On the Extraction of Uranium from Sea Water by a Complexing Resin

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Uranium Recovery from Sea Water, Sorbents Accumulating Uranium,
Uranium Uptake and Elution

A cross-linked polyacryl resin containing amidoxime or related functional groups is capable of concentrating uranium from natural sea water. The resin presents a uranium loading of more than 3000 ppm; moreover it has a higher selectivity, uptake rate, and attrition stability than hydrous titanium oxide.

In view of the anticipated exhaustion of terrestrial uranium reserves of the western world in the near future [1], the recovery of uranium from sea water is increasingly taken into consideration [2–11]. The oceans contain more than 4 billion tons of dissolved uranium, about the thousandfold of reasonably assured and estimated terrestrial resources in the cost range up to $ 50/lb U_3O_8 [1]. The concentration of uranium in sea water appears to be nearly constant at about 3.3 μg/litre [12]; its molar concentration is nearly 8 orders of magnitude lower than the total concentration of the major ions. In order to recover an economically significant quantity of uranium from sea water – about one ton per day – the vast sea water volume of nearly 10^9 cubic meters would have to be processed per day. Certainly, sea water is a very low grade uranium source; however, the advantage of the dissolved state and the almost exhaustless quantities of uranium should be kept in mind.

Owing to the relatively high carbonate concentration in sea water, uranium predominantly should occur as the tricarbonato uranylate anion $[UO_2(CO_3)_3]^{4-}$, an extremely stable complex with the formation constant of $\log \beta_3 = 22.6$ [6]. This complex is easily decomposed if the natural pH of sea water of 8.1–8.3 is lowered beneath 8.

Several methods of uranium accumulation from sea water such as solvent extraction, ion floatation or coprecipitation have been considered [6], but only the sorptive concentration using a suitable solid sorbent seems to be feasible. Hydrous titanium oxide possesses a uranium loading capacity in natural sea water of some hundred ppm [3]; it is used in a laboratory scale in Japan, China, France, the United States, and also in the Federal Republic of Germany. However, hydrous titanium oxide does not satisfy the stringent requirements of mechanical stability, high selectivity and uptake rate; moreover it lacks in greater uranium loading capacity.

We have determined the uranium uptake of a large number of inorganic, organic, and biological materials in natural sea water, but none of them proved to be suitable. Thereupon we have turned our attention to ion exchange resins and tested about 60 resins of different functional groups or polymer frameworks. Most of them appeared to be ineffective, only a few showed uranium loadings of 20 to 50 ppm. But nearly all uranium binding resins depressed the natural pH of sea water. However, such sorbents are unsuitable, since an acidification of sea water cannot be accepted with respect to economic and ecological reasons.

Until now we could detect only one resin capable of concentrating significant quantities of uranium from natural sea water at the natural pH. Some experimental values concerning both the uranium uptake and selectivity of hydrous titanium oxide* as well as the just mentioned resin are compared in Table I.

The resin is a cross-linked poly(acrylamidoxime). However, we have found some experimental evidence that it does not only contain amidoxime groups but also related functional groups. Hydrous titanium oxide shows a uranium uptake of 230 ppm, whereas the complexing resin attains to a loading of 3100ppm without reaching the saturation capacity. A higher selectivity of the resin can be derived from the concentration factors calculated with regard to natural sea water. In spite of the considerably higher uranium

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* The hydrous titanium oxide mentioned in this publication was bought from the Atomic Energy Research Establishment in Harwell, United Kingdom.

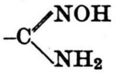
Sorbents	Functional Groups	Uranium Uptake [ppm]	Concentration Factors			
			U	Ca	Mg	Na
Hydrous Titanium Oxide	$>Ti(OH)_2$	230	$7.2 \cdot 10^4$	70	6.5	0.69
Complexing resin	 $-C(=NOH)NH_2$	3100	$9.7 \cdot 10^5$	31.8	12.8	0.29

Table I. Uranium uptake and selectivity of hydrous titanium oxide and the complexing resin.

loading – more than one order of magnitude – the resin accumulates less calcium and sodium than hydrous titanium oxide; the concentration factor of magnesium is only double the size. Moreover it can be derived from preliminary results that the uranium uptake of the resin is faster under the same conditions. For example at 30 °C the uptake rate (ppm/day) was found to be at least twice as high than for hydrous titanium oxide.

For testing the stability of the resin beads against attrition, the beads have been subjected to a fluidized bed in natural sea water for several months. The initially white colour of the resin changed to brown, however, nearly no attack of the glossy surface could be observed. The uranium loading of the beads is limited to a surface layer, the thickness of which increases with increasing loading.

Uranium can be eluted from the complexing resin by hydrochloric acid. Fig. 1 demonstrates six loading-elution cycles starting with a uranium content of the resin of 110 ppm.

After the uranium loading in natural sea water the elution was carried out with 6 bed volumes of 0.75 molar hydrochloric acid. An elution efficiency of more than 90% could be achieved. However, a serious disadvantage of the acid elution is a certain instability of the functional groups leading to a slight decrease of about 5% per cycle in uranium uptake. The attack of the functional groups by hydrochloric acid could clearly be established by the polarographic determination of hydroxylamine.

At present we are mainly concerned with the stabilization of the functional groups against acid eluants, the elution of uranium with carbonate solutions and the improvement of the uptake rate by optimization of the porosity and the specific surface of the resin. Detailed informations of our studies on the development of suitable sorbents for the extraction of uranium from sea water will be reported elsewhere.

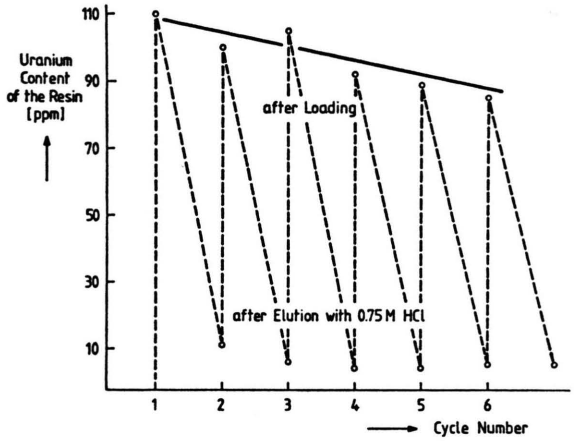


Fig. 1. Loading-elution cycles of the cross-linked poly-(acrylamidoxime) resin.

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