

## Enhancement of the Extraction of Uranium from Seawater

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### ABSTRACT:

Due to the limited uranium resources available for recovery through mining and ore processing and to the environmental problems associated with these operations, the future of nuclear power depends, to a large extent, on the feasibility of recovery of uranium from the ocean. While the amounts of uranium in the ocean are sufficient to fulfill the nuclear industry for many thousands of years, recovery of uranium from the ocean is hampered by its low concentration (3.3 parts per billion) and the presence of many other solutes in seawater at comparable or much higher concentrations. Thus, the only hope for economically viable recovery of uranium from the ocean lies in the development of adsorbents with high capacity and high selectivity for uranium as present in the seawater environment (pH 8.1, U(VI) oxidation state, anionic carbonate complexes). Moreover, it is quite unlikely that economically viable recovery of uranium could be achieved if the adsorbent could be used only once. Thus it is essential to develop adsorbents that can be used through multiple cycles of uranium adsorption followed by elution of the uranium to regenerate the adsorbent without significant degradation of their capacity and selectivity for uranium. Adsorbents used in the large majority of studies aimed at recovery of uranium from seawater are based on the use of radiation grafting to produce polymeric supports, in particular polyethylene, with attached amidoxime groups. This configuration has been concluded to offer the best candidate for use in recovery based on studies which were performed in the early 1980's. Substantial progress has been made in improving the amidoxime-based adsorbents.

The basic approach undertaken by the authors of the proposal, on the other hand, has been to test ligands which have not been included in the scoping studies of the 1980's or have been developed since then. So far, 18 such ligands have been tested, of which three, including B2MP (an organic phosphate), DAOx (an organic oxalate), and Br-PADAP (an azo compound) have been selected for further investigation. In addition, Winged™ Nylon 6 has been identified as a promising polymeric support in view of its large surface area and high chemical stability. Furthermore, improved grafting techniques intended to achieve high grafting density under "green chemistry" conditions, i.e., in aqueous media, have been developed. These techniques include the use of surfactants to enhance the solubility of ligands in water and the use of a homopolymerization inhibitor to promote grafting rather than homopolymerization. Furthermore, unlike amidoxime-based adsorbents, which require a chemical treatment step following the radiation grafting to convert a nitrile group to amidoxime, the adsorbents developed by the authors do not require an additional step after grafting. Highly effective regeneration has been demonstrated for the phosphate-grafted polymeric adsorbent over at least 21 adsorption/elution cycles without significant loss of capacity.

The currently proposed study is intended to build upon the progress made so far in developing alternative systems for removal of uranium from seawater. It will focus on the following objectives:

1. Continued searches will be conducted for high-capacity, high-selectivity ligands based on systematic characterization of structural features favorable to uranium adsorption. (For instance, phosphates have been found to be much more effective than the corresponding phosphonates). At the same time, development and testing of the three ligands selected so far will continue, focusing on issues such as high grafting densities and effective regeneration.
2. Testing will be conducted in non-spiked seawater (3.3  $\mu\text{g/L}$  U) and lightly spiked seawater (up to 10  $\mu\text{g/L}$  U). The authors have recently been able to refurbish an ICP-MS spectrometer for this purpose.
3. Improved grafting techniques will be developed and refined for specific ligands. These techniques will include the use of surfactants to allow grafting of ligands with low solubility in water, the use of homopolymerization inhibitors, modifying the chemical structure of ligands to introduce C=C bonds, investigating possible modification of the surface of the polymeric support, and mechanistic analysis of the effects of grafting conditions, in particular accumulated dose and dose rate.
4. Improvements in the characterization of adsorbents before and after contact with seawater will be implemented using techniques such as XPS, SEM-EDS, and zeta potential measurements to investigate the mechanism of uranium adsorption.
5. Effective techniques of multi-cycle regeneration of promising adsorbents without degradation of their performance will be developed and refined through testing of mild, preferably near-neutral eluant solutions.
6. The kinetics of adsorption and desorption of uranium will be investigated. This study is of great operational value and it will also greatly contribute to improved understanding of adsorption/desorption mechanism on promising adsorbents.