

Appendix E2

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Note

In this document the references are coded by Q-numbers (e.g. Q133). Each reference has a unique number in this coding system, which is consistently used throughout all publications by the author. In the list at the back of the document the references are sorted by Q-number. The resulting sequence is not necessarily the same order in which the references appear in the text.

Uranium from seawater

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Introduction

Seawater contains dissolved uranium, mainly as uranyltricarboxylate ions $[\text{UO}_2(\text{CO}_3)_3]^{4-}(\text{aq})$, with an average concentration of 3.34 mg uranium per cubic metre seawater. Since the total volume of seawater of the world is about 1.37 billion km^3 , the total amount of uranium in the oceans is about 4.5 billion Mg (1 Mg = 1 megagram = 1 metric tonne). This huge uranium resource is assured, but is it also an *energy* resource?

In the past a limited number of studies has been published on extraction of uranium from seawater. Some of the studies go into detail, e.g. ORNL 1974 [Q133], Burnham et al. 1974 [Q136], Mortimer 1977 [Q98], Sugo et al. 2001 [Q298] and Sugo 2005 [Q303]. Other studies are confined to only a part of the process, e.g. Koske 1979 [Q223], Saito 1980 [Q224], Burk 1989 [Q73] and Nobukawa et al. 1994 [Q72]. Brin 1975 [Q225] gives a concise bibliography. The comprehensive and leading international study INFCE-1 1980 [Q226] cites results of an unspecified study by the US Department of Energy in 1978. The INFCE study concluded that uranium from seawater was not a viable option.

Though uranium from seawater is still cited as an energy resource option for the future, e.g. MIT 2003 [Q280], few feasibility studies have been published after 1980, not surprising after the conclusions of INFCE in 1980.

Only in Japan some interest in extraction of uranium from seawater appears to exist nowadays, judging by the publications of Nobukawa et al. 1994 [Q72], Sugo et al. 2001 [298], Sugo 2005 [Q303] and JAERI 2005 [Q304].

Extraction from seawater, general outline

Technically it is possible to extract uranium from seawater.

The first stage of the extraction process is adsorption of the dissolved complex uranium ions from the seawater on solid adsorption beds. Because of the extremely low concentration of uranium and the relatively high concentrations of many other kinds of ions, very specific adsorbents are required.

After the first stage, the adsorption, a number of additional processes is needed to obtain the uranium (see Figure 1):

- cleansing of the adsorption beds, to remove organic materials and organisms
- desorption: elution of the adsorbed uranium ions from the adsorption beds with a suitable solution; dependent on the type of adsorbent, this process may be a two-stage process in itself,
- purification of the eluent: removal of other desorbed compounds, which are present in far higher concentrations than uranium ions,
- concentrating the solution,
- solvent extraction of uranium from the solution with a mixture of an organic solvent and a specific complexing agent (a organophosphor compound),
- concentrating and purification of the extracted uranium compound and conversion into yellow cake.

After the desorption stage follows also a regeneration process of the adsorbent. A significant part of the adsorbent will be lost in the first stages of the process chain and has to be replenished by fresh adsorbent during restoring the adsorption beds for the next cycle.

All processes have their unavoidable losses, an inherent feature of chemical equilibria, which are involved in the extraction process.

A five-stage process with an assumed yield of 80% of each stage, would have an overall yield of 33%. If each stage has a individual yield of 70%, the overall yield would be 17%. A reasonable estimate of the overall yield of a five-stage process chain, excluding the first stage (adsorption from seawater), may be in the range of 17-33%. If more stages are needed, the total yield may be lower.

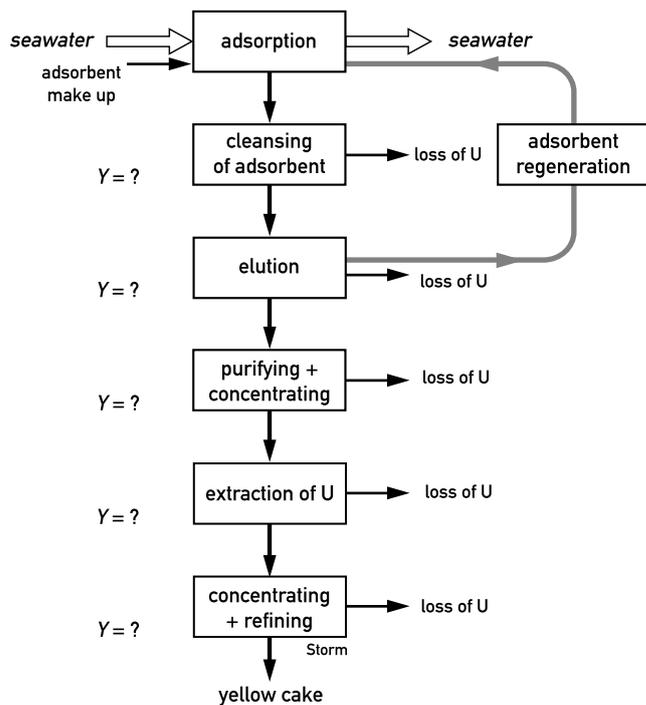


Figure 1
General outline of the extraction process of uranium from seawater

Adsorption from seawater

Because of the low concentration of uranium, very large volumes of seawater have to pass through the adsorption beds. With an assumed extraction efficiency of about 0.3, 1 gram of uranium would be adsorbed from 1000 m³ seawater. The contact time of the adsorption bed with seawater, the time needed to attain a reasonable load of uranium on the adsorption beds, may vary from several days to several months.

The adsorption stage requires very large facilities with dimensions measured in kilometers.

The adsorption rate strongly depends on the water temperature. Only locations in warm sea currents with water temperatures of more than 20 °C (e.g. the Gulf Stream in the Atlantic and the Black Current along Japan) are suitable to adsorption facilities, in order to keep the contact time of the adsorbent beds in seawater within reasonable limits. This is because the establishment of the chemical equilibrium between the complex uranium ions in seawater and the bound uranium ions on the solid adsorbent phase is slow and is speeded up by higher temperatures. If the adsorption is an exothermic process, and probably it is, the ratio adsorbed uranium/dissolved uranium will become less favourable the higher the temperature, because the equilibrium shifts to the endothermic reaction (desorption) at higher temperatures. So an optimum between adsorption rate and shifting equilibrium has to be found.

Two adsorption methods have been described in more or less detail: the titaniumhydroxide adsorption method and the polymer adsorption method. None of both has been actually tested other than in small-scale experiments.

Titaniumhydroxide adsorption method

One proposed method, introduced by British studies in the 1960s and reviewed by ORNL in 1974 [Q133], is based on adsorption of the dissolved uranium-complex ions on hydrous titaniumhydroxide gel, $Ti(OH)_4$, on small titania spheres. The adsorbent is packed in large horizontal beds. The seawater is refreshed either by pumps in a facility on the shore, or by tidal currents in a facility on a dam in a large estuary. The pump-fed facility seemed more economical than a tidal facility.

According to ORNL, very few parameters of the British studies were backed by solid experimental data. The loading of uranium, for instance, was assumed to reach 240 mg U/kg adsorbent after 4 days immersion time, but laboratory experiments showed no higher values than about 130-150 mg U/kg adsorbent after 9 days contact time. Dependent on the production process of the adsorbent, the load values may be even much lower. Considerable amounts of adsorbent are lost in the processing of the adsorbent: at least 15-65 kg titanium per kg uranium.

If an adsorption yield of 30% can be achieved, about 1 km³ seawater has to pass the adsorbent beds to get 1 Mg uranium adsorbed. Because of the low yield in the following processes (see Figure 1) to recover the uranium from the adsorbent, the required amount of seawater has to be a multiple of 1 km³, to get hold of 1 Mg uranium.

There are unsolved problems, such as clogging of the adsorption beds by organic materials from the sea. In addition there are large uncertainties in some parameters, such as adsorption yield and the recovery yield from the adsorbent. These factors make the feasibility of the concept speculative.

Polymer adsorption method

A recent Japanese concept (Sugo et al. 2001 [Q298] and Sugo 2005 [Q303]) is based on adsorption on a fibrous polymer. This material is called a graft polymer because the active agent, consisting of amidoxime groups, is chemically bound to it via a special chemical process involving electron beams. The adsorbent sheets are packed in stainless steel cages which are moored in a warm sea current, hanging from anchored buoys. The plant to recover the uranium from the adsorbent is situated on the shore.

Mooring the adsorbent at sea

In two mooring methods the cages with the adsorption beds are connected in units of 100 beds, spaced at 0.5 meter intervals, and hung under buoys (one unit per buoy) or large platforms (540 units per platform). Special crane ships hoist the beds aboard after a residence time of 60 days at sea and bring them to the shore for processing.

In a third approach, the adsorption beds (cages) are connected in units of 10 beds, and are hung from a long horizontal line connecting anchored buoys. The line is 23 kilometer long and forms a loop. Both ends are connected with a processing plant at the coast. Recovery of the beds is done in the same manner as a ski lift: winching up one end of the rope and easing the other. At the plant

the exposed beds are removed and fresh ones are attached on the outgoing line.

Table 1 Basic parameters of one adsorption bed, from Sugo et al. [Q298]

mass adsorbent	125 kg
mass spacer	104 kg
mass stainless steel mesh container	685 kg
total mass (cage + adsorbent)	1 Mg (average dry and wet)
adsorbed uranium	2 g uranium per kg adsorbent
immersion time (= 1 cycle)	60 days
adsorbent loss replenishment	1/4 of total mass of adsorbent per annum
diameter	4 m
height	0.4 m

Hypothetical uranium extraction plant

Based on the data from Sugo et al. [Q298] some parameters of a hypothetical uranium extraction plant can be roughly estimated, which are presented in Tables 2, 3 and 4.

Table 2 Parameters of a hypothetical extraction plant. Theoretical base case: without any process losses. Data from Sugo et al. [Q298]

annual uranium production	10000 Mg/a
annual operating time	300 days
number of cycles per annum	5
uranium production per cycle	2000 Mg
number of adsorption beds	8 million
total mass of adsorbent	1 million Mg
replenishment of adsorbent	250 000 Mg/a
daily number of beds to be processed	133 333 each day
mass of beds to be processed	133 333 Mg/day
loss of adsorption beds at sea	unknown, not mentioned in [Q298]
recovery yield uranium from adsorbent	unknown, not mentioned in [Q298]

Table 3 Parameters of three mooring methods (theoretical), based on data from Sugo et al. [Q298]

parameter	buoys	floating bodies	chain loops
number	80 000	148	350
area occupied at sea (km ²)	3200	1926	4025
number of ships unloaded per day	133	27	–
occupied coast line (straight, km)	–	–	350

Table 4 Parameters per Mg uranium (theoretical)

uranium grade per bed	0.025%	
number of beds to be processed	4000	
mass of adsorption beds to be processed	4000 Mg	
number of ships to be unloaded	4 (method 1)	1 (method 2)
adsorbent loss	25 Mg adsorbent/Mg U	

Each adsorption bed has to go through the following processes during each cycle:

- transport from sea to shore (10s to 100s of kilometers), as unit
- disassembling sea-going mooring unit of adsorption beds
- disassembling adsorption bed (cage)
- processing of the adsorbent, a multi-stage process (see Figure 1)
- replenishment adsorbent
- reassembling and repair
- reconnecting to mooring unit
- transport from shore to sea (10s to 100s of kilometers)

Uncertainties

The figures of the hypothetical plant above are calculated ignoring the losses in the processes of the recovery of uranium from the adsorbent. As is pointed out before (see Figure 1) the recovery yield certainly will be much less than 100%. If a yield of 50% is assumed, probably a high estimate, all dimensions in above tables have to be multiplied by 2. If the recovery is lower, e.g. 33% or 20%, the multiplier will be 3 to 5.

Moreover it is unknown which fraction of the adsorption beds will be lost and damaged during each cycle, caused by heavy waves at sea and by other causes. The number of adsorption beds to be handled during each cycle is theoretically 8 million, and practically a lot more, e.g. 16-40 million, dependent on the value of the multiplier mentioned above.

As long as the multiplier is unknown, the project is characterized by very large uncertainties, apart from the uncertainties posed by incorporating untested technology.

Unsolved problems

Several unsolved problems are, among others:

- dynamic behaviour of the mooring equipment at sea under conditions of high waves and strong winds. Violent movements and collisions may cause losses at sea of adsorption beds or even whole units of beds.
- recovery of the adsorption beds under adverse conditions
- problems for the shipping traffic posed by the buoys and floating platforms
- pollution of the adsorber beds by organic materials from the sea.

Costs

Some figures from the literature are listed in Table 5. All figures except the last two (Nobukawa et al. 1994 [Q72] and Sugo et al. 2001 [Q298]) refer to the titaniumhydroxide adsorption method.

Table 5 Estimates of costs and energy consumption of uranium from seawater

reference	energy consumption TJ/Mg (U)	costs \$(yr)/kgU	costs \$(2000)/kgU
Burnham et al. 1974 [Q136]	26 *	-	-
ORNL 1974 [Q133]	90 ** 1,2 ***	>> 796 >> 796	>> 2766
Brin 1975 [Q225]	~390 *	91-2600	289-8280
Mortimer 1977 [Q98]	20-600	260-780	728-2210
from ore:	21-78	60-221	
Koske 1980 [Q223]	5-10 ****	-	-
INFCE 1 1980 [Q226]	-	7000-9000 (1978)	18400-23700
Burk 1989 [Q73]	-	-	-
Nobukawa et al. 1994 [Q72]	-	40000 ¥/kg (1994)	370
Sugo et al. 2001 [Q298]	-		280-560

* only pumping energy, deduced from data in publication

** only pumps, pump-fed plant, pump head 20 m

*** pumps in tidal plant

**** deduced from data in publication; only pumps in first stage, pump head 0.5 m

The authors of ORNL 1974 emphasize that the cost figures they found are based on very optimistic assumptions, so the real values will probably be several times higher.

The figures of Sugo et al. are based on apparently unrealistic assumptions:

- The processes following the adsorption stage, to recover the uranium from the adsorbent (see Figure 1), and their inherent losses are ignored.
- The authors assumed an uranium load of 6 grams uranium per kilogram adsorbent under operational conditions, with the perspective of 10 g U per kg adsorbent. Their own experiments showed that a load of about 2 grams uranium per kilogram adsorbent could be reached after a residence time of 60 days and about 3 g U per kg adsorbent after 240 days immersion in seawater. The calculations of Sugo et al. are based on a contact time of about 60 days. Taking these two factors into account, their cost estimates may be low with a factor of at least 10.

Upscaling

The cost figures in Table 1 should be regarded as speculative, as no experiences with uranium extraction from seawater exist, even not on pilot plant scale. The sole empiric data known are the results of only a few adsorption experiments on gram scale.

As every chemical engineer knows, upscaling of complex chemical processes is not too simple. For a meaningful contribution to the world uranium supply, an extraction plant with an annual production capacity of at least 10 000 Mg uranium would be needed (the present uranium consumption is 67 000 Mg per annum). That would mean an upscaling of the adsorption process, coupled with the subsequent chemical processes, with a factor of ten billion.

Large cost escalations are intrinsic to new technology projects, as RAND 1981 [Q126] reports:

“• Severe underestimation of capital costs is the norm for *all* advanced technologies; the underestimation for energy process technologies mirrored that seen in major weapon systems acquisition, very large advanced construction projects, and major public work activities.

A number of advanced technologies brought to project completion had problems with reliability and performance.

• Capital costs are repeatedly underestimated for advanced chemical process facilities, just as they are for advanced energy process plants. Furthermore, the performance of advanced energy process plants constantly falls short of what was predicted by designers and assumed in financial analyses.

• Greater than expected capital costs and performance shortfalls not anticipated by conventional estimating techniques can be explained in terms of the characteristics of the particular technology and the amount of information incorporated into estimates at various points in project develop.”

According to RAND 1979 [Q127], escalations in cost estimates of energy process plants with factors 2 - 5 are not uncommon. The nuclear industry itself provides many examples of these observations and those in RAND 1981 [Q126].

There are no indications that the mechanisms described in the RAND studies would not apply to new large technology projects in 2005, including extraction of uranium from seawater. On the contrary, several factors leading to underestimation of the costs are clearly demonstrated in the publication of Sugo et al., such as:

- assuming an adsorption yield far higher than experimentally demonstrated
- ignoring unavoidable losses of materials at sea by heavy waves and by other causes
- ignoring unavoidable extraction losses in the chemical processes needed to recover the uranium from the adsorbent
- starting from an ideal situation and disregarding technical imperfections
- estimating costs on theoretical grounds, without practical experiences (e.g. in a pilot plant) with all components of the system separately, let alone integrated.

The evaluation by ORNL [Q133] is very critical on the cost estimates as done by the reviewed studies, because of similar reasons.

Energy requirements

Titaniumhydroxide adsorption method

Mortimer 1977 [Q98] concludes that most techniques he reviewed have an energy consumption equalling the energy content of the uranium.

A minimum value of the specific energy consumption for the extraction of uranium from seawater may be:

$$J_{\text{sea}} = 100 \text{ TJ/Mg} \text{ mainly electricity} \qquad \text{eq 1}$$

This figure is based on the elaborate study of ORNL 1974 [Q133], and includes energy costs of plant construction, chemicals and operation and maintenance of a pump-fed plant at sea, as large-scale tidal plants do not seem feasible. The process needs powerful pumps and consumes large amounts of electricity. Regeneration of the eluant by steam stripping is very energy-intensive and may alone consume thermal energy in the order of 200 TJ/Mg U.

The authors of ORNL 1974 emphasize that the values they found are based on very optimistic assumptions, so the real values most probably will be several times higher.

A rough estimate of the specific energy requirements including plant construction, chemicals, operation and maintenance, can otherwise be made using the costs in dollars and e , the energy/gnp ratio. Using the cost estimates quoted in INFCE-1 1980 [Q226] (taken from a 1978 US Department of Energy study) of 18400-23700 \$(2000)/kg and $e = 10,6 \text{ MJ}/\$(2000)$, we find:

$$J_{\text{sea}} = 195\text{-}250 \text{ TJ/Mg} \qquad \text{eq 2}$$

Above values are underestimated, because the chemical industry is more energy-intensive than the average economic activity. The figures agree fairly well with the estimates of Mortimer 1977 [Q98] and ORNL 1974 [Q133]. In all studies, as far as we can gather, the extraction losses (see above) have been left outside of account, so the cited figures are low estimates.

Table 6 Theoretical gross energy production from 1 Mg natural uranium in an LWR of current design

average burnup B	46 GW(th).day/Mg enriched uranium
enrichment assay	4.2 % U-235
feed/product ratio enrichment	7.84
heat production	507 TJ(th)/Mg U(natural)
gross electricity production	162 TJ(e)/Mg U(natural)

In Table 6 the physical process losses of uranium are ignored, as well as the energy requirements of the processes needed to convert uranium ore into reactor fuel, to operate, maintain and refurbish the nuclear power plant and to clean up the nuclear wastes safely.

The net energy production of an LWR nuclear power system is much lower than the theoretical maximum of 162 TJ/Mg, and may be in the range of about 70-100 TJ/Mg natural uranium, see [Q6]. Equation 2 shows that the energy requirements of the complete process probably will be much higher than even the theoretical energy production possible with the recovered uranium.

From an energetic point of view, uranium from seawater using the titaniumhydroxide method can't be considered an option for the global energy supply.

This is confirmed by the conclusion of INFCE-1 1980 [Q226]:

"Therefore it would be unrealistic to expect uranium from seawater to contribute significant amounts of the world's uranium demand for thermal reactors on an acceptable time scale."

Polymer adsorption method

Based on the concept of Sugo et al. some parameters of a hypothetical uranium extraction plant can be deduced, see Tables 1-4. The plant has an assumed annual production capacity of 10 000 Mg uranium from seawater.

The effective 'ore grade' of the adsorbent beds is $G = 0.025\% \text{ U}$ (see Table 4). This value is quite near the energy threshold of about $0.02\% \text{ U}$ of conventional ores (see [14]). If the yield of the recovery of uranium from the adsorbent is lower than the recovery yield from conventional ore of the same grade, the effective grade of the adsorbent may significantly lower than $0.025\% \text{ U}$. If, for instance, a recovery yield from conventional ore $Y = 60\%$ is assumed, and from the adsorbent $Y = 30\%$, which is not unthinkable (see Figure 1), two times as much adsorbent has to be processed as conventional ore, to recover the same mass of uranium.

Although the adsorption process itself requires no energy input because the seawater is continuously refreshed by the sea current, handling of the adsorbent units and processing the materials to recover the uranium may require huge amounts of energy, equipment and materials.

The transport of the adsorbent to the shore and back to sea, occurs not like ore by large trucks and belts or like seawater by pumping through pipelines over short distances, but by cranes, ships and other equipment over long distances, may be hundreds of kilometers. Moreover, the energy requirements of all processes each adsorbent cage has to go through, cited under Table 4, are to be taken into account. The replenishment of adsorbent beds requires energy-intensive materials, such as stainless steel and the amidoxime polymer.

The specific energy consumption of the production of the adsorbent, a polymer with the amidoxime groups, may be high, because of the special chemical composition of the adsorbent and the need for electron beams to bind the active groups to the polymer. For each Mg uranium at least 25 Mg polymer adsorbent is consumed.

By reason of above considerations, it seems extremely unlikely that the specific energy consumption of the method of Sugo et al. will be less than the specific energy content of the recovered uranium.

Conclusions

Two methods of recovery of uranium from seawater have been studied in enough detail to get an impression of their feasibility and specific energy requirements: the titaniumhydroxide adsorption method and the Japanese polymer adsorption method.

None of both methods has been tested as a complete process chain. The sole empirical base consists of some small scale laboratory experiments.

Both methods have so many and such far-reaching uncertainties and unsolved problems, that their feasibility may be considered speculative.

Uranium from seawater by the titaniumhydroxide adsorption method can't be considered an energy resource, nor from tidal nor from pump-fed systems, because the specific energy consumption of the whole chain of processes almost certainly will surpass the energy to be generated from the recovered uranium.

INFCE-1 1980 [Q226] concludes:

"Therefore it would be unrealistic to expect uranium from seawater to contribute significant amounts of the world's uranium demand for thermal reactors on an acceptable time scale."

It seems extremely unlikely that the specific energy consumption of the Japanese polymer adsorption method will be less than the specific energy content of the recovered uranium.

With the present state of technology, uranium from seawater can't be considered an energy resource.

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