
Recovery of Uranium from Seawater: Aminophosphinates as Selective Extractants

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ABSTRACT:

The objective is to prepare a polymer-supported extractant for the recovery of uranium from seawater. The DOE has set a goal “to double the Japanese sorption capacity in three years.” Results from our NEUP-funded 2011-2013 grant show that primary amine polymer has a high uranium affinity, removing 14.8 mg U / gpolymer (11.4 mmol U /molligand) from artificial seawater. Polymeric diamidoxime removes 2.34 mg U/gpolymer (3.79 mmol U/molligand). Since diamidoximes have higher affinities than monoamidoximes, the results suggest at least a tripling of uranyl capacity by the primary amine (calculated on a mole basis) and quadrupling when ligands with two primary amines per ligand are used.

Three approaches are taken in the proposed research:

(A) *Focus on the primary amine ligand and quantify the effect of increasing ligand density:* Since polystyrene-bound tris(aminoethyl)amine, with two neighboring –NH₂ groups available binding, had a 50% increase in capacity over the polymer with isolated –NH₂ groups (16.0 vs. 11.4 mmol U /molligand), polymers with a higher number of proximate –NH₂ groups will be studied (see structure A).

(B) *Probe the mechanism of uranyl binding with amidoxime analogues:* Results suggest that the imine in the amidoxime may have a role in increasing the basicity of the primary amine through pi-donation and that this is responsible for the high uranyl affinity. A series of amidines (B) will be prepared with aromatic groups bearing substituents (OCH₃, CH₃, F, Cl) that vary pi-donation onto the –NH₂. The effect will be quantified by constructing a Hammett plot of the uranyl distribution coefficients vs. substituent sigma constants.

(C) *Prepare immobilized ligands with the amine proximate to an auxiliary group:* Our BES-sponsored research has shown that neighboring (auxiliary) groups influence cation binding at a given ligand. The phosphinic acid has a high affinity for UO₂²⁺ when immobilized onto polystyrene. Aminophosphinates (structure C) can be prepared through a modified Strecker synthesis and offer the best possibility for an auxiliary interaction to provide a ligand with high affinity and selectivity for the uranyl ion.

Amines and aminophosphinates as ligands are thus promising approaches to meeting the DOE goal.

The final part of the project is the modification of fibers in supercritical CO₂ to thus avoid irradiation as the source of free radicals for grafting for preparation of the final product for seawater application.

