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Adsorption/Membrane Filtration as a Contaminant Concentration and Separation Process for Mixed Wastes and Tank Wastes

Dr. Mark M. Benjamin
University of Washington
P.O. Box 352700
Seattle, Washington 98195-2700
Phone: 206-543-7645
E-mail: markbenj@u.washington.edu

Gregory Korshin
University of Washington
P.O. Box 352700
Seattle, Washington 98195-2700
Phone: 206-543-2394
E-mail: korshin@u.washington.edu

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Dr. Mark M. Benjamin, University of Washington

Gregory Korshin, University of Washington

Research Objective

Separate Sr and Cs from other constituents Hanford tank wastes (Na, Al, NO_3 , Ca) in a form that allows them to be further processed and, ultimately, disposed of appropriately.

Research Progress and Implications

This report describes progress through May, 1998, which is a little past mid-way through the second year of a three-year project. The goal of the research is to develop a treatment system for the separation of contaminants in low-organic Hanford tank wastes into various sub-groups that are relatively easy to treat further to yield products that are amenable to final disposal. The main target contaminants are Sr and Cs, although heavy metals and actinide-group elements are also targets.

Effort during the first half-year of the project was devoted primarily to development of experimental and analytical techniques that could be used to test and quantify the treatability of Sr and Cs in the extremely complex matrix of the tank wastes. The treatment technologies to be tested for isolation of Sr from other waste constituents included adsorption of Sr onto various mineral solids and membrane separation of particulate from dissolved Sr. The proposed technology for treating Cs was electrochemically controlled, reversible binding of the Cs to hexacyanoferrates. Results obtained during the remainder of the first year suggested that hematite ($\alpha\text{-Fe}_2\text{O}_3$) and iron-oxide-coated sand (IOCS) were the best adsorbents for Sr among the oxides tested, and work during the second project year followed up on that result.

Sr adsorption from simulated tank solutions containing $\sim 3 \text{ M NaNO}_3$, $\sim 2 \text{ M NaOH}$, $\sim 0.5 \text{ M Al(NO}_3)_3$, $3 \times 10^{-5} \text{ M Sr(NO}_3)_2$, and $0.11 \text{ M Ca(NO}_3)_2$ was evaluated in systems containing hematite. The hematite (with the adsorbed Sr) and any other solids were then separated from the solution using ultrafiltration or microfiltration membranes. When the hematite was dosed at a concentration of 100 mg Fe/L in batch systems, nearly 100% of the Sr adsorbed onto the hematite. However, when this Sr:Fe ratio was scaled up and used in a continuous flow system using ultrafiltration for solid/liquid separation, Sr removal from solution was near 100% for only a short time before the removal efficiency began to decline. Over the course of two hours, the water flux through the membrane decreased from ~ 165 to $\sim 150 \text{ L/m}^2\text{-hr}$, and Sr removal declined from $\sim 100\%$ to $\sim 40\%$.

The results for treatment using IOCS were much more favorable. The simulated waste has been treated by passage through three columns in series, using a 5-min empty bed contact time in each column. A fourth column was prepared as well, and the system has been run continuously for 38 days in an arrangement where three columns are in use and the fourth is being regenerated at any given time. To date, the Sr concentration in the final effluent (from the third column in the series) has been undetectable. Each column has been regenerated (using a solution at pH 3) five times, with no apparent deterioration in performance. We propose to continue using this system for Sr treatment, exploring the effects of competing metal ions and organic complexing agents, over the next several months.

The separation of cesium from simulated Hanford waste (SHW) was pursued using an electrochemically controlled system built around an electrode modified with Co(II) hexacyanoferrate. The active phase in this electrode is $\text{Men[CoFe(CN)}_6]$, where Me is a mono- or di-valent cation that is reversibly exchangeable for cesium. The oxidation state of the iron is controlled electrochemically

by an external potentiostat. The active phase was formed by direct contact between Co(II) and hexacyanoferrate ions in the host electrode. Theoretically, the amount of cesium that can be retained by the electrode is controlled by the amount of the active phase and the oxidation state of the hexacyanoferrate iron. The reduction of Fe(III) to Fe(II) in a Cs-containing solution perturbs the charge balance of the hexacyanoferrate matrix and initiates the influx of Cs ions whose summary charge restores the electroneutrality. When the Fe(II) is electrochemically oxidized to Fe(III) in a regenerating solution, the cesium is expelled from the hexacyanoferrate matrix, and the electrode's capacity to bind Cs is restored. In theory, these cycles can be repeated indefinitely.

To study the performance of the cesium-active electrodes, three types of experiments have been conducted. First, the reactions of several non-electrochemically controlled cesium-active hexacyanoferrates (Fe, Co, Cu, Zn, Ni, Cd) were examined at varying pHs, ionic strengths, reaction times. Cobalt hexacyanoferrate was found to be superior to others in terms of pH stability and selectivity to cesium. The kinetics of incorporation of cesium into the active matrix depended to some extent on the preparation technique (e.g., freeze-drying, thermal treatment); this issue will be studied in more detail in the coming year. The pH stability of hexacyanoferrates at pH greater than 11 or 12 might be a fundamental limitation of their applicability of this approach for treating highly basic Hanford wastes without adjusting their pH.

In the second group experiments, the electrochemistry of hexacyanoferrate-modified graphite electrodes was studied. Activation substantially increased the current through the electrode. The typical peaks associated with the incorporation/ expulsion of counter-cations were observed and quantified.

In the third group of experiments, the charge passed through the electrode in solutions containing from $<10^{-5}$ to $>10^{-2}$ M cesium was measured chronoamperometrically and compared with the amount of cesium released in a regenerating solution. The amount of cesium taken up by the electrode was from 50 to 120% of the total charge associated with the oxidation/ reduction of the iron. Sodium in the concentration range up to 5 M did not interfere with the performance of the electrode.

The focus of current and planned experiments is on the stability of the modified electrodes at high pH, kinetics of cesium incorporation and release, effects of mass transfer to the electrode surface, the reuse of the regenerating solutions, and effects of interfering species on the electrode surface and the active phase. Ways to increase the amount of the active phase in the electrode, accelerate the kinetics of its reactions with cations and improve the electrochemical control are being investigated.

Planned Activities

Sr removal by IOCS will be investigated as a function of the concentration of Ca, heavy metals, and organic complexing agents. The regenerability of the IOCS over many regeneration cycles will be explored, and the possibility of reusing the regenerant solution will be explored, so that the volume of regenerant requiring further processing will be minimized. These tasks will be carried out simultaneously over the next six to eight months.

Cs removal by reversible incorporation into Co hexacyanoferrates will be explored further, with a focus on the kinetics of mass transfer and Cs binding and release, the reversibility of the binding over many cycles, and the effects of potentially competing ions. These studies will be carried out in parallel over the next nine months.