to be a problem. The bags will simply be anchored in the ocean and left there until they saturate. The system should be designable so that losses of the activated carbon will be minimal. However, fouling of the bags by the many

well known mechanisms which are common in seawater is anticipated to present a very significant problem. If it is very significant, it might limit the area of operation of this system to clear southern waters where fouling will be much lower than in the northern waters.

ECONOMICS:

It is expected that the initial capital investment will be reduced by more than a factor of ten over the seawater pumped/titanium hydroxide adsorbent process analyzed by Exxon. This is because we will not have to pump seawater and will have a much simpler adsorbent system.

If we use the literature number of 500 mg U/kg C, this is equivalent to one pound of uranium per ton of activated carbon. Since a pound of yellowcake is worth about \$45.00, the value increase of the activated carbon will be \$45.00 per ton due to the uranium alone. However, one must also consider the value of the other minerals expected to be recovered. The potential for activated carbon to recover gold and silver from the ocean has been reported by the Russians. (6) If we assume that these elements are also recovered in their relative concentration proportions in the ocean, the gold and silver will add approximately \$9.00 and \$16.00 per ton of carbon respectively. Thus one might expect a value increase of the carbon of approximately \$70.00 per ton of carbon. If the activated carbon can be made for approximately the price of its heating value, due to the value of the other products produced in the same plant, its value will be approximately \$20.00 per ton. Thus the process that contacts the activated carbon with seawater will increase the value of the activated carbon from its initial \$20/ton to a final value of approximately \$90/ton (the value of the uranium, gold, silver and heating value of the carbon). It can be seen that this level of value increase could allow for carbon losses and other process expenses and still show a profit.

It should also be noted that the adsorbed uranium, in a concentration of one pound per ton of activated carbon, will be capable of supplying approximately 10 times more thermal energy (after isotope enrichment) for a nuclear power plant than would be available from the combustion of the activated carbon. Thus, a considerable amount of activated carbon could be lost in the ocean and there would still be a net energy gain for the process.

EXPERIMENTS:

Our singular goal in the set of experiments described in this section is to quantify the sorption uptake of uranium by activated carbon from seawater and other test solutions.

In establishing an experimental procedure, there were a number of decisions that had to be made early. They included the choice of type of activated carbon, the particle size of the activated carbon, the contacting method (with seawater), the source of seawater, the chemical analysis method that would be used, and the extent to which synthesized or doped seawater would be used. These decisions will be discussed below.

A survey of commercially available activated carbons, which included consulting a number of companies that produce activated carbon, led us to choose an activated carbon produced by Calgon. This activated carbon, called "Type NAP", has an exceptionally high surface area ($1,525 \text{ m}^2/\text{g}$) and is derived from bituminous coal, which is an abundant source. A data sheet, provided by Calgon, is presented in Table 1.

Table 1

Typical Properties of Type NAP Pulverized Activated Carbon

Surface Area m^2/g (BET method).....	1525
Iodine Number.....	1265
Molasses Number.....	550
Ash, Weight %.....	15
Moisture, Weight %.....	2
CCl_4 Adsorption, Weight %.....	92
Screen Size:	
Smaller Than 100 Mesh U.S. Sieve Series, Weight %.....	90
Smaller Than 350 Mesh U.S. Sieve Series, Weight %.....	70

Consistant with the choice of the NAP activated carbon, we also decided to use a relatively finely divided activated carbon so as to minimize the required contact time (with seawater) as discussed in the previous section. After attempting a number of flow through methods, we concluded that this approach to contacting the activated carbon with seawater would not work for us. The permeability of the fine carbon powder was too low to allow an acceptable flow rate of the water. We thus decided to use a large container of seawater (250 gallons), and stir in a small amount of the activated carbon (1-5 gms). The activated carbon was then allowed to settle over 1-2 days. The seawater was decanted off and the activated carbon was collected off the bottom. When we used higher concentration doped samples in distilled water for some of the measurements, smaller vessels were used, but the same stirring and settling technique was retained as the contacting method.

Seawater was obtained from the "Sea-lab" at LLNL. This laboratory

receives regular shipments of seawater supplied by the University of California Oceanography Laboratory at Bodega Bay, California. An analysis of the seawater performed by Thomas Hirshfeld at LLNL, using a laser fluorescence technique, showed that it contained uranium at a concentration of 1.8 ppb. This is lower than the more usual measured 3.3 ppb, which might be explained by dilution of the seawater by river outfalls, or possibly some loss on the walls of the shipping vessel. We were unable to pursue this discrepancy within the scope of this effort.

The chemical analysis of the samples was performed by Los Alamos Scientific Laboratory using their neutron activation analytical facility developed under the NURE program. A review of the capability indicated that it would be sufficiently sensitive and accurate for our needs. An added advantage was that the facility automatically analyzed not just for uranium, but also for 31 other elements. Thus, for the same analysis price, we were able to look for possible extraction of other elements. However, we did not find measurable uptakes of any other elements.

For the first set of experiments we used natural seawater, analyzed to have a uranium concentration of 1.8 ppb, and the NAP activated carbon. Four grams of activated carbon was stirred into 250 gallons of undoped, but filtered seawater, and the carbon was allowed to settle out over two days. The seawater was then decanted off and the carbon removed from the bottom of the tank. We usually recovered more than three out of the four grams added to the water. The results are presented in Table 2. The fraction of the uranium in the seawater that was measured to be on the activated carbon is presented as well as the partition coefficient for each experiment. The partition coefficient is defined as: concentration of uranium on the activated carbon/the concentration of uranium in the water (seawater). Since both

concentrations are in grams/gram, the partition coefficient has no units. The partition coefficients were erratic, with the highest being 1,100. These were discouraging results since our economic analysis presented above indicated that we would need a partition coefficient of $1-5 \times 10^5$.

Table 2

Uranium Extraction from Natural Seawater using Activated Carbon
 (Each test used 250 gallons of seawater (1.8 ppb U) and 4g of activated carbon)

Test	Uranium on Activated Carbon (ug/g)	% Uranium Removed from Seawater	Activated Carbon Based Partition Coefficients
1	0.7	0.20	400
2	0.3	0.05	140
3	0.2	0.04	89
4	1.7	0.40	920
5	1.0	0.20	530
6	2.0	0.40	1,060

In the next set of experiments we tried doping the activated carbon with a number of chelates as well as the proven titanium hydroxide in an attempt to increase its sorption capabilities and thus the partition coefficient. It was reasoned that the nonpolar backbone of the additive might be sorbed on the activated carbon surface, leaving the polar chelation ends available for bonding with the uranium. The samples were prepared by dissolving the

additive in an appropriate solvent, adding the activated carbon, and then removing the solvent in a rotary vacuum evaporator. The results of these experiments are presented in Table 3. It can be seen that we were unsuccessful in significantly increasing the partition coefficient based on activated carbon. We also calculated a partition coefficient based on the weight of the additive used. These numbers are considerably higher due to the additive being a small part of the weight of the activated carbon. The highest partition coefficient based on activated carbon was 1,600, which is far too small compared to the needed 10^5 .

Table 3

Doped Activated Carbon in Natural Seawater

(Each test used 250 gallons of seawater (1.8 ppb U) and 4g activated carbon)

Dopant #	Uranium on Activated Carbon (ug/g)	Grams of Dopant Added	Partition Coefficients	
			Based on:	
			Activated Carbon	Dopant
1	0.60	0.04	330	32,800
	2.90	0.20	1,600	32,700
	1.20	0.70	650	3,900
2	0.90	0.40	490	5,400
3	0.80	0.20	440	9,200
4	1.20	0.20	660	13,200

Dopant # 1 = 2,2,6,6-tetramethylheptane-3,5-dione

2 = 2,2,6,6-tetramethylheptane-3,5-dione; 0.1% aerosol

3 = titanium hydroxide

4 = humic acid

At this point we were concerned that our poor results were due to microorganisms in the seawater being preferentially sorbed on the activated carbon. This would then plug the pores of the activated carbon and coat its surface area so that the uranium would not be sorbed. In order to check this possibility, we performed a set of experiments using distilled water (free of such organics) solutions of uranyl nitrate. Due to the limited supply of distilled water (was not available in 250 gallon quantities) we used much smaller quantities of water and higher concentrations of the uranyl ion. The results are presented for undoped activated carbon in Table 4. It can be seen that the partition coefficients are similar to those obtained with seawater. We thus concluded that our poor results were not due to plugging of the activated carbon by microorganisms.

Table 4

Activated Carbon in a Distilled Water Solution of $U(NO_3)_6$
 (Each test used 500 ml of solution and 3g of activated carbon)

Uranium Concentration (ppb)	Uranium on Activated Carbon (ug/g)	% Uranium Removed from Water	Partition Coefficients
312	46	86	1,050
	40	76	500
3,120	380	73	450
	420	80	675
	350	67	340
	370	70	400
	360	69	370
	320	62	270
	370	70	400
	390	75	470

After encountering the above failures, which appear to show that our original concept will not work with activated carbon, we decided to carefully review our approach, and the assumptions that we made. One of our primary, unwritten assumptions was that it would never be economical to add a soluble material to the seawater to precipitate out the uranium. However, upon carefully reviewing the commonly referenced extraction process using titanium

hydroxide, we concluded that this is probably what is actually happening in this process. The uranyl ion is not being adsorbed on the titanium hydroxide particles like in an ion exchange process, but rather it is more likely that the uranyl ion is forming an insoluble compound with dissolved titanium hydroxide, which then precipitates out on the titanium hydroxide particles. This is consistent with the fact that the titanium hydroxide is slightly soluble in seawater, to the extent that its equilibrium solubility would allow it to reach a concentration in seawater of approximately 100 ppb, which is 40 times greater than the concentration of the uranium. Therefore, the titanium hydroxide particles are continually dissolving as the uranium is adsorbed on their surfaces. This is not consistent with the conventional ion exchange model, but is consistent with a model of the formation of an insoluble uranyl-titanium hydroxide compound which precipitates out on the titanium hydroxide particles. An additional supporting piece of information is that the uranium is found only on the outer surface of the titanium hydroxide particles in such an extraction processes.

The difference might be subtle, but could be profound if capitalized on. It has already been shown in the Exxon analysis that the solubility losses associated with saturating the seawater with titanium hydroxide are an acceptable economic loss. Even though the titanium hydroxide is 40 times more soluble in seawater than the concentration of the uranium, this is still a very small concentration. Therefore, the approach of adding a material to the seawater to reduce the solubility of the uranium now becomes reasonable, which is in contrast to our original perception of the situation. Thus we now have the beginnings of a new, reasonable process. We have a method of making the uranyl ion much less soluble in seawater, consisting of adding titanium hydroxide to the seawater in just sufficient amounts to approach saturation,

which is significantly different than the alternate titanium hydroxide processes since far less material is used. If we add to this the observed trend that the effectiveness of activated carbon in sorbing material out of water increases as their solubilities decrease, we can devise or invent a significantly new process. It consists of adding just enough titanium hydroxide to the seawater to form the insoluble uranyl-titanium hydroxide compound, and then sorb this compound out on activated carbon.

The first step in proving the validity of our precipitation-sorption model, and thus demonstrate the potential feasibility of this proposed process, is to run some experimental tests. In designing the tests it was decided that we would have to use the 250 gallon tank, since the smaller vessels would use such small amounts of materials that our neutron activation analysis diagnostics would not be sensitive enough to make the necessary measurements. We also decided, for the first tests, to use fresh water instead of seawater in order to minimize the variables. Unfortunately, this committed us to using our tap water, due to our inadequate supply of distilled water. However, we felt it would be good enough for these first scoping tests since it is known to be relatively low in minerals. (However, we had no mineral analysis of it.)

We doped the water with uranium nitrate, $U(NO_3)_6$, which form the uranyl ion once it is in solution. There is also probably sufficient carbonate ion concentration in the water to form some of the uranyl carbonate complex. We then added a small amount of $Ti(OH)_4$ (in the form of $TiCl_4$ which converts to $Ti(OH)_4$ once it is in the water) in varying amounts bracketing the estimated solubility limit of approximately 0.12 grams (for 250 gallons of seawater). 3 grams of activated carbon were then stirred into the

water and allowed to settle. The data are presented in Table 5. It can be seen that the partition coefficients are very significantly improved over any of the earlier tests. The numbers for activated carbon are as high as 2.4×10^5 , which is within our projected economic range if the system used seawater. One interesting observation is that the maximum activated carbon partition coefficients were obtained at a titanium hydroxide addition of approximately 0.4 grams for all three uranium concentrations tested. However, the number of tests are insufficient to determine if this is an artifact or if it is a real effect.

We also calculated the partition coefficient based on the added titanium hydroxide, and these results are also given in Table 5. It can be seen that these partition coefficients much higher, up to 3×10^6 . However, they are consistent with other reported measurements where the titanium hydroxide precipitate is collected. In such experiments partition coefficients as high as 1.5×10^6 have been reported. (1)

Table 5

Activated Carbon in Fresh (Tap) Water Doped with $U(NO_3)_6$ and $Ti(OH)_4$

(Each test used 250 gallons of water and 3g of activated carbon)

Uranium Concentration (ppb)	Uranium on Activated (ug/g)	% Uranium Removed from Water	Grams of $Ti(OH)_4$ Added	Partition Coefficients	
				Based on:	
				Activated Carbon	$Ti(OH)_4$
2.0	78	12	0.18	44,000	780,000
	93	15	0.18	54,000	960,000
	275	43	0.36	240,000	2,250,000
	113	18	0.72	69,000	350,000
5.0	110	7	0.023	23,000	3,040,000
	195	12	0.046	44,000	2,940,000
	305	19	0.23	76,000	1,050,000
	532	34	0.46	160,000	1,200,000
10.0	223	7	0.046	24,000	1,580,000
	826	26	0.44	112,000	870,000
	328	10	0.72	37,000	190,000

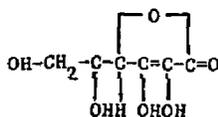
We then tried a number of potential chelating agents, obtained from a variety of sources, using the same experimental procedure. The tests included using some peat moss collected from the Sacramento River Delta in northern California. The peat moss was tested with sea water and showed an average

partition coefficient of 700, which was too low to be of interest. The remainder of the tests were carried out in fresh (tap) water and the results are presented in Table 6. Of the materials tested, only L-ascorbic acid showed similar effectiveness to titanium hydroxide.

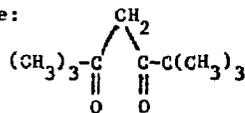
Table 6
Activated Carbon Sorption of Uranium from Fresh (Tap) Water With Dopant
(Each test used 250 gallons of water with dopant, and 3g activated carbon)

Dopant #	Uranium Concentration (ppb)	Uranium on Activated Carbon (ug/g)	% Uranium Removed from water	Grams Dopant Added to water	Partition Coefficients Based on:	
					Activated Carbon	Dopant
1	2.0	134	21	1.0	85,000	340,000
		207	33	5.0	153,000	246,000
	5.0	84	5	0.07	18,000	770,000
		123	8	0.7	27,000	140,000
	10.0	682	22	0.07	87,000	3,800,000
		113	4	0.7	12,000	60,000
166		5	0.7	18,000	90,000	
		221	7	0.7	24,000	125,000
2	5.0	139	9	0.048	30,000	1,900,000
		118	2.5	0.07	12,000	510,000
	10.0	144	4.5	0.73	15,000	77,000
		118	2.5	0.73	12,000	50,000
3	10.0	360	11	0.1	40,000	1,300,000
		150	5	0.1	9,500	300,000
		92	3	1.0	9,400	37,000
4	10.0	140	4.5	0.04	15,000	1,000,000
		125	4	0.4	13,000	100,000
5	5.0	103	6.5	0.05	22,000	1,300,000
	10.0	227	7.2	0.2	24,000	390,000
6	10.0	176	5.5	0.2	19,000	300,000
7	10.0	147	4.6	0.2	15,000	250,000

Dopant # 1 = 1-ascorbic acid:



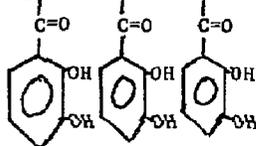
2 = 2,2,6,6-tetramethylheptane-3,5-dione:



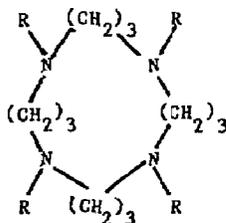
3 = Tri-n-butyl phosphate: $(\text{C}_4\text{H}_9\text{O})_3\text{PO}$

4 = Quinone

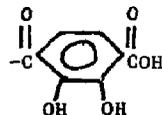
5 = $\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_2)_3\text{N}(\text{CH}_2)_4\text{NCH}_2\text{C}_6\text{H}_5$



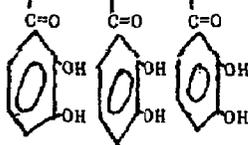
6 =



where R =



7 = $\text{CH}_3(\text{CH}_2)_7\text{N}(\text{CH}_2)_3\text{N}(\text{CH}_2)_4\text{N}(\text{CH}_2)_7\text{CH}_3$



At this point, we ran some new standards. The standards consisted of adding the activated carbon and uranium to the 250 gallon tank under essentially the same conditions, only without any dopants. The results are presented in Table 7. Much to our surprise, the partition coefficients were

far higher than those obtained earlier in either the seawater tests or with the much smaller distilled water tests. We are unable to explain this difference without further testing. There is a possibility that there may have been some small amount of dopant material stuck to the walls of the container that affected the results, or the impure tap water may have had some minerals that made a contribution. However, these larger partition coefficients tend to infer that the relative degree of improvement due to adding titanium hydroxide to the water may not be as large as indicated by the earlier tests.

Table 7

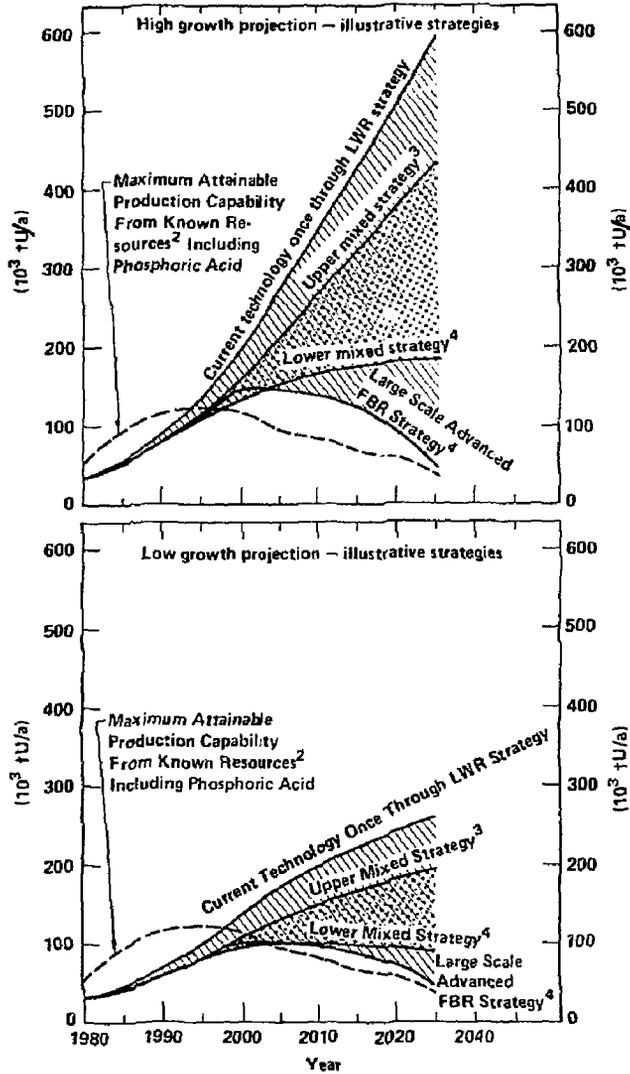
Activated Carbon with Fresh (Tap) Water Solution of $U(NO_3)_6$
 (Each test used 250 gallons of water and 3g of activated carbon)

Uranium Concentration (ppb)	Uranium on Activated Carbon (ug/g)	% Uranium Removed from Water	Partition Coefficient
2.0	32	5	17,000
4.0	60	5	16,000
5.0	66	4	14,000
	81	5	17,000
10.0	620	20	77,000
	270	9	30,000
	200	7	22,000
	440	14	52,000
	320	10	35,000

The contract was terminated at this point, and no further work was done. Unfortunately, this left a number of potentially interesting experiments unfunded. We would recommend, if there is further work funded in this area, that our results with the titanium hydroxide added to the water be verified and quantified for a number of operating conditions. We would also recommend most important of all, the procedure should then be carried out on natural seawater.

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1. Data were not supplied nor included for USSR, Europe nor China.
2. Reasonable assured and estimated additional resources.
3. With oxide-fuelled FBRs.
4. With carbide-fuelled FBRs.

Figure 1. Comparison of annual world uranium supply and demand to 2025 (modified INFCE diagram).

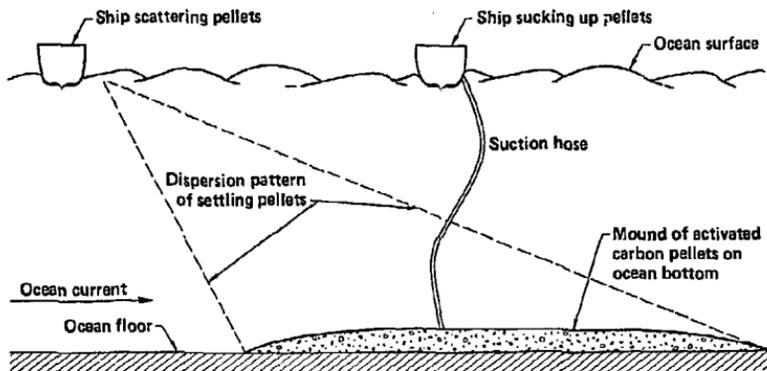


Figure 2. Uranium from Seawater Recovery Process using Settling Activated Carbon Adsorption Pellets.

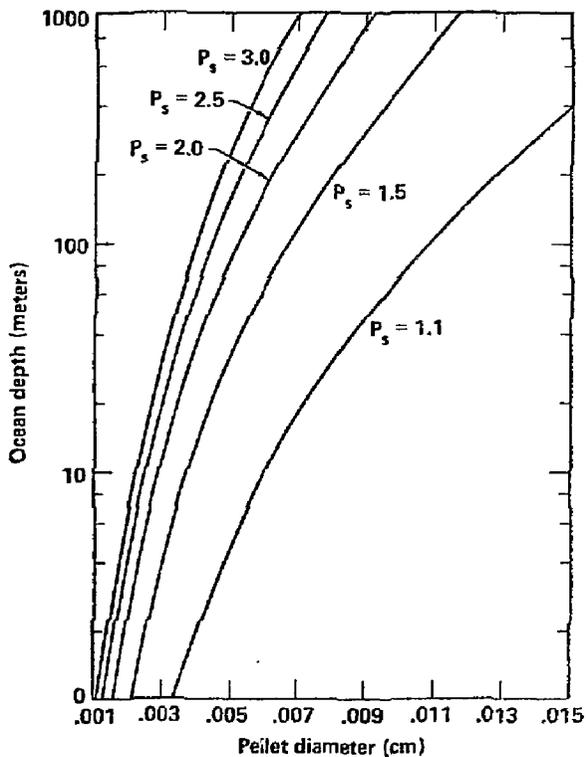


Figure 3. Required ocean settling depth for activated carbon pellets to reach a uranium concentration of 500 mg U/kg C as a function of pellet diameter and pellet density (P_s).

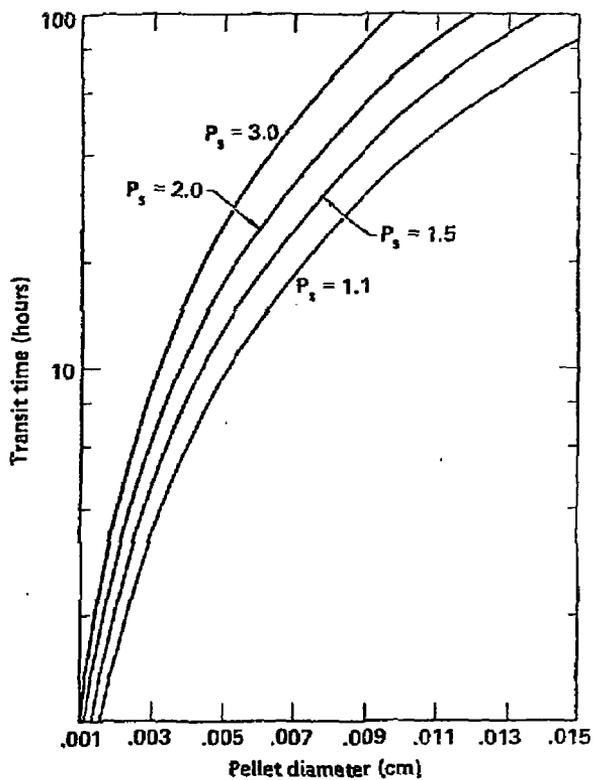


Figure 4. Required ocean settling time for activated carbon pellets to reach a uranium concentration of 500 mg U/kg C as a function of pellet diameter and pellet density (P_s)

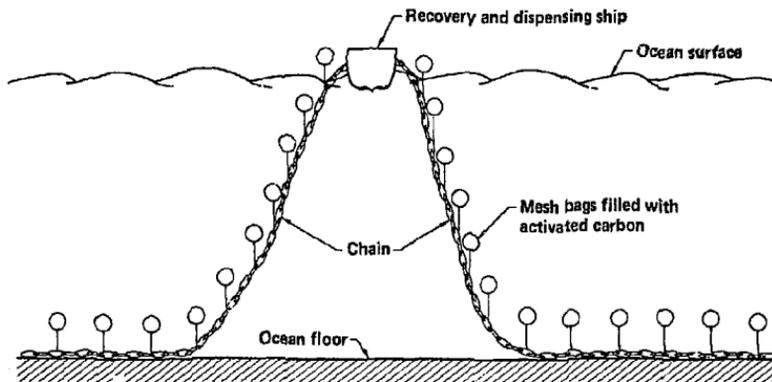


Figure 5. Uranium from Seawater Recovery Process using Activated Carbon Pellets Contained in Mesh Bags.

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Available from
National Technical Information Service
U.S. Department of Commerce
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