

simulate a radiation Universe. Hoyle, Fowler, Burbidge and Burbidge¹³ were led, for reasons independent of those of the present article, to consider temperatures exactly in the region $T_{10} \simeq 1$. These authors give the following differential equation between the time t and the density ρ , in such a superstar:

$$dt = \left(\frac{1}{24\pi G \rho} \right)^{1/2} \frac{d\rho}{\rho} \quad (14)$$

and also the following relation for an object of mass M :

$$\rho = 2.8 \times 10^8 \left(\frac{M_{\odot}}{M} \right)^{1/2} T_{10}^3 \text{ g cm}^{-3} \quad (15)$$

Eliminating ρ and $d\rho$ we have:

$$dt = \left(\frac{M}{2.44 \times 10^4 M_{\odot}} \right)^{1/4} \frac{dT_{10}}{T_{10}^{2.5}} \quad (16)$$

whereas the differential form of equation (6) is:

$$dt = -2.08 \frac{dT_{10}}{T_{10}^3} \quad (17)$$

The difference of sign arises because equation (16) was given for a contracting object. For re-expansion of an object the sign must be reversed, so that the time-scales are identical if $M \simeq 5 \times 10^5 M_{\odot}$. It may be significant that this is about the largest mass in which the temperature $T_{10} \simeq 1$ can be reached without the object being required to collapse inside the Schwarzschild critical radius. If collapse inside this radius followed by re-emergence be permitted, larger masses can be considered. The time-scale is then increased above equation (17) and this has the effect of giving a smaller He/H ratio than that calculated above. If an object is inside the Schwarzschild radius and neutrinos do not escape from it, the conditions are closely similar to the cosmological case. On the other hand, the calculation must be slightly changed for objects that do not enter the Schwarzschild radius, since neutrinos are certainly not contained within them. Thus if the same time-scale were used, that is, $M \simeq 10^5 - 10^6 M_{\odot}$, absence of neutrinos would reduce the right-hand side of equation

(12) by a factor of 2. A corresponding calculation leads to $n/(n+p) = 0.22$, also in reasonable agreement with observation, especially as all material need not have passed through massive objects. However, a more detailed discussion of massive objects will be required to decide whether the required amount of helium cannot only be produced but also ejected from them.

This brings us back to our opening remarks. There has always been difficulty in explaining the high helium content of cosmic material in terms of ordinary stellar processes. The mean luminosities of galaxies come out appreciably too high on such a hypothesis. The arguments presented here make it clear, we believe, that the helium was produced in a far more dramatic way. Either the Universe has had at least one high-temperature, high-density phase, or massive objects must play (or have played) a larger part in astrophysical evolution than has hitherto been supposed. Clearly the approximate calculations of this present article must be repeated more accurately, but we would stress two general points: (1) the weak interaction cross-sections turn out to be just of the right order of magnitude for interesting effects to occur in the time-scale available; (2) for a wide range of physical conditions (for example, nucleon density) roughly the observed amount of helium is produced.

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EXTRACTION OF URANIUM FROM SEA WATER

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THERE is now a world surplus of uranium; the production capacity of mines and ore treatment plants in the United States, Canada and South Africa far exceeds the present demand for all civil and military purposes so that the relatively modest uranium supplies to cover British nuclear power requirements seem to be assured for some years. When the work described here was started, more than ten years ago, this situation was far from evident. It is true that the existence of large reserves in these areas was suspected on geological grounds but there was little reason to expect that production capacity could overtake demand so rapidly. In Britain, we were about to embark on a nuclear power programme which it was thought might lead in course of time to dependence on uranium for much of our national electricity supply, yet no reserves of uranium had been discovered in these Islands which were in any way commensurate with requirements.

The possibility of recovery of uranium from natural waters, including sea water, by ion-exchange resins had been considered by the late Dr. F. H. Burstall and his group at the Chemical Research Laboratory (now the

National Chemical Laboratory), Teddington, shortly after the War, but it was decided that the effort should be directed towards exploitation of the then known ores overseas. Later some experiments were made at Harwell¹ on the recovery of uranium from sea water by newly developed techniques of continuous counter-current extraction. The solvent—dibutyl phosphate dissolved in butex (dibutoxy diethyl ether) or kerosene—was contacted with acidified sea water in a rotary annular column; extraction appeared to be quantitative and 60 μg of uranium was obtained from 20 l. It was evident, however, that although such a process would be technically feasible on a large scale the solvent losses and reagent costs would render it economically unattractive. Nevertheless, the comparative ease with which uranium could be quantitatively extracted from such an extremely weak solution containing high concentrations of other salts gave encouragement to the idea that in the long term some economically acceptable method might be found.

The total volume of the oceans has been estimated² to be 1.37×10^9 cubic kilometres and, assuming a uniform concentration throughout, the dissolved uranium should

Table 1a. MOLAR CONCENTRATIONS IN SEA WATER; URANIUM AND ASSOCIATED IONS

U	HCO ₃ ⁻	H ⁺	CO ₃ ²⁻
1.43 × 10 ⁻⁸	2.3 × 10 ⁻³	10 ^{-7.8} - 10 ^{-8.2}	2.2 × 10 ^{-4*}

Table 1b. MOLAR CONCENTRATIONS IN SEA WATER—OTHER MAJOR IONS

Na ⁺	Mg ⁺⁺	Cl ⁻	SO ₄ ²⁻
0.47	0.054	0.54	0.03

* Calculated from the dissociation constant for bicarbonate ion in sea water ($K_{\text{HCO}_3} = 10^{-9.02}$).

amount to 4.16×10^9 metric tons. Moreover, the uranium concentration in sea water is probably stationary; a large amount, estimated at 27,000 tonnes annually, contributed by rivers, appears to be balanced by an equal amount carried down with the bottom deposits³.

The uranium concentration (3.34 µg/l.) (ref. 4) is remarkably constant; only second-order variations occur between samples obtained from the Atlantic and Pacific oceans and from near the surface to depths of at least 400 m.

The molar concentrations of uranium and of closely associated species in sea water are given in Table 1a, and concentrations of other major constituents are given in Table 1b (ref. 2).

A very interesting feature is that the uranium occurs in true solution as the tricarbonate complex, $\text{UO}_2(\text{CO}_3)_3^{-4}$. This was early established at Harwell⁵ where it was also shown that less than about 0.1 per cent of the uranium is associated with suspended matter. Russian workers⁶ came to the same conclusion regarding the chemical form of the uranium independently. Thus the ocean is virtually a limitless reservoir of uranium in solution in a well-defined chemical environment. There are, however, two major obstacles to using this reservoir as an economic source of uranium. First it is in a strongly complexed form at extreme dilution in presence of relatively high concentrations of other ions; and secondly, to bring any extraction agent into contact with the very large volumes of sea water that would be involved is not an easy operation. To be successful, an extractant must function efficiently at the usual pH and ionic strength of sea water and must be virtually insoluble.

Possible Organic and Inorganic Absorbents

An obvious step following the successful solvent extraction experiments with dibutyl phosphate was to incorporate functional groups of similar type in solid insoluble organic resin matrices. Extraction could only be expected by reagents which form a complex with the uranyl ion sufficiently strong to compete with the uranyl tricarbonate complex in sea water for which the stability constant is about 2×10^{18} . Calculation showed that the stability constant of the competing uranyl complex would have to exceed 10^{12} . Although a number of ligands were known to form uranyl complexes with stability constants of this order, such as β-diketones and 8-hydroxyquinolines, the effective stability constant when the ligand had been incorporated in a resin matrix could not be predicted, so a fairly wide range of functional groups was chosen for investigation in the first instance. Resins were prepared⁷ containing mono- and di-basic phosphoric and phosphonic acids, 8-hydroxyquinoline, kojic acid, salicylic acid, amino-carboxylic acid and amino-phosphoric acid functional groups. These were tested first in a simulated sea water enriched about 1,000-fold in uranium and afterwards in fresh sea water in a small laboratory on the Mole at Portland Harbour. Samples of chelating resins available at the Chemical Research Laboratory, Teddington, were tested there by Daborn and Milward⁸ using the enriched artificial sea water, and the most promising of them, a condensation product of formaldehyde and resorcinol arsonic acid, was sent to Harwell for further investigation. Greater quantities of some of the more promising resins were specially prepared for us by the Permutit Co., Ltd. A number of commercially available resins was also tested, including the carboxylic acid resin 'Zeo-Karb 226' and an α-hydroxy phosphonic acid resin supplied by Permutit.

The Portland tests were with fresh sea water which was pumped by a stainless-steel pump through a coarse filter into a head tank whence it flowed through a glass-wool filter into the test system. The connecting tubing and vessels were made of polythene, polyvinyl chloride or glass. The resin was held between two sintered glass disks 9 in. apart in a column of internal diameter 1 in. and subjected to upward-flowing sea water. At first, all the preparations showed only a low uptake, the maximum being 10 µg of uranium/g dry resin. However, the form of the resin proved to be critically important and a standard pretreatment procedure was evolved. The resins, initially in the damp H⁺ form, were converted to the Na⁺ form by 1.0 M sodium carbonate solution and then washed with redistilled water until fully swollen. Where particular mesh sizes were required the fully swollen resin was wet-sieved through stainless-steel mesh. After sizing it was reconverted to the H⁺ form, with 0.5 M hydrochloric acid, washed with distilled water, dried for 48 h and bottled. Quantities, normally 2 g, were converted as required to the Na⁺ form with 1.0 M sodium carbonate solution before placing in the column for testing. Although there was considerably greater uptake with several of the resins, only one reached values high enough to be of practical interest, namely, the arsonic acid resin. The early preparations of this material both rapidly lost weight in flowing sea water and were soluble in the sodium carbonate eluant used to remove the uranium. Improvements in the method of preparation which were made by Jones and Packham⁹ at Teddington, and by Lane, Holdaway, Robinson and Willans at Harwell¹⁰, increased the uniformity of product and enhanced matrix stability and general properties. The uptake of uranium by some typical organic materials is shown in Table 2.

Table 2. UPTAKE OF URANIUM FROM SEA WATER BY ORGANIC ABSORBENTS

Resin	Functional group	Time of contact (days)	Uptake µg/g of dry H ⁺ form
'Deacidite FF'	- R ₂ NCl	84	0.2
'Zeo-Karb 226'	- COONa	36	1.5
Polystyrene methylene phosphonic acid	- CH ₂ PO(ONa) ₂	88	25
8-hydroxyquinoline	- N = N(C ₆ H ₄) ₂ N ₂ ONa	81	13
Resorcinol arsonic acid resin	- AsO(ONa) ₂	112	1,010

Although the solubility shown by the original arsonic acid resin in sea water was largely overcome there still remained a steady loss of capacity which was traced to a slow hydrolytic attack on the carbon-arsenic bond¹¹. This appeared to be an inherent weakness in any form of arsonic acid resin which seemed to exclude it as an absorbent for the economic extraction of uranium from sea water. Fortunately, alternative possibilities had arisen.

Although the concentration of uranium in the sea is far below the saturation level, deposition appears to be taking place at a rate equal to the rate of inflow from rivers. The mechanism is not properly understood but uptake by inorganic material seems to occur. In agreement with this, deposition of uranium from carbonate-containing waters in the Goodsprings District of Nevada has been attributed to absorption by hydrated ferric oxide and basic zinc carbonate. These considerations, coupled with our observation that ferruginous deposits in the filter on the inlet side of the sea-water plant at Portland contained some uranium, led us to investigate a number of inorganic materials as possible absorbents. They were precipitated on glass wool and packed into a glass column for testing. Sea water flowed upwards through the bed at the rate of 2.5 cm/min. Basic zinc carbonate, hydrated titanium hydroxide and certain lead compounds were the only materials which exhibited an effective uptake (Table 3).

Several other lead compounds showed comparable uptakes (lead naphthalene tetracarboxylate gave 1,074 µg/g in 35 days), but unfortunately all were unstable either in sea water or in the sodium carbonate eluant

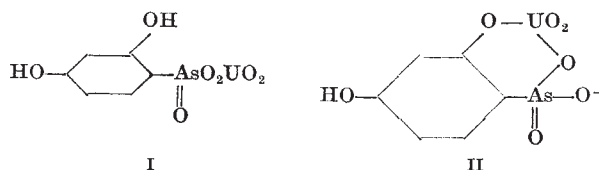
Table 3. UPTAKE OF URANIUM FROM SEA WATER BY INORGANIC ABSORBENTS

Compound	Time of exposure (days)	Uptake ($\mu\text{g/g}$ of metal base)
Basic zinc carbonate	23	512
Titanium hydroxide	21	268
Lead sulphide	21	338
Lead pyrophosphate	21	479

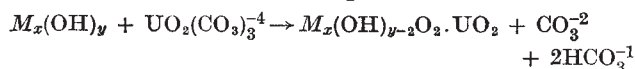
which led to a low uptake when re-used after elution. Moreover, the lead compounds and basic zinc carbonate dissolved too rapidly in the flowing sea water to be economically possible. For example, basic zinc carbonate loses $0.5 \mu\text{g}$ zinc/ml. to sea water flowing at 2.5 cm/min through the bed. With titanium hydroxide, however, the loss under the same conditions was undetectable.

After appropriate contact with sea water, the arsonic acid resin and the inorganic materials listed in Table 3 contain between 0.02 and 0.1 per cent of uranium in terms of dry weight; that is, within the same range as the uranium content of the ores now being worked in the main uranium-producing territories.

The stoichiometry of the reactions between some of these materials and sodium uranyl tricarbonate solutions was examined. Saturation of the arsonic acid resin occurred with an arsenic/uranium atomic ratio of unity. Conductivity determinations on the arsonic acid monomer indicated that the uranyl complex is uncharged, and this is borne out by the behaviour of the resin itself which exhibits no cation exchange capacity when saturated. The structure of the complex is therefore more probably I than II:



Analysis of the wet, basic zinc carbonate precipitate invariably gave a ratio $\text{Zn}/\text{CO}_3 = 3$, implying the formulation $2\text{Zn}(\text{OH})_2\text{ZnCO}_3$. This ratio is maintained at all uranium loadings. When absorption takes place from sodium uranyl tricarbonate solution, one mole equivalent of carbonate and two of bicarbonate are released into the solution for each mole equivalent of uranyl absorbed, so that carbonate is not taken up by the absorber. Hydrated titanium oxide behaves in the same way. The absorption mechanism can therefore be represented as follows:



Although this equation may be representative of the conditions when macro concentrations of sodium uranyl tricarbonate are used the absorption reaction in sea water may be different. Tracer experiments with uranium-233 in simulated sea water gave results which, for hydrated titanium oxide, were more indicative of the participation of a partially neutralized species $M_x(\text{OHO})_y$.

During the course of this work a report was published describing Russian experiments on the extraction of uranium from natural saline waters containing $60 \mu\text{g}$ uranium/l. (that is, about 20 times sea water concentration) by absorption or co-precipitation processes¹². Optimum results were obtained with calcium phosphate, aluminogel and ferri-gel; titanogel was also said to be satisfactory, uptakes being in the range $70\text{--}170 \mu\text{g}$ uranium/ml. of absorber. These results, which we have confirmed, indicate a different order of uptake compared with that from solutions with a uranium concentration as low as that in sea water. Those reagents which gave the highest uptakes from Russian lake-waters absorbed relatively insignificant amounts of uranium from sea water.

More recently experiments have been reported by Bayer¹³ on the uptake of copper and uranium from sea

water by various organic chelating agents containing, for example, the glyoxal *bis*-2-hydroxyanil grouping. The uptake of uranium from 100 l. of sea water from the Gulf of Naples was $50 \mu\text{g}$ for a bed 2 cm diameter and 30 cm deep, that is, $< 50 \mu\text{g/g}$ absorbent. This is of the same order of uptake as we obtained with some other chelating agents (Table 2).

Properties of Selected Absorbents

Titanium hydroxide is an amorphous material the properties of which depend on the method of preparation. Two forms have been distinguished and designated *ortho* and *meta*: the first, a fully hydrated form, is obtained at room temperatures and the second, a partially hydrated form, is obtained after long standing in air at room temperature or by heating. Although no appreciable difference could be detected in the total uptake of uranium from sea water, the two forms exhibit considerable differences in rate of uptake. Most of the experiments described here were made with titanium hydroxide which was precipitated by means of caustic soda, but it was found, later on, that precipitation with ammonia resulted in a more active product. In some experiments, the absorbent was supported on glass wool, muslin or pumice; in others it was used alone, in the form of granules. The muslin was impregnated by soaking it first in titanium tetrachloride solution (15 per cent titanium tetrachloride in 15 per cent hydrochloric acid) for 5 min, draining off for 30 min and then soaking in 8 N caustic soda solution (A.R.) for 5 min. Before being put into sea water, it was washed with distilled water. Normally the muslin was attached to a frame suspended beneath a vessel in Portland Harbour. The experiments with glass wool were made in glass columns 16 in. \times 2 in. with filtered sea water. Glass wool (60 g) was thoroughly wetted with the titanium tetrachloride solution (155 ml.), after which the 8 N caustic soda solution (250 ml.) was stirred into the mixture and stirring continued for 15 min. The treated glass wool plug was positioned and protected in the column by plugs of untreated glass wool at either end, allowed to drain and exposed to flowing sea water without further washing. Granular titanium hydroxide was made by mixing the same reagents in the ratio 155 ml. titanium chloride solution to 250 ml. 8 N sodium hydroxide while stirring vigorously to avoid an appreciable rise in temperature. The precipitate was washed by decantation with distilled water until the pH of the washings was less than 8. A slurry of the titanium hydroxide was poured on to trays so as to form a layer 0.5 in. thick and allowed to dry in air for 21 days. When the dried material was placed in distilled water it broke up into granules which could then be separated into different size ranges by sieving.

The uptake curves, shown in Fig. 1, are typical of the results obtained when the methods of preparation described here were used. The precipitate on muslin appeared to be rather finer and more disperse than that on glass wool and the absorption was faster but they both reached the same maximum uptake. Similarly, the smaller granules showed a faster initial rate of uptake than larger granules but, with each, absorption levelled off after a time and the larger granules gave a lower apparent saturation level. If the granules are assumed to be spherical, the ratio of the initial uptake rates proves to be roughly proportional to the ratio of the surface areas. On this model the outer layers of the particles would appear to be progressively saturated until, with the 0.3-mm diameter particles, for example, the thickness of the saturated zone reaches 0.03 mm in 20 days, whereafter the absorption rate falls off rapidly. The irregular shapes of the granules and their porous nature allow such a model to be regarded only as a crude representation; nevertheless it conforms with the idea that the larger the granule the greater is the volume which is inaccessible for uranium absorption.

The model also implies that granules of diameter less than 0.06 mm would be completely accessible.

It has been mentioned that the rate of uptake was higher when the titanium hydroxide had been precipitated with ammonia instead of caustic soda. Granules (14-24 mesh, diameter about 0.9 mm) produced by the ammonia route gave an uptake of 60 µg/g in one day when exposed to flowing sea water. This is more than ten times the initial rate obtained with the same size of granules prepared by the caustic soda method.

Titanium hydroxide is without detectable solubility in flowing sea water, but 0.1 µg/ml. was found in sea water which had been shaken with the precipitate for 72 h. No significant changes in specific uptake occurred after prolonged contact with sea water and after elution with M sodium carbonate solution. In the experimental work, the uranium content was frequently determined after complete dissolution of the sample, but for any large-scale extraction process selective leaching of the uranium would be necessary. Partition coefficients have been determined for a number of alkaline leaching solutions, and, in order to obtain results applicable to conditions of high dilution, trace concentrations of uranium-233 were used (Table 4).

Table 4. PARTITION COEFFICIENTS FOR ELUTION

Reagent	Partition coefficients (U per g Zn or Ti/U per ml.)	
	Basic zinc carbonate	Titanium hydroxide
0.25 M Na ₂ CO ₃	168.0	1,311
0.5 M Na ₂ CO ₃	96.4	602
1.0 M Na ₂ CO ₃	49.8	206
0.25 M ammonium carbonate		45
0.5 M ammonium carbonate		1

Elution of uranium from basic zinc carbonate supported on glass wool is rapid with 1.0 M sodium carbonate, four or five bed volumes giving complete separation. But with titanium hydroxide, elution is slow; for example, less than 60 per cent of the uranium was removed by eight bed volumes of 1 M sodium carbonate eluant. A mixture of sodium bicarbonate (2 vol.) and sodium carbonate (1 vol.) gave 75 per cent elution in eight bed volumes and 1 M ammonium carbonate gave 65 per cent elution in two bed volumes and 93 per cent in eight. Dilute nitric acid is also a possible eluant for titanium hydroxide but ammonium carbonate appears to give the best results. The results in Table 4, obtained by batch equilibration at trace uranium concentration with the uranium initially in the aqueous phase, probably represent true equilibrium conditions since that for 1 M sodium carbonate was confirmed by approaching from the opposite side with titanium hydroxide containing natural uranium absorbed from sea water.

The solubility of titanium hydroxide in these eluants was determined: (a) by shaking with the precipitated

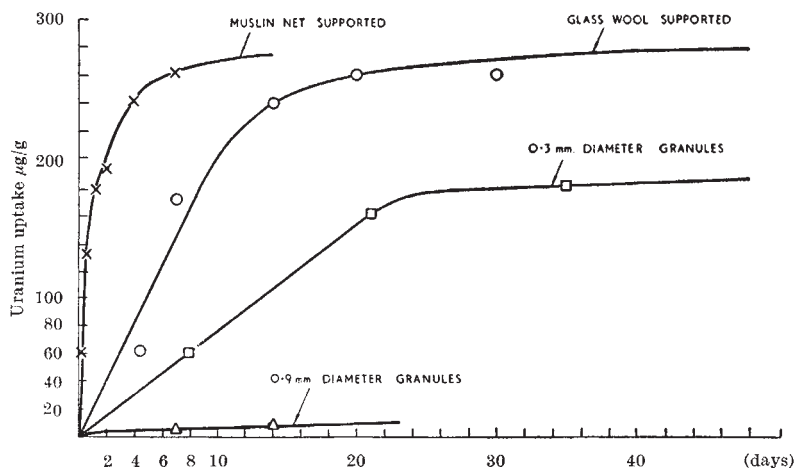


Fig. 1. Uptake of uranium from sea water by titanium hydroxide; typical results

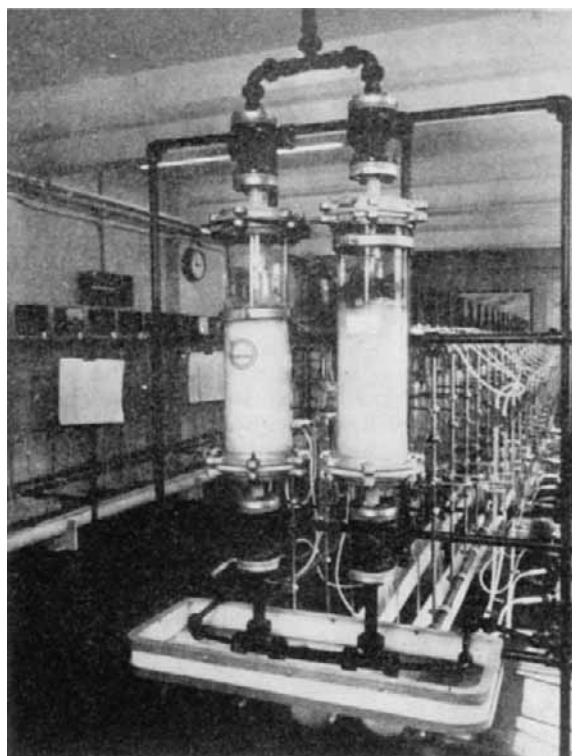


Fig. 2. Sea-water test equipment at Binclives Laboratory, Portland Harbour

floc for three days; (b) by passing the eluant through a bed of granular material at a flow rate of 1 cm/min.

Table 5. SOLUBILITY OF TITANIUM HYDROXIDE IN ELUANTS

Eluant	Solubility µg Ti/ml.
(a) Ti(OH) ₃ , precipitate shaken for 3 days	
1.0 M Na ₂ CO ₃	0.48
0.5 M ammonium carbonate	1.4
1.0 M ammonium carbonate	14.1
(b) Ti(OH) ₃ , granules in flowing eluant	
1.0 M Na ₂ CO ₃	0.1
1.0 M ammonium carbonate	11.4

The loss of absorbent in the eluant, although appreciable, would therefore not have a serious effect on the life of the bed.

Engineering Aspects

The engineering problems associated with the large-scale extraction of uranium from sea water are formidable but do not appear to be insoluble. Clearly it is desirable for the extraction plant to be sited so that it can be supplied with fresh uranium-bearing water by natural transport processes. In many coastal areas there is a residual drift superimposed on the purely oscillatory tidal motion which could maintain an adequate supply of uranium provided the rate of extraction was not too great. Certain ocean currents transport very large amounts of uranium. The volume of water transported by the Norwegian Current, which flows past the Orkneys and Shetlands, and along the coast of Norway towards the Arctic Sea, is about 3 × 10⁶ m³/sec, which is equivalent to about 250,000 tons of uranium per annum; much greater quantities, carrying in excess of a million tons of uranium per annum, pass through the Florida Straits and the Japan Strait in comparatively narrow channels.

Where there is a plentiful supply of fresh uranium-bearing water it would be possible to consider the advantages of means whereby only a small fraction of the uranium is extracted. Titanium impregnated muslin suspended beneath a vessel in Portland Harbour functioned in this way, giving very rapid uptake. Large-scale application of this technique, though possible in principle, would require a great deal of development to make it workable even before considering cost.

Other methods, in which the flow of sea water has to be channelled or controlled by engineering works, tend to require a high percentage extraction in an absorber system of specific design. Mass transport calculations have been made for different possible geometric arrangements of absorber, making the assumption that uptake was determined only by transport in the aqueous phase and that the diffusion coefficient of uranium species in sea water is about 3×10^{-6} cm²/sec. We obtained a value of 1.8×10^{-6} cm²/sec in the laboratory using the isotope uranium-233. The calculations showed that absorbers consisting of packs of parallel tubes lined with the absorbent placed across a channel would give a comparatively low yield unless the tubes were excessively long; for optimum absorption a considerable head of water would be required. Experiments were carried out in the south entrance to Portland Harbour using a cubic metre steel-framed cell containing asbestos cloth loaded with basic zinc carbonate folded over glass rods so as to give 1/8 in. spacing between layers. Uptake was slow and the percentage extraction was probably small, although this could not be accurately determined; saturation was reached after four weeks, yielding 0.25 g of uranium*.

The requirement for a greater head of water than could be obtained in a simple tidal channel led to an investigation of a fixed bed of absorbent particles operating against a head of sea water. Such a system, based on utilizing tidal energy in a manner similar to tidal power schemes, could be more easily visualized in engineering terms than any of the others considered. Two lagoons would be created, the sea water flowing into one on the rising tide, forming an upper lagoon, and out of the other, the lower, on the falling tide. The plant itself would consist of intermediate lagoons containing the packed beds, situated between the upper and the lower tidal lagoons. Sea water would flow into the plant lagoons from the upper lagoon, down through the packed beds and out along conduits into the lower lagoon. A difference in head of water would exist between the two lagoons which would depend on the level of the tide and the pressure drop through the bed. The beds would thus be operating continuously at all states of the tide, at a rate responding to the variations of head. The plant lagoons would be equipped with gates so that the flow of water could be cut off, enabling the beds to be eluted. The beds themselves would be partitioned so that sections could be eluted in a counter-current manner with a number of bed volumes of eluant, provided from the treatment plant located on the adjacent coast.

In order to obtain some idea of the problems and costs involved, a design investigation was made for a hypothetical plant operating in the Menai Straits. For this it was assumed that there is sufficient north-easterly drift of the water of the Irish Sea past Anglesey to maintain adequate supplies of fresh uranium-bearing water; there appears to be good reason for believing this but experiments were not carried out to establish it. The scheme would involve the construction of dams and sluice gates across the

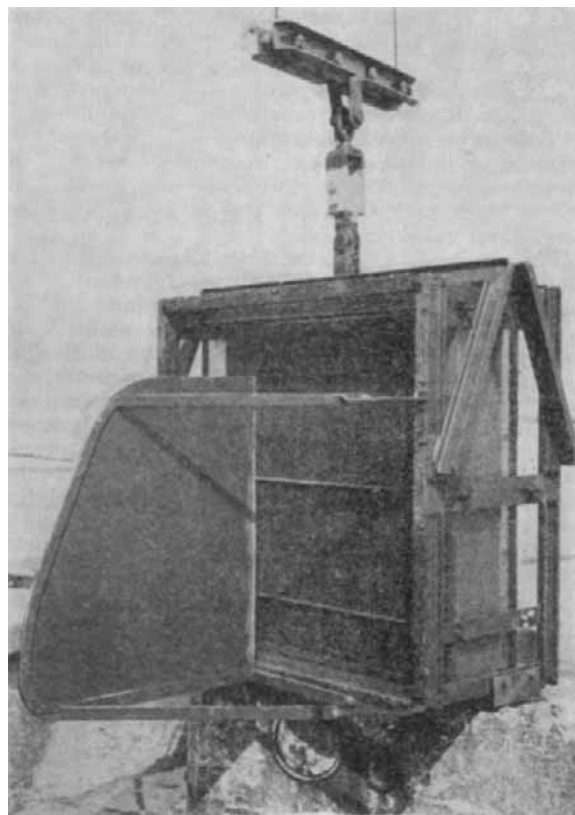


Fig. 3. Cell, 1 sq. metre cross-section, used in south entrance to Portland Harbour, showing frame bearing asbestos cloth impregnated with basic zinc carbonate

northern entrance between Anglesey and Great Orme's Head, and the division of the enclosed area of Beaumaris Bay into an upper lagoon and a lower lagoon by means of a dam and gates associated with absorber beds running in an approximately southerly direction from the neighbourhood of Puffin Island. A plant providing for the associated chemical operations would be located on shore at the southern end of the beds. Site investigations were not carried out and many assumptions had to be made regarding hydrological and geological factors and further uncertainty was introduced into the cost estimates by the novel engineering problems likely to be encountered. Fortunately we were able to make a comparison with results from the very thoroughly investigated Passamaquoddy Tidal Power Project through the courtesy of John W. Leslie, chief of the Engineering Division, Army Engineer Division, New England, U.S. Army Corps of Engineers, and this has enabled us to attach considerably greater confidence to our estimates of cost, particularly of the sea dams and gates. It would appear that the Menai site could produce almost 1,000 tonnes of uranium (1,300 short tons of U₃O₈) per annum, assuming adequate absorber performance, at a cost of £10,000-£20,000 per tonne (11-22 dollars per lb. U₃O₈). This is based on a twenty-year amortization; a lower unit cost would be achieved if the amortization period were extended from twenty to forty years. For comparison, the cost of extraction of uranium from shales has been estimated as 40-50 dollars per lb. U₃O₈ (ref. 14) and from granite as 100 dollars¹⁵.

Performance of Titanium Hydroxide Absorber compared with Plant Requirements

The cost and performance of the absorber are, of course, key features. In making the estimate it was assumed that the active absorbent would be supported on low cost inert material in the form of small particles or granules.

* Mr. N. R. Daly, Atomic Weapons Research Establishment, Aldermaston, has kindly determined the isotopic ratios for this oceanic uranium, namely:

Sample	235/238	236/235	233/235	234/235
A	0.007255 ± 0.000012	0.00005	0.00005	0.0077
B	0.007250 ± 0.000008	0.00007	0.00006	0.0080
Normal for uranium	0.007258			0.0078

Table 6. PERFORMANCE OF BEDS OF SUPPORTED TITANIUM HYDROXIDE IN FLOWING SEA WATER

Support	Bed diam. (cm)	Bed height (cm)	Ti content (g)	Flow rate (cm/sec)	Uptake (mgU)	Time (h)	% Extraction
Muslin	7.6	33	13	0.3	1.215	24	33
Glass wool	5.1	61	12	0.04	0.306	33	93
Glass wool	5.1	61	12	0.04	1.3	166	79
Glass wool	5.1	20	5	0.2	0.821	26.6	62
Glass wool	5.1	20	5	0.75	0.926	7.25	70

A satisfactory bed filling in such a form has not yet been produced but data for beds containing titanium hydroxide supported on muslin and on glass wool are given in Table 6.

Although the glass-wool-supported beds give an adequate performance at flow rates within the range expected in the plant (0.55–0.79 cm/sec) they would not be suitable for large-scale operations both for physical and for economic reasons. It has been shown, however, that titanium hydroxide granules appear to behave as composite particles containing an inaccessible and therefore inert core surrounded by a layer of active absorbent. Beds of these granules should perform similarly to the beds of composite particles specified for the plant. Adequate flow rates were obtained for pressure drops likely to be obtained in the plant using comparatively small granules (mean diam. 0.1 cm), but a larger size would almost certainly be required in practice in order to avoid blocking of the bed.

The results in Table 7 show that uptake rates of the required order can be obtained with titanium hydroxide granules (diam. ~ 0.1 cm) and that a considerable latitude exists for optimizing the absorptive activity of the bed. If these unsupported titanium hydroxide granules were used in the plant instead of the cheaper supported material, the increase in cost would be about £5,000 per tonne (5.50 dollars per lb. U_3O_8). Although preliminary experiments with pumice particles about 1/8 in. in diameter were not very promising, it should be possible to find some other low cost support, such as hydrated silica granules, which is acceptable.

It has not been possible to extend the range of these experiments on account of the closure of the sea water laboratory at Portland, and the present results do no more than indicate that a reasonably favourable basis exists for further development. This would require a substantial effort in bed-material development and manufacture, elution technology and so on. In the Portland experiments blockage and contamination of the absorber beds were avoided by filtration of the sea water through glass wool; the engineering implications of this have not been taken into account and other, unforeseen, difficulties might arise. If we assume that operational difficulties can be overcome there appears to be some hope that the ocean can provide a ready supply of medium cost, if not low cost, uranium.

This article summarizes work which will ultimately be published in full. The contributions of some of our

Table 7. COMPARISON OF EXPERIMENTAL RESULTS USING $Ti(OH)_3$ GRANULES WITH PLANT REQUIREMENTS

Exp.	Size range of granules, 14–24 mesh (mean diam. ~ 0.1 cm)					
	Bed depth (in.)	Pressure drop (ft.)	Flow rate (ft. ³ /ft. ² /h)	Ti content (kg)	Uptake mgU in 24 h	% Extraction
Experimental results for columns 1 in. in diameter						
A	25	16	180	0.105	0.071	3
B	1.9	0.25	70	0.008	0.026	3
C	0.5	0.067	70	0.002	0.12	14
Extrapolated to plant, per sq. ft.						
A	15.6	4.0	70	13	8.3	7.7
B	15.6	2.0	70	13	38	24
C	15.6	2.0	70	13	150	~ 100
Required in the plant						
	2.0	70–100	2.1	125	80	

Notes: (1) The experimental uptake for A represents 1/7 of the uptake determined after 7 days.

(2) Absorbents A and B were made by sodium hydroxide precipitation, but different batches; C was by ammonia precipitation.

(3) Results for B and C are typical of several experiments.

(4) The extrapolations are on a simple linear basis; in B, it is assumed that transport in the aqueous phase is not rate determining. This seems to be approximately correct for the range of conditions specified in Table 7 although not for Table 6.

(5) The figures given for plant requirements are typical; satisfactory designs for other performances are not excluded. During actual operation there would be considerable variation depending on the state of the tide.

(6) The quantity of titanium given represents that actually used in the experiments with extrapolations according to note 4. The quantity given for the plant is the minimum needed for a four-day cycle of exposure followed by elution.

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A RECONSTRUCTION OF THE CONTINENTS FOR THE UPPER PALÆOZOIC FROM PALÆOMAGNETIC DATA

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AT a recent meeting on continental drift, sponsored by the Royal Society, I reported¹ some new palæomagnetic results from South American rocks and compared these with data from other Gondwanic continents.

It is my purpose here to describe a later stage of this work in which palæomagnetic data from the Gondwanic continents of South America, Africa and Australia are

compared with those from the Laurasian continents of North America and Europe.

Since the preliminary results of my South American palæomagnetic work were published²⁻⁴, I have carried out thermal and alternating-field demagnetizing experiments in order to determine more precisely the directions of the fossil magnetization by selectively destroying