

Project ID: **60041**

Project Title: **Removal of Radioactive Cations and Anions from Polluted Water Using Ligand-Modified Colloid-Enhanced Ultrafiltration**

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PROJECT SUMMARY/PROGRESS REPORT

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Publication Date: 06/14/99

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RESEARCH OBJECTIVES

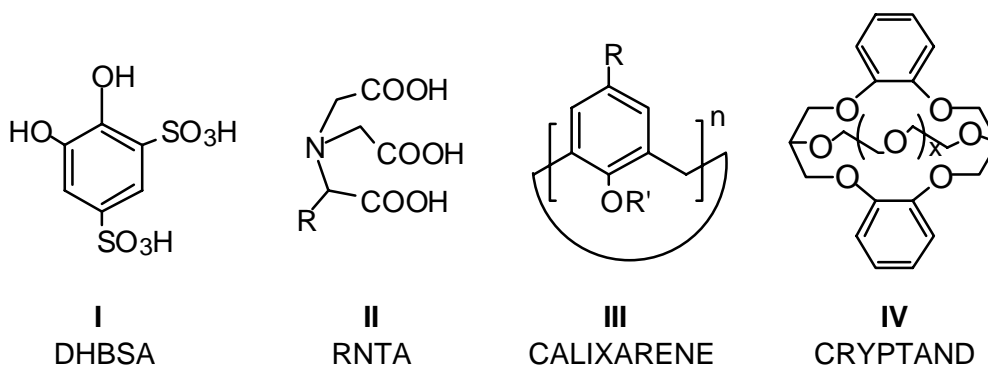
The objectives of this project are to determine the feasibility of and develop optimum conditions for the use of colloid-enhanced ultrafiltration (CEUF) methods to remove and recover radionuclides and associated toxic non-radioactive contaminants from polluted water. The target metal ions are uranium, plutonium, thorium, strontium and lead along with chromium (as chromate). Anionic or amphiphilic chelating agents, used in conjunction with polyelectrolyte colloids, provide a means to confer selectivity required for removal of the target cations. This project entails a comprehensive study of the effects of solution composition and filtration unit operating parameters on the separation efficiency and selectivity of ligand modified colloid-enhanced ultrafiltration (LM-CEUF) processes. Problem areas identified by the Office of Environmental Management addressed by this project include removal of hazardous ionic materials from ground water, mixed waste, and aqueous waste solutions produced during decontamination and decommissioning operations. Separation and concentration of the target ions will result in a substantial reduction in the volume of material requiring disposal or long-term storage.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work after 20 months of a 3-year project. In the proposed method, a soluble cationic colloid and an anionic ligand are added to the waste stream to be treated. The resulting feed solution is placed in an ultrafiltration (UF) cell that has a membrane with pore sizes sufficiently small to reject the colloid along with any colloid-bound species. Target cations that form anionic complexes with the ligands are electrostatically bound to the polymer and retained during the filtration step. A similar uses amphiphilic ligands with surfactant micelles as the colloid. The degree of retention of the target ion X is expressed as a rejection coefficient, R_x (%), where $[X]_{\text{per}}$ and $[X]_{\text{ret}}$ refer to the concentrations of X in

$$R_x (\%) = \{ 1 - [X]_{\text{per}} / [X]_{\text{ret}} \} \times 100\% \quad (1)$$

the permeate (filtrate) and retentate (retained) solutions, respectively. Separation behavior was evaluated for the following metal ion-ligand systems: UO_2^{2+} with CO_3^{2-} and 1,2-dihydroxy-3,5-benzenedisulfonic acid, DHBSA (I); Th^{4+} with DHBSA; and Pb^{2+} with nitrilotriacetic acid derivatives (II, RNTA). Polycyclic phenol derivatives, calixarenes (III) and macrobicyclic polyether cryptands (IV) were evaluated as potential ligands for use with LM-CEUF. Structures of the ligands investigated are shown below.



Ultrafiltration studies; separation and regeneration. For each system the effects of metal ion and ligand concentration, pH, added salt (NaCl), and colloid concentration were investigated. In most cases the colloid used was polydiallyldimethylammonium chloride (PDADMAC). The $\text{UO}_2^{2+}\text{-CO}_3^{2-}$ system at pH 7-8, solutions with $[\text{CO}_3]:[\text{UO}_2]_{\text{total}}$ ratio greater than 4.0 gave $R_{\text{UO}_2} \cdot 99.91\%$. This corresponds to UO_2^{2+} concentrations in the permeate as low as 0.1 micromolar, a reduction of about ~1000-fold in a single separation step. In the presence of 0.2 M or 0.5 M NaCl the R_{UO_2} values decreased to ~95% and ~80%, respectively. When the feed solution was adjusted to pH 2.4, uranyl rejection decreased to 70-75%. The combined effects of lowered pH and increased salt concentration may provide a suitable method to remove UO_2^{2+} and recycle the polymer. DHBSA (I) was evaluated as a ligand for UO_2^{2+} and for Th^{4+} . With both metal ions rejection exceeded 99.9% in the pH range 5.0-6.5 when the ligand:metal ratio was 2.0 or greater. The presence of 0.2 M NaCl caused R_{UO_2} and R_{Th} to decrease slightly to 99.8% and 99.5%, respectively. Preliminary studies indicated that acid stripping at low pH (1-2) gave ligand recoveries of about 50%. NTA derivatives (II) with anionic ($\text{R} = \text{CH}_2\text{SO}_3^-$, SNTA) and hydrophobic ($\text{R} = \text{C}_{10}\text{H}_{21}$, DNTA) substituents were tested for removal of Pb^{2+} . The latter was studied using cetyl pyridinium nitrate (CPN) micelles as the colloidal phase. At low ionic strength SNTA gave R_{pb} values in the range 99.0-99.9% while DNTA gave R_{pb} values in the range 99.7-99.9%. In the presence of 0.05 M salt, R_{pb} decreased to 50-55% for SNTA with PDADMAC, but was hardly affected ($R_{\text{pb}} = 99.5\%$) for DNTA with CPN. Acid stripping, combined with Pb^{2+} precipitation using oxalate, allowed ligand recoveries of 96% and 85% for SNTA and DNTA, respectively.

Evaluation of new ligands. The UF behavior of the tetrasulfonate calixarene (III, $n = 4$, $\text{R} = \text{SO}_3^-$, $\text{R}' = \text{H}$) with PDADMAC was evaluated in the presence 0.0-0.5 M NaCl. Rejection values were greater than 99.8%, even in the presence of 0.5 M NaCl, indicating that calixarene derivatives (e.g., $\text{R}' = \text{CH}_2\text{CO}_2\text{H}$) hold promise as ligands for LM-PEUF at high concentrations of electrolyte. Several macrobicyclic polyethers cryptands (IV) have been evaluated as prototype ligands for selective removal of Sr^{2+} . These compounds have carbon atoms at the bridgehead positions instead of nitrogen atoms, thus making them suitable for use in neutral or acidic media. The complex formation constants (K_{ML}) have been

measured in water for Na^+ , K^+ , Ca^{2+} , Sr^{2+} , and Ba^{2+} with a series of related cryptands (IV; $x = 1,2,3$). Cryptand IV ($x = 2$) forms strong complexes with Sr^{2+} ($\log K_{\text{SrL}} \sim 8.0$) and shows excellent selectivity ($K_{\text{SrL}}/K_{\text{ML}} > 200$) for Sr^{2+} over other alkali and alkaline-earth cations. Smaller and larger cryptands (IV; $x = 1,3$) form weaker complexes generally and have lower selectivity for Sr^{2+} ($K_{\text{SrL}}/K_{\text{ML}} \cdot 10$).

PLANNED ACTIVITIES

During the next year, we will continue ultrafiltration studies on the LM-CEUF systems for UO_2^{2+} , Th^{4+} , and Pb^{2+} , with particular attention to the chemical (pH, salt concentration) and physical (applied pressure, membrane pore size) factors that affect recovery of ligand and polymer. The membrane binding behavior of new ligands for other target cations (Pu^{4+} , Sr^{2+}) will be investigated. UF techniques will be used to evaluate metal ion separation behavior for those ligands that show suitable behavior. Separations of other actinides (e.g., Pu) using LM-CEUF will be studied by collaborators at LLNL. Following evaluation of ligands in single cation studies, ligands displaying suitable performance will be tested using mixtures containing other cations and anions (e.g., CrO_4^{2-}).