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URANIUM RECOVERY FROM SEAWATER BY ADSORPTION

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ABSTRACT

Results are presented of a 10 weeks field experiment producing uranium from seawater by the so-called "adsorber-loop-concept". For the adsorption process polyamidoxin (PAO) granulate has been used with grain sizes between 0.3 - 1.2 mm diameter. The performance of the adsorber and the efficiency of the adsorption process - especially with regard to high volume flows of seawater - are presented.

INTRODUCTION

According to the estimates of the International Atomic Energy Agency (IAEA) the reasonably assured resources (RAR) for terrestrial uranium within the cost limit of 130 US $/kg U amount to 2×10^6 t. The estimated additional resources - category I (EAR-I) total about 1.2×10^6 t U. To these amounts the estimated additional resources - category II (EAR-II; "believed to exist") and the speculative resources (SR) may add several million tons (1). In comparison the world oceans with a total water volume of about 1400×10^6 km^3 and an average uranium concentration of 3.3×10^{-9} contain 4.6×10^9 t uranium, which exceeds the terrestrial resources by a factor of 10^3.

If 1 % of this amount could be made available for the use in nuclear power plants the presently known resources are multiplied by a factor of more than 10. Therefore considerations about the extraction of uranium from seawater have been performed since the middle fifties and with increased intensity since 1980 (2,3)

Work has been done in this field in Great Britain, in the United States, in Japan and in the Federal Republic of Germany. The present paper reports about the German activities and the results of field experiments which were performed to prove that the uranium extraction from seawater is technically feasible.

FUNDAMENTALS OF PROCESS ENGINEERING

According to the very low concentration level of 3.3 ppb uranium is considered as a trace constituent of seawater. Its recovery from the ocean in a technical scale therefore is typically and adversely characterized by enormous volumes of water that have to be processed in production plants. Assuming an extraction effiency of 0.5, about 0.6×10^6 t of seawater have to be put through a suitable recovery unit for 1 kg uranium.

Of the several principal processes which could be considered for the production of uranium from seawater such as flotation, liquid extraction, coprecipitation or adsorption, the adsorption process is the only one which does not require the use of additional chemicals and is therefore not hazardous for the marine environment. In the adsorption process seawater has to be brought into contact with an appropriate adsorber material that acts on the dissolved uranium with a certain selectivity relative to the other elements which are present in seawater too.

It has been shown in extensive tests by different working groups in the United Kingdom, Germany, Japan and elsewhere that hydrous titanium oxide (HTO) and organic ion exchange resin based on polyamidoxim (PAO) are suitable adsorber materials which can be used as granulates with grain sizes around 1 mm and smaller. The essential question is how to perform the necessary contact between the adsorber granulate and seawater.

The standard way in chemical process engineering is the use of either "fixed" or "fluidized" adsorber beds through which the seawater is pumped. Fixed beds as in ion exchange columns require rather high energy for the water flow especially at higher flow velocities because of their high hydraulic resistance. In fluidized beds the energy requirements are considerably smaller but the upstream water velocity is limited by the sinking velocity of the adsorber grains in order to avoid a flushing of the bed layer. Both concepts have been treated in several publications and presentations with regard to the design of a technical production plant for seawater uranium (4-12).

Because of the high water volumes to be processed on one hand and the low water velocities through the adsorber bed configuration on the other rather large bed areas are consequently required which in turn increases the costs of investment for the plant.

For a more quantitative discussion of typical specifications and main dimensions of a technical production plant for seawater uranium a few equation will be discussed in order to identify adsorber dependent properties that influence and determine the plant lay out.

It is obvious that the production rate P of a plant depends on the mass of seawater processed in the plant and the adsorption efficiency, defined as ratio of adsorbed uranium to total uranium transported through the adsorption unit.

$$P = V \cdot \rho \cdot c \cdot \eta \cdot 24 \qquad (1)$$

with

P : production rate of the plant or production per unit time (t/d)
V : volume flow of seawater (m^3/h)
ρ : density of seawater (1.028 t/m^3)
c : relative mass concentration of uranium in seawater (3.3×10^{-9})
η : adsorption efficiency; ratio of adsorbed uranium to total uranium transported through the adsorption unit

For a given production rate of uranium the necessary water flow can be calculated from the rearranged equation (1)

$$V = \frac{P}{\rho \cdot c \cdot \eta \cdot 24} \qquad (1a)$$

With the flow velocity w of the seawater in the cross section F of the adsorber bed the volume flow can be calculated according to

$$V = F \cdot w \cdot 3600 \qquad (2)$$

with

F = area of the adsorber bed (m^3)
w = superficial velocity of seawater in the adsorber bed (m/s); for the calculation of w the cross section F is assumed to be empty and not diminished by granulate particles.

Rearranged for F equation (2) reads

$$F = \frac{V}{w \cdot 3600} \qquad (2a)$$

With these equations the required seawater flow for a production rate of 2.74×10^{-3} t U/d (which corresponds to an anual production of 1 t uranium at 100 % plant availability) can be calculated as function of the adsorption efficiency according to (1a), and the resulting bed area in turn can be determined in

Table 1: Seawater flow V as function of the adsorption efficiency, bed area F as function of seawater flow V and seawater velocity w (for a production rat P = 2.74 x 10^{-3} tU/d)

η	0.3	0.5	0.6	0.7	0.8	1.0
V (m^3/h)	112300	67300	56200	48200	42100	33500
			F (m^2)			
w (m/s)						
0.01	3120	1870	1560	1330	1170	930
0.05	624	374	312	266	234	186
0.10	312	187	156	133	117	93
0.20	156	94	78	67	59	47
0.30	104	62	52	44	39	31
0.40	78	47	39	33	29	23
0.50	62	37	31	27	23	19

dependence of this volume flow and the seawater velocity in the bed according to (2a). Some results of these calculations are presented in Table 1. The combination of an adsorption efficiency of 0.3 and a seawater velocity of 0.01 m/s results in a bed area of more than 3000 m^2 whereas corrsponding figures of 0.7 and 0.40 m/s require only about 30 m^2 of bed area, both for an anual production of 1 tU.

The advantages of rather high seawater velocities in the adsorption unit are obvious with regard to plant dimensions and lay out. Because of their drastic limitations with respect to flow velocity the classical bed configurations of either fixed or fluidized adsorber beds cannot be regarded as successful solutions for the contact process. Therefore a new concept has been tested for the contact between adsorber and seawater which will be presented in somewhat more detail in the following section.

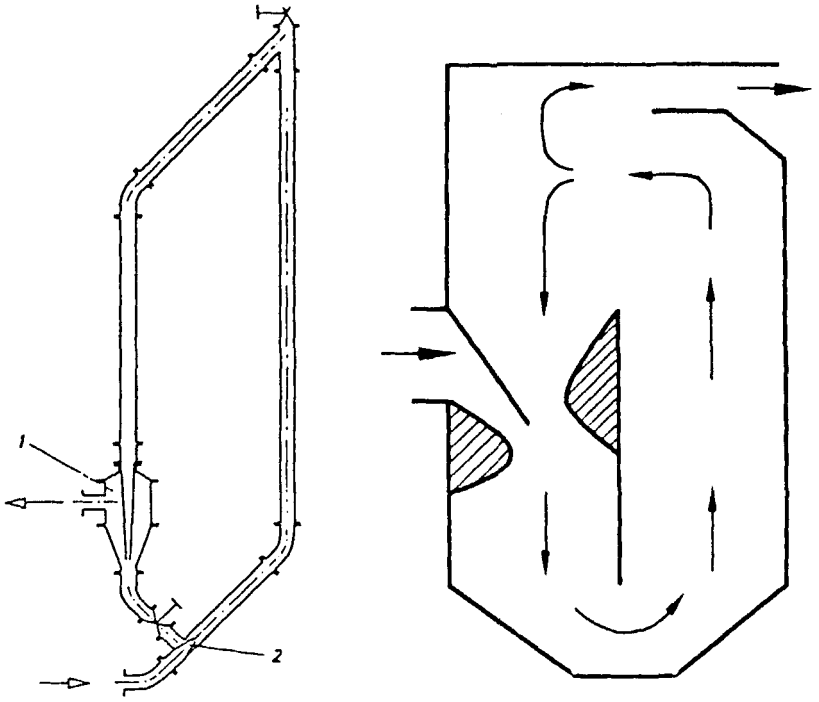

Fig. 1: a) Experimental loop b) Technical loop

ADSORBER LOOP CONCEPT

The adsorber loop concept has been developed to use standard, commercially available PAO adsorber granulate with a grain size 0.3 - 1.2 mm diameter and a density of 1.1 t/m^3. The sinking velocity of this granulate is in the order of a few centimeters per second and therefore the material cannot be used in a standard fluidized bed at higher upstream velocities. The new concept is based on a loop like design of the adsorption unit (13) and shall be explained with help of figure 1a.

At the start of the process the adsorber granulate is stored in the separation volume 1. The seawater flow enters the loop system through a diffusor 2, which acts partly as a suction-pump. At the outlet of the diffusor the seawater is mixed with the adsorber granulate coming from above. After having arrived at the top of the loop the flow is diverted downward back to the separation volume, where the granulate suspension is separated, with

the depleted seawater leaving at the top and the adsorber granulate collecting in the sedimentation cone from where it is, by gravity and suction, added to and mixed with the entering seawater again.

The principal flow scheme of the experimental loop in figure 1a has been slightly changed and adapted to plant applications in figure 1b. Here in the technical loop the seawater flow again enters the loop system through a diffusor like channel, is mixed with granulate from above and diverted downward.The direction of the seawater/granulate mixture is changed from downward to upward flow at the cone shaped bottom of the loop. After having arrived at the top the flow is slowed down and diverted horizontally. The granulate suspension is separated in this part of the loop, again with the depleted seawater leaving at the top and the adsorber granulate collecting in the sedimentation cone.

As can be expected from Figure 1 seawater velocities are required in the loop that are considerably higher than the sinking velocity of the suspended PAO-granulate in order to avoid deposition of the material at the bottom. It has been determined experimentally that velocities in the order of 0.10 m/s are well suited to keep the suspension flow in circulation. An upper limit for the water flow can be derived from the hydrostatic head which is required for higher flow rates and from the need for rather slow motion at the top in order to accomplish an effective separation of seawater and granulate. It has been shown in several experiments that an hydrostatic height of less than 1 m is sufficient to provide flow velocities of 0.40 m/s within the loop.

With regard to the adsorption behaviour such a loop unit can be compared with a fluidized bed. Though the adsorber granulate is carried along with the seawater flow in the loop, because of their higher density the particles do move relatively to the surrounding water: they are dragging behind during upward flow and are moving ahead on the way down. This relative velocity of about 1.5 cm/s is comparable to the relative motion in a fluidized granulate layer where the particles are stationary and the water is passing by.

According to this process similarity adsorption in loop units should give similar results as in fluidized beds, if the loops are handled properly. This means that there should neither too much depleted seawater together with the granulate be recycled and remixed with the entering seawater in order to avoid a reduction of the uranium concentration nor the granulate be stored too long in the sedimentation cone and thus kept from being loaded.

The two critical parameters for the adsorber loop concept are the volume mixture ratio (granulate volume to loop volume) and the contact time. Both can be adjusted easily within a wide

range, the former by adding or subtracting granulate material, the latter by varying the loop height. So for a contact time of 8 seconds a loop height of 3.0 to 4.0 m is required with a seawater velocity of 0.40 m/s.

ANALYTICAL PROCEDURES

Before in the following the conducted field trials and their results are described some information shall be presented about the analytical methods and procedures which were used during the experiments and on which the collected data are based.

To determine the amount of adsorbed uranium throughout the experiment adsorber granulate samples were taken two times a day. The sampling had to be carried out very carefully in order to obtain a representative grain size distribution. The uranium content of the samples was analyzed in a small field laboratory using the spectrophotometric method of determination of hexavalent uranium with arsenazo III. This method had been adopted to the special requirements and shall be described briefly.

After drying at 110 °C the adsorber material (about 0.5 g containing not more than 100µ g of U) is weighed into a small porcelaine crucible and then incinerated at about 1000 °C. The unburned residue containing the uranium is then dissolved in 2 ml concentrated nitric acid. With the aid of 20 ml of salting-out solution (aqueous solution of 80 % ammonia nitrate and 1% EDTA) the dissolved residue is carried over into a separation funnel. After adjusting the solution to pH 1 with concentrated ammonia 20 ml extraction solution (20 % tributyl phosphate in toluene) are added and the solution is then shaken for ten minutes. After phase separation the aqueous phase is discarded and the organic extract is washed by shaking with two portions (10 ml each) of wash solution (65 % ammonia nitrate, 0.5 % EDTA, adjusted to pH2) for a few seconds. Finally 25 ml buffered Arsenazo III solution (0.06 % Arsenazo III, 0.9 % sodium hydroxide and 3 % monochloro acetic acid) are added and the uranium is extracted from the organic phase by shaking for three minutes. After 45 minutes the extinction is measured at 655 nm against a reagent blank.

FIELD TRIALS AND RESULTS

In order to test the performance of the newly developed loop concept and to establish the suitable process parameters a field experiment was designed for a working time of about two months with a nominal plant capacity of 1 kg U/year. The experimental set-up consisted of 4 loops with the approximate dimensions 0.4 m x 0.5 m in cross section and a height of 4.0 m. Each loop had a process volume of 800 l and could be supplied with seawater by its own pump.

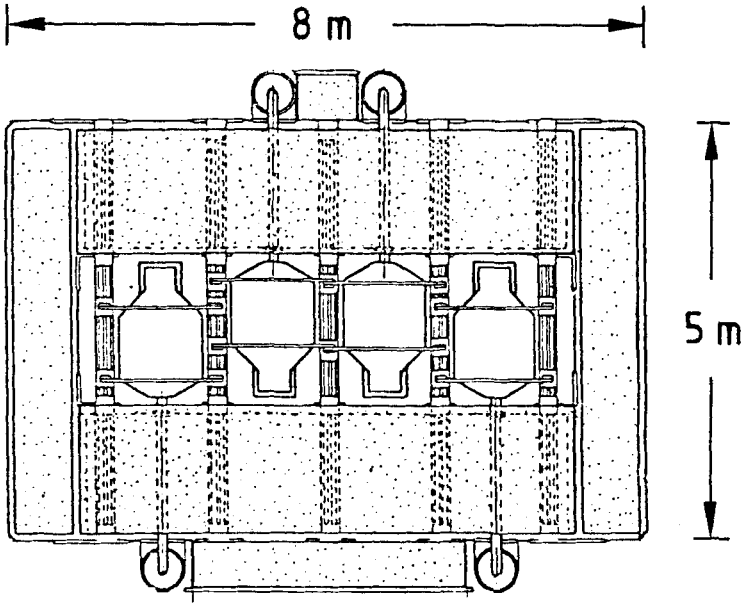

Figure 2: Top view of the loop float

All 4 loops were suspended from a floating platform with dimensions 8 m x 5 m (Figure 2) and were operated in parallel. As can be seen from Figure 3 the 4 loops are immersed in the surrounding seawater and suspended with their head parts from the float. Therefore there is nearly no hydrostatic head to be supplied by the pumps besides the frictional losses inside the loops. The seawater flow through each loop was in the order of 15 - 20 m^3/h, and this flow was contacted and processed with about 240 l of adsorber granulate (PAO) in each loop.

The field trials were performed in clear ocean water with very low suspended matter and at temperatures between 23 and 30 °C. Elevated temperatures are advantageous for the adsorption rate as has been shown in separate studies.

The significant experimental data for these runs are summarized in Table 2.

The results of these experiments are shown in Figures 4 and 5. In Figure 4 the increase of the uranium concentration on the

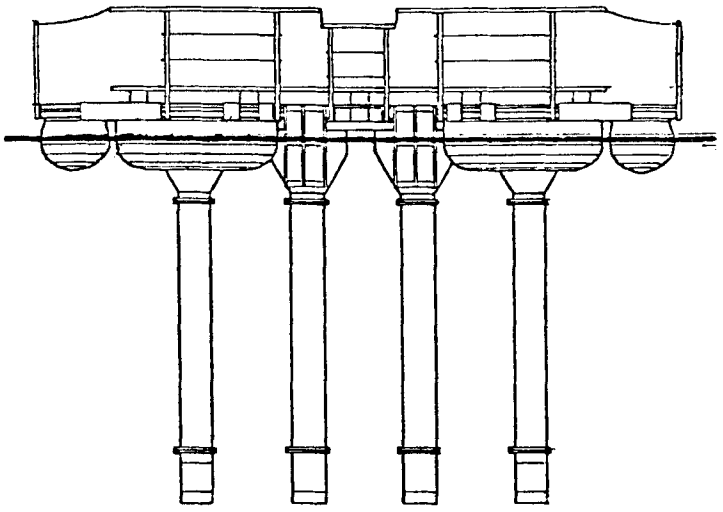

Figure 3: Side view of the float with 4 adsorber loops

adsorber granulate is shown in dependence of the elapsed time of the experiment. The result of all 4 loops have been plotted together which in part is responsible for a certain scattering of the data. As can be seen from the plot after about 46 days of operation (1100 h) a uranium concentration of about 190 ppm has been analysed on the adsorber. With an adsorber mass in process of 190 kg per loop this equals an uranium amount of 36.1 g per loop or a total of 144.4 g (4 x 36.1 g) uranium.

In Figure 5 the increase of the uranium concentration on the adsorber granulate has been shown as function of the processed seawater, again for all 4 loops together. The corresponding data are 190 ppm uranium and 20 000 m^3 seawater according to an average seawater flow of 18 m^3/h through each loop. On the basis of 3.3 ppb for the uranium concentration in seawater 20 000 t of seawater represent 66 g uranium, thus resulting in an adsorption efficiency of 0,55 (36.1 g U adsorbed relative to 66 g U transported through 1 loop). After a total process time of 70 days and an uranium concentration on the adsorber of about 250 ppm the experiment was stopped. The loaded adsorber material was eluted by Uranerz Bonn GmbH, a company with experience in uranium prospection and mining. A total of 120 g U as yellow cake has been prepared as final result of this field trial. The difference between the theoretical yield and this value is due to the elution efficiency (0.8), to a residue concentration on the eluted PAO-

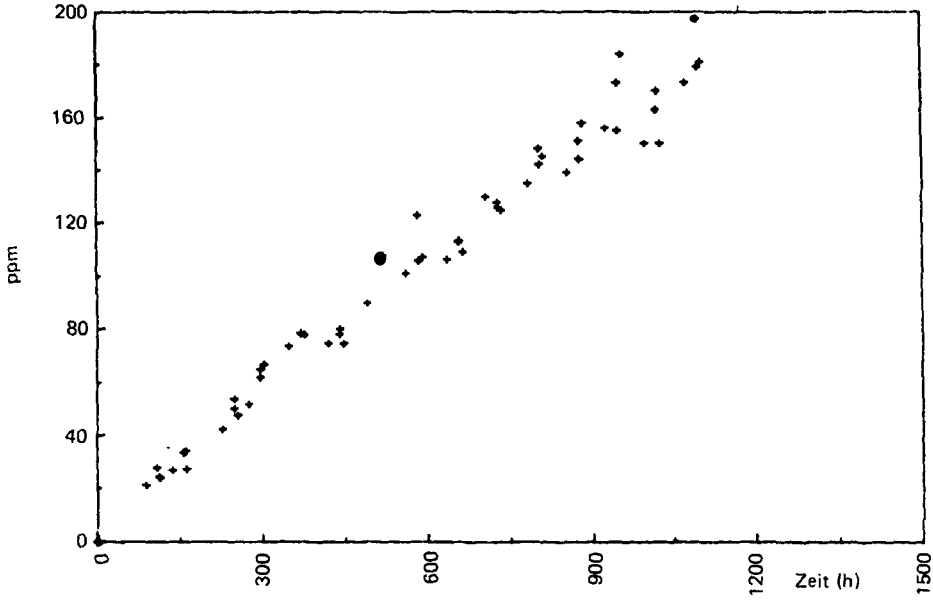

Figure 4: Increase of the uranium concentration on the adsorber granulate as function of time (for all 4 loops)

Table 2: Significant experimental parameters and data for the field trials with adsorber loops

Number of adsorber loops	:	4
Amount of adsorber material per loop	:	190 kg / 240 l
Sea water flow / average flow	:	15-20 / 18 m^3/h
Duration of the experiment	:	1647 - 1672 h (68,6 - 69,7 d)
Total processed seawater per loop	:	28.900 - 31.100 m^3
Uranium concentration on the adsorber	:	245 - 266 ppm
Total uranium extraction (per loop)	:	48,5 g
Total uranium content in the processed seawater (per loop)	:	99 g
Over all adsorption efficiency	:	0,49

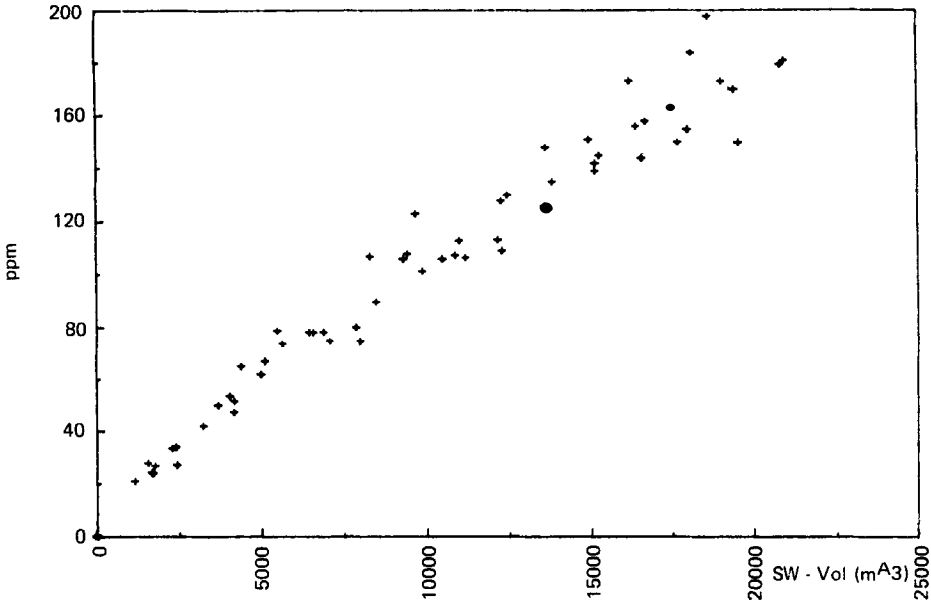

Figure 5: Increase of the uranium concentration on the adsorber granulate as function of the processed seawater

granulate (20 % or 50 ppm) and some spare material which was not eluted.

Based on these figures the anual production capacity of this semi-technical plant is about 1 kg U in accordance with the original design criteria for this experiment. It should be pointed out however that for longer periods of operation the adsorber material has to be exchanged because of a decline in adsorption rate. Though the increase in U-concentration seems to be linear in Fig. 4 and 5 up to 200 ppm the loading rate is reduced at higher concentrations around 250 ppm (overall adsorption efficiency 0,49;see Table 2) which recommends an exchange of the adsorber material.

CONCLUSIONS

It has been shown that the extraction of dissolved uranium from seawater by adsorption is technical feasible, if suitable adsorber material is available. With PAO-granulate an adsorption efficiency of 55 % has been accomplished without optimization of the relevant process parameters.

Because of the new loop concept for the adsorption process a total plant area of about 8 m^2 and a total plant volume of about 3.5 m^3 is sufficient to produce 1 kg uranium per year from seawater.

For a technical production plant a ship-based concept can be designed in which the described adsorber loops are adapted to the hull of the vessel. Thus a ship with the dimensions 300 m length and 35 m beam could hold a production plant for seawater uranium with an anual capacity of 100 t U.

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