

Project 86800

Reactive Membrane Barriers for Containment of Subsurface Contamination

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RESULTS TO DATE: This report summarizes work after 33 months of a three year project. A no cost extension for an additional 12 months has been approved.

This report focuses on progress made in the last 12 months, with prior results briefly summarized. We emphasize that the key to our work is an increase in barrier properties. Thus, much of our work has focused on poor, thin barriers composed of PVA. WE have done so because experiments are then able to be conducted over reasonable times. At the same time, we have developed and experimentally verified theories showing how our short experiments can be extrapolated to real situations.

Acid Barriers

Initial studies were performed with acid as a model contaminant, zinc oxide as the reactive material, and inclusions of mica or clay flakes. Permeability reductions of 10 to 4000 times were observed in flake-filled composite membranes. The inclusion of zinc oxide increased the time to permeate across the film by as much as 3000-fold. Both of these effects can be predicted theoretically without adjustable parameters. We have also shown that these effects can be combined to yield still better barriers.

Polyvinyl Alcohol Contaminant Barriers

Polyvinyl alcohol (PVA) membranes containing zero-valent iron (Fe0) particles were developed and tested as model barriers for a variety of environmental contaminants. Results were present in previous reports and have been published (Shimotori, T.; Nuxoll, E. E.; Cussler, E. L. and W. A. Arnold, 2004. A Polymer Membrane Containing Fe0 as a Contaminant Barrier. *Environmental Science and Technology*, v. 38(7), pp. 2264-2270).

PVA membranes containing crystalline silicotitanate to capture cesium (Cs+) have also been developed. First, the lag time of cesium ion through PVA barrier membranes was measured. These membranes contained no CST and results were reproducible. The lag time for Cs+ for these membranes was found to be approximately 3 minutes. Adding CST to the PVA membrane greatly increases the barrier's lag time for cesium. Membranes with similar thicknesses but different loadings of CST were tested. The y-axis is plotted as $C/C(o)$ to normalize for upstream concentration. The increases exceed 30-fold.

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 CsNO3 and used to challenge a CST containing barrier membrane. The very surprising result was a 5-fold increase in lag time compared to experiments using distilled 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.

Addition of CST to a barrier membrane greatly increases the barrier's ability to contain cesium. The experiments correlate well to theory. 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 and a decrease in the effective upstream concentration owing to CST adsorption of cesium from solution (see Modeling below).

HDPE membranes containing Fe0 Compared with diffusion experiments using PVA-based membranes, those using HDPE-membranes take much longer due to HDPE's low permeability. Previously, a flow-through cell connected to a pump and reservoir was adopted for the HDPE experiments. This setup, however, could not keep the contaminant concentration in the upstream cell constant. This decrease of the upstream concentration may bias the evaluation of membrane performance. A new apparatus was implemented consisting of two closed-cells, with a small cell on the downstream side and a large cell on the upstream side. The two cells are separated by membrane, and the joint is doubly sealed by epoxy glue and silicone glue and held together by a U-clamp. This new apparatus allowed us to keep the upstream concentration more constant and to collect consistent data. Diffusion coefficients for carbon tetrachloride and chloroform were determined to be 1.34×10^{-13} m²/s and 3.00×10^{-13} m²/s, respectively in HDPE. These values are comparable to those reported by past studies using other chlorinated solvents.

In the previous report, glycerol was used as an additive to make Fe0/HDPE membranes to prevent oxidation of iron particles. We have also succeeded in making Fe0/HDPE without glycerol by covering the batch mixer and heated press with a plastic bag and flushing it with N₂ continuously during the membrane preparation. Comparison of HDPE and Fe0/HDPE prepared in this manner showed no significant difference in the breakthrough lag time for these membranes. Without glycerol, the iron is ineffective. This suggests that glycerol is key to a successful reactive membrane.

Another improvement made is the achievement of longer lag times using Fe0/HDPE/glycerol membranes. This is done by simply doubling the iron content. In the previous report, all lag times were below 1500 min using Fe0(10wt%)/HDPE/glycerol. Using Fe0(20wt%)/HDPE/glycerol, we observed 9420 min and 18900 min for the membrane thickness of 166mm and 269 mm, respectively. Doubling of the iron content was expected to double the lag time, but the effect was actually more than double. Still, estimations imply that only 1-2 % of iron is used for the reaction with carbon tetrachloride. Increasing this reactive iron fraction will be key to further increases in lag time.

Other configurations

In an attempt to increase the water content in a polyethylene membrane to stimulate reaction of Fe0 while keeping its permeability low, a 15%PVA-85% PE co-polymer was used instead of HDPE. It was hoped that hydrophilic PVA portion of the polymer would provide water for the reaction and that the hydrophobic PE would keep the permeability low.

Swelling of the polymer in water was negligible, suggesting low water content in the co-polymer. Using the same method for Fe0/HDPE/glycerol membrane production, pure 15%PVA-85%PE membranes and Fe0(10wt%)/15%PVA-85%PE/glycerol membranes were prepared. The two formulations were compared in diaphragm diffusion experiments, and the results showed: (1) the permeability of 15%PVA-85%PE membrane is almost as large as that for a PVA membrane, and (2) no measurable effect of Fe0 was observed. Using a co-polymer is not effective, and we will not pursue this further at this time.

Modeling

Our theories depend on the sacrificial reagent reacting faster than diffusion across the membrane. In more quantitative terms, the second Damkohler number must be large. Because this is a potentially crippling flaw in other reactive barrier systems, we have studied it carefully.

Past modeling efforts suggested two membrane performance parameters which quantify the solute flux after contaminant breakthrough: the leakage and the kill time. The kill time is the time at which the total amount of solute that has passed through the barrier is deemed unacceptable. The leakage quantifies not

only how much contaminant leaks through, but also how long it is there. We have successfully evaluated the leakage and kill time as a function of particle loading and reaction rate.

Previous theories and equations were modified to explain the performance of the CST/PVA membranes that were better than expected. One possibility is the settling of the CST. However, we can see a second, more fundamental reason why the membranes are behaving better than expected. This is the result of the nonlinear isotherm operating in this system.

For an instantaneous, irreversible reaction, the lag time is $t_{lag} = (l^2) * C_{20} / (2 * D * H * C_{10})$ where l is the membrane thickness, C_{20} is the concentration of CST, D is the diffusion coefficient of Cs^+ , H is the partition coefficient of Cs^+ , and C_{10} is the initial upstream concentration of Cs^+ . If the reaction is instantaneous but stops at some equilibrium concentration C_{ie} , which is roughly the shoulder of the isotherm for Cs^+ sorption by CST, the lag time becomes $t_{lag} = (l^2) * C_{20} / (2 * D * H * [C_{10} - C_{ie}])$. This does predict that the lag times should be longer than those expected from the previous equation. However, at this point we are unsure if this argument is more appropriate than an uneven distribution of CST.

So far, our modeling has been focused on behavior of the mobile reactant (contaminant). A new phase of our modeling efforts looks at the behavior of a mobile product as a result of reaction between a contaminant and immobile reagent. The mobile product can be a degradation product of the contaminant or a dissolution product of the reactive material, but the form of the diffusion equation should be same for both. This modeling of a mobile product is particularly important if the product is of environmental concern. It is therefore significant for this study. We have chosen to study the acid barriers containing zinc oxide to validate the model. Rather than only monitor the lag time of the acid, we also measured to release of zinc ion (Zn^{2+}) into the downstream and upstream cells. This relevant equations are solved numerically or analytically with simplifying assumptions. Both methods produce nearly identical results that closely match the experimental data. One interesting characteristic of this concentration profile is that the downstream concentration initially increases, reaches a peak, then decreases. This peak time coincides with the breakthrough time of the acid.