Recovery of Uranium from Seawater:
Preparation and Development of Polymer-Supported Extractants

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ABSTRACT
A new series of polymer-supported extractants is proposed for the removal and recovery of uranium from seawater. The objective is to produce polymers with improved stability, loading capacity, and sorption kinetics compared to what is found with amidoximes. The target ligands are diphosphonates and aminomethylidiphosphonates. Small molecule analogues, especially of aminomethylidiphosphonates, have exceptionally high stability constants for the uranyl ion. The polymeric diphosphonates will have high affinities due to their ability to form six-membered rings with the uranyl ion while the aminomethylidiphosphonates may have yet higher affinities due to possible tridentate coordination and their greater acidity. A representative set of the polymers to be prepared are indicated below.

The preparations to be developed will be from readily available starting materials in a minimum number of steps. The structures will be analyzed through FTIR and XPS spectra, supplementing zero point charge determinations and elemental analyses. The uranyl distribution coefficients will be determined from synthetic seawater containing 5 ppm UO$_2^{2+}$ to allow for accurate analysis by ICP. With solutions having higher concentrations of the uranyl ion, adsorption isotherms and loading capacities will be determined. Polymers with high distribution coefficients will be evaluated with authentic seawater samples and uranyl levels of 3 ppb using radiotracer techniques. Rate studies will measure the sorption kinetics. Regeneration of the polymers after loading with the uranyl ion will be studied with a series of regenerants, including sodium carbonate, 1-hydroxyethyl-1,1-diphosphonic acid, and oxalic acid.

The optimum ligand will be immobilized onto polypropylene, thus allowing for its application to uranium recovery from seawater. The approach taken will be the formation of polypropylene fibers grafted with vinylbenzyl chloride using supercritical CO$_2$ technology. The scCO$_2$ allows the monomer and free radical initiator (benzoyl peroxide) to enter deep within the polymer to give high grafting yields. The aromatic groups can then be functionalized in exactly the same way that the beads were modified. Uniform functionalization is expected because the porosity of the fiber permits accessibility of the reagents. Removal of the scCO$_2$ solvent is obviously implemented simply by reducing the pressure. Conditions that minimize homopolymer formation and any degradation of the polypropylene have been defined with maleic anhydride as the monomer and should extend to vinylbenzyl chloride.