

PROJECT ID 60041-OK - SUMMARY/PROGRESS REPORT

Title: Removal of Radioactive Cations and Anions from Polluted Water Using  
Ligand-Modified Colloid-Enhanced Ultrafiltration (60041-OK)

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Number of Post-doctoral Students involved on project: 1

## RESEARCH OBJECTIVES

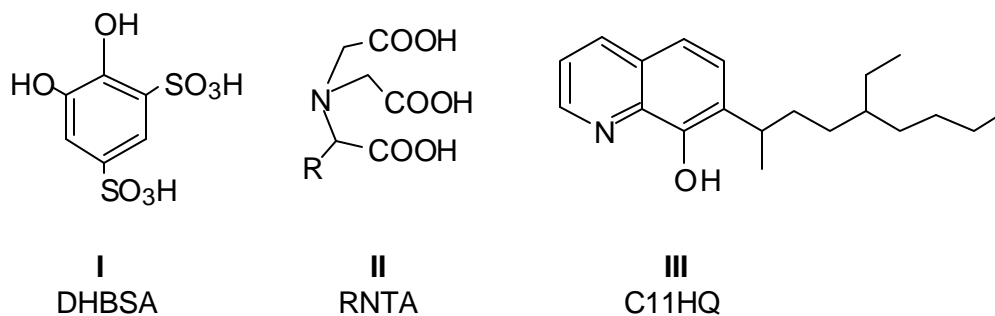
The objectives of this project are to determine the feasibility of and develop optimum conditions for the use of colloid-enhanced ultrafiltration (CEUF) methods to remove and recover radionuclides and associated toxic non-radioactive contaminants from polluted water. The target metal ions are uranium, plutonium, thorium, strontium, cadmium, 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 2 years and 4 months of a 3-year project. In the method under study a soluble cationic colloid and an anionic or amphiphilic ligand are added to the waste stream to be treated. The ligands are attached to the colloid via electrostatic or hydrophobic interactions. The resulting feed solution is placed in a cell with an ultrafiltration (UF) membrane having pore sizes sufficiently small to reject the colloid along with any colloid-bound species. Target cations that form complexes with the ligands are retained during the filtration step. 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 target species, X, in the permeate

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

(filtrate) and retentate (retained) solutions, respectively. Separation behavior was evaluated for the following metal ion-ligand systems:  $\text{UO}_2^{2+}$  with  $\text{CO}_3^{2-}$  and 1,2-dihydroxy-3,5-benzenedisulfonic acid, DHBSA (I);  $\text{Th}^{4+}$  with DHBSA;  $\text{Pb}^{2+}$  with nitrilotriacetic acid derivatives (II, RNTA); and  $\text{Cd}^{2+}$  with undecyl-8-hydroxyquinoline (III,  $\text{C}_{11}\text{HQ}$ ). The ligand structures 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. For electrostatic attachment of ligands, polydiallyldimethylammonium chloride (PDADMAC) was used as the colloid. Micellar-based separations employed the cationic surfactant cetyl pyridinium nitrate (CPN) or the neutral surfactant hexaoxyethylene-*n*-dodecyl ether (C<sub>12</sub>(EO)<sub>6</sub>). For the UO<sub>2</sub><sup>2+</sup>-CO<sub>3</sub><sup>2-</sup> system at pH 7-8, R<sub>UO<sub>2</sub></sub> = 99.9% when the [CO<sub>3</sub>]:[UO<sub>2</sub>]<sub>total</sub> ratio is greater than 4.0. This result corresponds to UO<sub>2</sub><sup>2+</sup> permeate concentrations 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<sub>UO<sub>2</sub></sub> values decreased to ~95% and ~80%, respectively. Uranyl rejection decreased further, to ~70%, when the feed solution is adjusted to pH 2.4. The combined effects of lowered pH and increased salt concentration provide a potential method to remove UO<sub>2</sub><sup>2+</sup> and recycle the polymer. DHBSA (I) was evaluated as a ligand for UO<sub>2</sub><sup>2+</sup> and for Th<sup>4+</sup>. With both metal ions rejection exceeded 99.9% in the pH range 5.0-6.5 for ligand:metal ratios equal to or greater than 2.0. The presence of 0.2 M NaCl caused R<sub>UO<sub>2</sub></sub> and R<sub>Th</sub> to decrease slightly to 99.8% and 99.5%, respectively. Acid stripping (pH 1-2) gave ligand recoveries of about 50%. NTA derivatives (II) with anionic (R = CH<sub>2</sub>SO<sub>3</sub><sup>-</sup>, SNTA) and hydrophobic (R = C<sub>10</sub>H<sub>21</sub>, DNTA) substituents were tested for removal of Pb<sup>2+</sup>. The latter was studied using CPN surfactant micelles as the colloidal phase. At low ionic strength SNTA gave R<sub>Pb</sub> values in the range 99.0-99.9% while DNTA gave R<sub>Pb</sub> values in the range 99.7-99.9%. In the presence of 0.05 M salt, R<sub>Pb</sub> decreased to 50-55% for SNTA with PDADMAC, but was hardly affected (R<sub>Pb</sub> = 99.5%) for DNTA with CPN. Acid stripping, combined with Pb<sup>2+</sup> precipitation using oxalate, allowed ligand recoveries of 96% and 85% for SNTA and DNTA, respectively. An 8-hydroxyquinoline derivative, C<sub>11</sub>HQ (III) was tested for removal of Cd<sup>2+</sup> using CPN and C<sub>12</sub>(EO)<sub>6</sub> surfactant micelles as the colloidal phase. For both types of surfactant, R<sub>Cd</sub> values in the range 99.0-99.7% were obtained at pH 9. The presence of added salt (10 mM NaCl) had no effect on rejection, R<sub>Cd</sub> = 99.5-99.6% in either surfactant. High Cd<sup>2+</sup> rejections were maintained in the mixtures containing either Ca<sup>2+</sup> (R<sub>Cd</sub> = 99.7%) or Zn<sup>2+</sup> (R<sub>Cd</sub> = 98.8%). Lowering pH to 6.0 resulted in ligand recoveries of ~88% (CPN) and ~50% (C<sub>12</sub>(EO)<sub>6</sub>).

**Additional studies.** The UF behavior of a cyclic phenol (calixarene) tetrasulfonate anion with PDADMAC was evaluated. Rejection values were greater than 99.8%, even in the presence of 0.5 M NaCl, indicating that calixarene derivatives are

promising ligands for LM-PEUF at high electrolyte concentrations. A macrobicyclic polyether cryptand was evaluated and found to form strong complexes with  $\text{Sr}^{2+}$  ( $\log K_{\text{SrL}} \sim 8.0$  in water) with excellent selectivity ( $K_{\text{SrL}}/K_{\text{ML}} > 200$ ) for  $\text{Sr}^{2+}$  relative to other alkali and alkaline-earth cations. Decyl thiourea,  $\text{C}_{10}\text{H}_{21}\text{NHC}(=\text{S})\text{NH}_2$ , was tested using CPN as the colloid. Preliminary studies showed excellent rejection of  $\text{Hg}^{2+}$  in acidic solution ( $R_{\text{Hg}} = 99.8$  at pH 2).

## **PLANNED ACTIVITIES**

During the next year, we will continue ultrafiltration studies on the LM-CEUF systems for removal of  $\text{UO}_2^{2+}$ ,  $\text{Th}^{4+}$ , and  $\text{Pb}^{2+}$ . Focus will be on the chemical (pH, salt concentration) and physical (applied pressure, membrane pore size) parameters that affect separation efficiency as well as ligand and polymer recovery. UF techniques will be used to evaluate membrane binding and metal ion separation behavior of new ligands for other target cations ( $\text{Pu}^{4+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sr}^{2+}$ ). Separations of other actinides (e.g., Pu) using LM-CEUF will be studied by collaborators at LLNL. Following evaluation in single cation studies, ligands displaying suitable performance will be tested using mixtures containing other cations and anions (e.g.,  $\text{CrO}_4^{2-}$ ).