Barrier Films for Cesium or Carbon Tetrachloride

Andy Warta[1], Tsutomu Shimotori[2], William A. Arnold[2] and Edward L. Cussler Jr.[1], (1)Chemical Engineering and Materials Science, University of Minnesota, 421 Washington Ave SE, 151 Amundson Hall, Minneapolis, MN 55455, (2)Civil Engineering, University of Minnesota, 500 Pillsbury Dr S ERoom 122 CivE, Room 122 CivE, Minneapolis, MN 55455

Introduction

During and after World War II the United States has operated a nuclear weapon and fuel program. Primarily managed by the Department of Energy and Department of Defense, there are several sites where these programs were undertaken. One such site, the Hanford Site in Washington State, has been the focus of environmental research for decades due to the presence of radioactive cesium (^{137}Cs) in the soil and water around the site. The nuclear decay sequence of ^{137}Cs includes emission of high energy γ-radiation.

It is estimated during the operating life of the Hanford Site 500,000,000 m^3 of wastes were percolated to the ground including more than 40 kCi of ^{137}Cs (Garten, 2000). A second source of ground contamination was leakage of waste containers, many of which are stored underground in the 200 Area of the Hanford Site. Of the more than 28 MCi of ^{137}Cs stored in the 200 Area, an additional 40 kCi has leaked into the ground (Garten, 2000). Almost all of the radioactive material that leaks from canisters is ^{137}Cs. Of the radioactivity contained in the canisters, 40% is from ^{137}Cs. The balance of the radioactivity (primarily ^{90}Sr) stays in the sludge while ^{137}Cs is in the supernatant of the canisters. It is the liquid in the supernatant that can leak out into the surrounding soil (Gephart, 1998).

This work aims to create a reactive barrier membrane that incorporates an ion-exchanger, a crystalline silicotitanate (CST) that has a high selectivity for cesium. The CST is able to adsorb cesium from very dilute solutions and stand up to radiation (Zheng, 1996). Incorporating CST into a polymeric membrane will give a flexible barrier that can be placed around a contaminated zone and prevent radioactive cesium, which has a half-life of 30 years, from further polluting soil and water near processing plants.

The polymer used in the cesium study is polyvinylalcohol (PVA) which is highly permeable. This polymer choice was also used in previous studies which incorporated Fe^0 nanoparticles to make a barrier for carbon tetrachloride (CT) (Shimotori et al. 2004). PVA is a good model polymer for experiments, but has low mechanical strength and high permeability to water. Further research shows theories correlate well for both experiments using the model PVA system and high density polyethylene (HDPE), a much less water permeable polymer with better mechanical strength. This correlation allows for using results from PVA experiments to predict the performance of less permeable barrier membranes, for cesium and carbon tetrachloride.

Theory

Before designing a barrier to stop cesium or carbon tetrachloride from spreading out of contaminated areas, it is useful to have a measure of how well a barrier is expected to perform when a sacrificial reagent, CST or Fe^0 respectively, is added. Begin by imagining two well-stirred volumes of solution, separated by a thin barrier membrane, such as that shown in the inset to Figure 1. The "upstream" volume initially contains the contaminant while the "downstream" volume and membrane are initially contaminant-free. The gradient in contaminant concentration will cause a flux of contaminant across the membrane. The concentration of contaminant in the "downstream" volume is given by

$$c_1 = \frac{DHAc_{10}}{\ell}\left(\frac{1}{V_{upstream}} + \frac{1}{V_{downstream}}\right)\left(t - t_{lag}\right) \tag{1}$$

where D is the contaminant's diffusion coefficient in the membrane; H is its partition coefficient, that is the concentration in the membrane at equilibrium with that in the adjacent solution; c_{10} is the contaminant concentration in the loaded "upstream" solution; A and l are the membrane area and thickness, respectively; $V_{upstream}$ and $V_{downstream}$ are the two volumes and t and t_{lag} are the time and the time before any significant flux across the membrane occurs (Cussler, 1997). This equation is an approximation and much simpler than the complex exact solution (Daynes, 1920), but provides a good fit to experimental results.

The key concept for this work is the idea of the lag time, t_{lag}. This is the time before which contaminant has yet to begin leaking into the "downstream" volume. The lag time for a barrier with no reactive additive is given by

$$t_{lag} = \frac{\ell^2}{6D}\ . \tag{2}$$

After the contaminant begins to breakthrough the barrier membrane, the flux across the membrane becomes constant. The expected concentration profile for the "downstream" volume is shown in Figure 1.

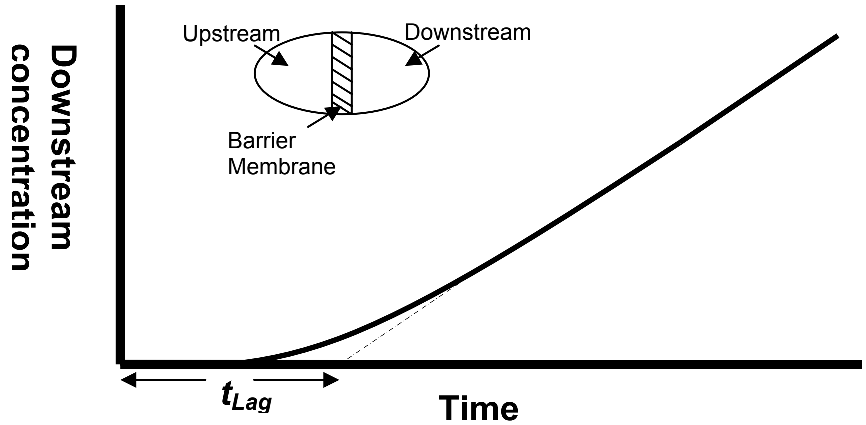

Figure 1: Expected concentration profile in the "downstream" volume of a contaminant diffusing across a barrier membrane. Inset Model of a diffusion

The goal of this research is to contain the spread of radioactive cesium or carbon tetrachloride. If we can increase a barrier's lag time for a contaminant, we can accomplish our goal. The lag time for a barrier membrane can be increased by adding a sacrificial reagent that reacts with the contaminant. If the reaction between reagent and contaminant can be taken as an instantaneous irreversible reaction, the new lag time is given by

$$t_{lag} = \left(\frac{\ell^2}{2\nu DH} \right) \frac{c_{20}}{c_{10}} \qquad (3)$$

where c_{20} is the concentration of sacrificial reagent within the barrier membrane (Yang, 2001). The stoichiometric coefficient v depends on the chemistry of the reaction. It is possible for the lag time due to the reaction to increase 100 or even 1000 times. For example, a barrier membrane with a lag time of one year could potentially become good for one century.

Results

The research aims at developing a barrier membrane for cesium ion to be used in the containment of radioactive waste at plutonium processing plants. To do this, a cesium scavenger, CST, was added to PVA membranes. These membranes were challenged with Cs^+ containing solutions and the lag times were measured. In every case the barrier membranes containing CST did significantly better than non reactive membranes.

First, the lag time of cesium ion through PVA barrier membranes was measured. These membranes contained no CST. The lag time for Cs^+ for these membranes was found to be approximately 3 minutes. Adding CST to the PVA membrane was expected to greatly increase the barrier's lag time for cesium. Equation 3 predicts that the greater the concentration of CST in the membrane, the larger the lag time will be. The relative increase of lag times for barriers with and without CST are shown in Figure 2.

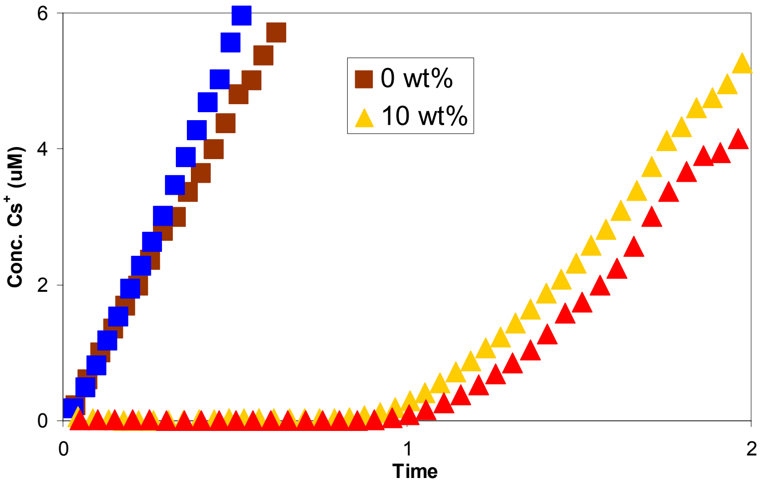

Figure 2: Downstream concentration profiles for $CsNO_3$ diffusing through PVA membranes showing lag times for cesium ion. The addition of CST to the membrane results in an increase in the lag time over the pure polymer.

Membranes with similar thicknesses but different loadings of CST were tested with the results appearing in Figure 3. The y-axis is plotted as $C/C_{(o)}$ to normalize for upstream concentration.

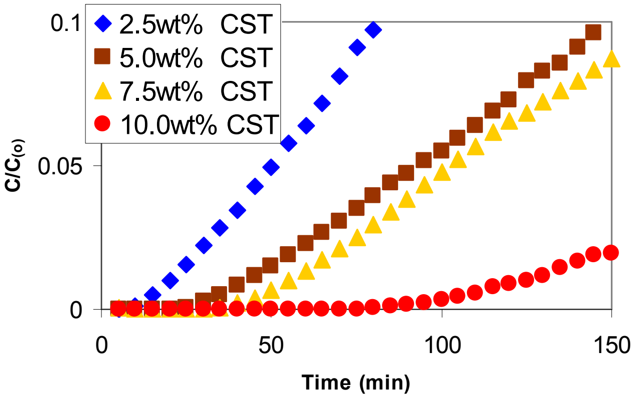

Figure 3: Effect of CST loading on cesium breakthrough curves. Addition of 10 wt% CST increases the lag time by over 30 times.

This work centers on developing barriers that can be used in areas already contaminated with radioactive cesium to prevent further ground and water pollution. A final set of tests were done to examine the ability of a CST containing barrier membrane to stop Cs^+ in a real groundwater sample, as all of the previous experiments were done using distilled water. An uncontaminated groundwater sample from the Hanford, WA plutonium processing site was spiked with $CsNO_3$ and used to challenge a CST containing barrier membrane. The very surprising results are shown in Figure 4.

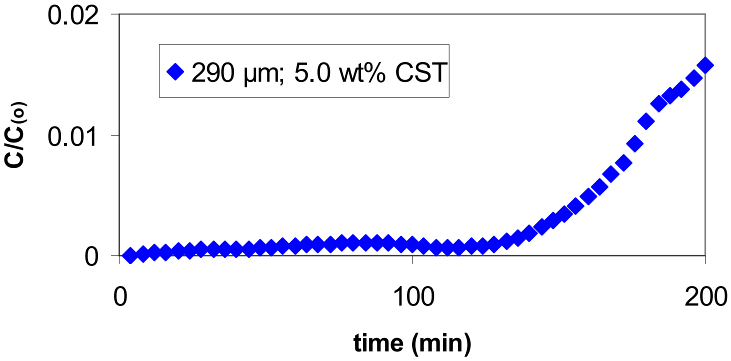

Figure 4: Breakthrough curve for cesium spiked Hanford, WA water. The 150 minute lag time is almost five times greater than predicted results and nearly 50 times greater than for a non-CST containing membrane.

Discussion

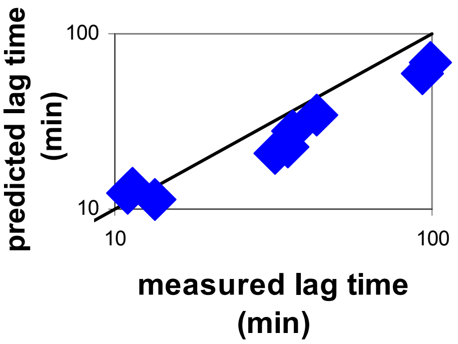

Figure 5: Experimental results show good correlation with theory.

Addition of CST to a barrier membrane greatly increases the barrier's ability to contain cesium. PVA membranes with no CST have lag times of around 3 minutes. Addition of different amounts of CST increases the lag time, as predicted by Equation 3. This equation also predicts the effect of increasing the membrane thickness and decreasing the upstream concentration of cesium. The experiments correlate well to theory, as shown in Figure 5. In fact, the lag times are found to be better than theory predicts. This is possibly due to settling of CST particles within the membrane during fabrication (Nuxoll, 2005) and a decrease in the effective upstream concentration owing to CST adsorption of cesium from solution.

The results of the experiments with groundwater from Hanford, WA are even more encouraging. Theory predicts a lag time for the membrane used to be about 31 minutes. The experimental lag time was found to be 150 minutes. Additional experiments also show similar increases in experimental lag times for barriers challenged with cesium spiked Hanford water. At this time we are unable to explain this increase in lag time. Possible causes could be an increase in the cesium capacity of CST, or a decrease in the partition coefficient of the membrane in the presence of groundwater. We will explore these explanations in the future. Regardless of the cause, greatly increased lag times mean we have an even better barrier.

The increased lag time caused by CST in PVA is significant, but PVA is not a practical polymer, the lag times are not long enough to be of use for containment. PVA was chosen for this work precisely because it is highly permeable and thus gives fast experiments. The factor by which lag times are increased is independent of the polymer used. Results using HDPE with Fe^0 for stopping carbon tetrachloride show the increase in lag time is independent of the polymer used.

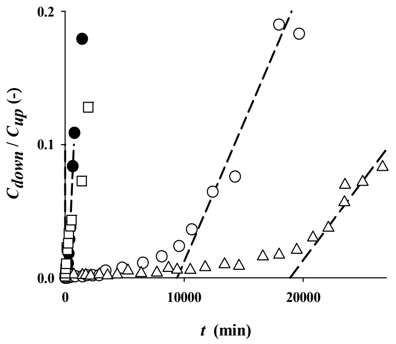

Figure 6: Breakthrough curves for HDPE (●), Fe^0/HDPE (○), and an exhausted Fe^0/HDPE membrane (□) prepared with glycerol. The dashed lines indicate the regression used to determine the lag time.

References

Cussler EL, 1997, *Diffusion* Cambridge University Press, Cambridge.

Daynes H, 1920, Proc. Roy. Soc., A97, 286.

Garten Jr CT, Hambry DM, Schreckhise RG, 2000, *Radiocesium discharges and subsequent environmental transport at the major US weapons production facilities,* The Science of the Total Environment Volume 255, 55-73.

Gephart RE, Lundgren RE, 1998, *Hanford Tank Cleanup: A Guide to Understanding the Technical Issues* 4th Edition, Battelle Press, Columbus.

Nuxoll EE, Siegel RA, Cussler EL, 2005, *Layered Reactive Barrier Films*, J. Membr. Sci., Volume 252, 29-36.

Shimotori T, Nuxoll EE, Cussler EL, Arnold WA (2004). *A polymer membrane containing* Fe^0 *as a contaminant barrier,* Environ. Sci. Technol., Volume 38(7), 2264-2270.

Yang C, Nuxoll EE, Cussler EL, 2001, *Reactive Barrier Films*, AIChE J., 47 (2), 295-302.

Zheng Z, Philip CV, Anthony RG, 1996, *Ion Exchange of Group I Metals by Hydrous Crystalline Silicotitanates,* Ind. Eng. Chem. Res. Volume 35, No. 11, 4246-4256.