# Environmental Management Science Program

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## Removal of Radioactive Cations and Anions from Polluted Water Using Ligand-Modified Colloid-Enhanced Ultrafiltration

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## Research Objective

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 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 groundwater, aqueous waste solutions and mixed waste. Separation and concentration of the target ions will result in a substantial reduction in the volume of material requiring long-term storage.

## Research Progress and Implications

This report summarizes work after 8 months of a 3-year project. In the proposed method, a soluble cationic polymer 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 polymer along with any polymer-bound species. Target cations that form anionic complexes with the ligands are electrostatically bound to the polymer and retained during the filtration step. The degree of retention of solute X is expressed as a rejection coefficient, $R_X(\%)$, where

$$R_X(\%) = \{ 1 - [X]_{per} / [X]_{ret} \} \times 100\% \qquad (1)$$

$[X]_{per}$ and $[X]_{ret}$ refer the to the concentrations of X in the permeate (filtrate) and retentate (retained) solutions, respectively. In our initial work, dialysis and UF techniques were used to test the effectiveness of carbonate as a ligand for removal of uranyl cation from water.

**Equilibrium Dialysis (ED) Studies.** Dialysis experiments have been shown to yield the same rejections as observed in ultrafiltration, so most of our results were obtained using this simple technique. The effects of uranyl and carbonate ion concentration, pH, added salt (NaCl), and polymer concentration were investigated using small (10 mL) dialysis cells with cellulose acetate membranes having a molecular weight cutoff of ~6000 Da. Unless otherwise noted, the retentate side of the cell contained 11.65 mM PDADMAC (concentration based on monomer) along with varying concentrations of $UO_2^{2+}$. Retentate and permeate compartments initially contained equal concentrations of carbonate ($NaHO_3/Na_2CO_3$). A set of baseline studies were carried out to determine the distribution of $UO_2^{2+}$ between permeate and retentate for initial conditions where (i) no carbonate or PDADMAC were present, (ii) PDADMAC, but no carbonate was present, and (iii) carbonate,

but no PDADMAC was present. For case (i) the $UO_2^{2+}$ distribution was 1:1, while for case (ii) electrostatic interaction resulted in net expulsion of ~90% of the uranyl cations into the permeate. In case (iii) a modest rejection of $UO_2^{2+}$ was observed ($RUO_2$ ~30-60%). The implications of these results are (i) that loses of $UO_2^{2+}$ on the dialysis cell walls or membrane are negligible and (ii) that uranyl cation can be removed after the first separation stage by conversion of the carbonate complexes back to cationic $UO_2^{2+}$. The result for case (iii) indicates the presence of residual membrane charges, resulting in net rejection of anionic $UO_2$-carbonate complexes without polymer present. This would tend to enhance the separation process. Based on the results of these preliminary studies, a series of ED experiments were carried out where the $UO_2^{2+}$, pH, and salt content were varied (10 mM total $CO_3$). At pH 8.3 ± 0.4, uranyl rejection varied from 99.93 to 99.98% for [$UO_2^{2+}$] total in the range 0.1-1.0 mM. At pH 10.6 ± 0.1 the rejection values decreased slightly ($RUO_2$ = 99.48-99.81%) for the same range of initial uranyl concentrations. This corresponds to about 1-4 µM $UO_2^{2+}$ in permeate. The decreased rejection at higher pH may be attributed a shift in the species distribution favoring cationic and monoanionic uranyl complexes {$(UO_2)_x(OH)_z^{2x-z}$, $(UO_2)_2CO_3(OH)_3^-$} relative to the more highly charged $UO_2(CO_3)x^{2-2x}$ species, and to the higher ionic strength of the solutions. ED studies carried out at pH ~ 8.2 in the presence of 0.2 M NaCl gave values of $RUO_2$ that varied from 33 to 44%. This dramatic decrease in the $RUO_2$ is attributed to the increased salt concentration which diminishes the polymer-anion interactions. ED studies at low pH showed the feasibility of acid stripping to remove $UO_2^{2+}$ and recover the polymer. At pH 2.3, the [U]per/[U]ret ratio after dialysis was about 1.2. Although the uranyl-carbonate complexes were dissociated, the $[U]_{per}/[U]_{ret}$ ratio was smaller than that found when solutions containing only PDADMAC and $UO_2^{2+}$ were treated by dialysis. This diminution of the ion expulsion effect is most likely due to the increased ionic strength resulting from the presence of ~5 mM HCl and $NaHCO_3$.

**Ultrafiltration Studies.** The separation behavior in an ultrafiltration (UF) unit was investigated using a 400 mL stirred cell equipped with a 10,000 Da MWCO membrane. Unless noted, feed solution composition was 5 mM PDADMAC, 0.25 mM $UO_2^{2+}$, 0.25-2.5 mM $NaHCO_3$, pH ~7-8. At pH 7-8, solutions with a [$CO_3$]:[$UO_2$] total ratio greater than 4.0 gave $RUO_2$ = 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. Addition of 0.2 M or 0.5 M NaCl to the feed solution resulted a decrease of the $RUO_2$ values to ~95% and ~80%, respectively. These results are comparable to the those obtained from ED studies. When the feed solution was adjusted to pH 2.4, uranyl rejection decreased to 70-75%. A similar result ($RUO_2$ ~80%) was obtained for UF runs using solutions at pH 7-8 containing $UO_2^{2+}$ and PDADMAC, but no $NaHCO_3$. This behavior can be attributed to charge polarization effects that are not observed in ED studies. The combined effects of lowered pH and increased salt concentration may provide a suitable method to remove $UO_2^{2+}$ and recycle the polymer.

## Planned Activities

During the next year, we will continue ultrafiltration studies on the $UO_2/CO_3$ system, with particular attention to the chemical (i.e., pH, salt conc.) and physical (applied pressure, membrane pore size) factors that affect recovery of ligand and polymer. The feasibility of extending the $UO_2/CO_3$-system to other actinides (e.g., Pu) will be investigated with collaborators at LLNL. The membrane binding properties of ligands selective for other target cations ($Th^{4+}$, $Pu^{4+}$, $U^{4+}$, $Pb^{2+}$, $Sr^{2+}$) will be investigated. Ligands to be studied include polycarboxylic acids, disulfonated catechols, and derivatives of polycyclic phenols (calix[N]arenes). ED and UF techniques will be used to evaluate metal ion separation behavior for those ligands that show suitable behavior. Following evaluation of ligands in single cation studies, ligands displaying suitable performance will be tested using mixtures containing other cations and anions (e.g., $CrO_4^{2-}$).