Environmental Management Science Program (EMSP) Annual Report

Project Number: 86800

Project Title: Reactive Membrane Barriers for the Containment of Subsurface Contamination

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Research Objectives

The treatment or remediation of contaminants at some sites is neither technically nor economically feasible. Containment or stabilization of these subsurface contaminants, therefore, may be the only viable alternative for the protection of human and ecological health. The overall goal of the proposed research is the development of reactive membrane barriers which dramatically enhance containment. Reactive particles in these barriers serve to either immobilize or transform contaminants within the membrane, and thus increase the time to breakthrough. These membranes are a powerful, novel, and versatile technique to contain and stabilize subsurface contaminants. This work focuses on reactive membrane barriers containing either zero-valent iron (Fe^0) particles (which can reduce metals and chlorinated solvents) or crystalline silicotitanate (CST, a selective ion exchanger of cesium and strontium) particles.

The specific objectives of this project are to manufacture, test, and model the performance of the reactive membrane barriers described above. Specific tasks are to:

1. Manufacture and test polyvinyl alcohol (PVA) membranes containing reactive particles with and without inert particles/flakes.
2. Manufacture and test high density polyethylene (HDPE) membranes containing reactive particles with and without inert particles/flakes.
3. Test the performance of the membranes with groundwater collected from one or more DOE sites to determine whether interference by components in the groundwater matrix occurs.
4. Use mathematical and/or numerical models to develop a set of analytical guidelines that facilitate the development of reactive barrier films to allow their application at contaminated DOE sites.

Research Progress and Implications

This report summarizes work after nine months of a three year project.

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 reduced permeability can occur either because of chemically reactive groups in the membrane or because of mica or clay flakes aligned parallel to the membrane surface which increase the diffusion path length.

The inclusion of zinc oxide increased the time to permeate across the film by as much as 3000-fold. Mica flakes reduce both the permeation time and the leak rate by as much as 100 times. 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.

Contaminant Barriers

Polyvinyl alcohol (PVA) membranes containing zero-valent iron (Fe^0) particles were developed and tested as model barriers for a variety of environmental contaminants. PVA was selected as a model polymer material because it is easy to synthesize and has high permeability which allows quick measurement of breakthrough lag time. Fe^0 was selected as the immobilized reactant, for Fe^0 is known to reductively transform oxidized contaminants such as chlorinated solvents, nitroaromatic compounds, and heavy metal ions. Carbon tetrachloride (CCl_4), cupric ion (Cu^{2+}), nitrobenzene, 4-nitroacetophenone, and chromate (CrO_4^{2-}) were selected as model contaminants.

The theory for diffusion through a membrane without reaction predicts that the downstream concentration changes according to the following equation *at the beginning of the breakthrough*:

$$\frac{C_{down}}{C_{up}} = \frac{PA}{LV_d}\left(t - t_{lag}\right) \text{ where } t_{lag} = \frac{L^2}{6D_m} \qquad (1)$$

where C_{down} and C_{up} are the contaminant concentrations in the downstream and upstream cells, D_m is the diffusion coefficient for the selected contaminant in the membrane, P is permeability of the membrane for the contaminant ($P = H_m D_m$ where H_m is a membrane-water partition coefficient for the contaminant into the membrane), L is the membrane thickness, V_d is the volume of the downstream cell, A is the cross-sectional area of the membrane available for diffusion, and t and t_{lag} are time and breakthrough lag time, respectively.

For a membrane containing a reactive material that consumes contaminants via an irreversible reaction, the equation changes to:

$$\frac{C_{down}}{C_{up}} = \frac{PA}{LV_d}\left(t - t_{lag}\right) \text{ and } t_{lag} = \frac{L^2 C_0}{2\nu P C_{up}} \qquad (2)$$

where ν is a stoichiometric coefficient of the reaction. In this work, ν is 1 for carbon tetrachloride (i.e. the major product in a short experiment is chloroform), 1 for Cu^{2+}, 3 for nitrobenzene and 4-nitroacetophenone, and 1.5 for CrO_4^{2-}. In equation (2), C_0 is the initial

concentration of the reactive material (*e.g.,* Fe^0 in this study) in the membrane. This equation assumes a constant C_{up} and an instantaneous reaction (i.e. the reaction is much faster than diffusion through the membrane).

Breakthrough curves of carbon tetrachloride, Cu^{2+}, nitrobenzene, 4-nitroacetophenone, and CrO_4^{2-} through pure PVA and Fe^0/PVA membranes are shown in Figure 1. The lag times without reaction are less than two minutes. The lag times with reactions are much larger, as Figure 1 shows. The dashed lines, which were obtained by regression of selected data points at the beginning of the breakthrough, are related to the steady-state flux of the contaminant. A clear increase in the breakthrough lag time was found for carbon tetrachloride and Cu^{2+}. The lag times shown for Fe^0/PVA membranes against carbon tetrachloride and Cu^{2+} are 352 min and 374 min, respectively, while the corresponding lag times for PVA membranes are respectively 1.4 min and 1.0 min (after adjustments). The similar slopes of the breakthrough curves for PVA and Fe^0/PVA revealed that the permeability was not affected by the presence of Fe^0. Similar, but smaller effects of the Fe^0 were observed for the nitroaromatic species and chromate.

Eq 2 can predict the diffusion lag time for the Fe^0/PVA membranes by assuming that all of the iron in the membrane is consumed before the breakthrough. The required parameters (L, C_0, C_{up}, v) are all known from the experiments, and P is obtained from a diffusion experiment using a pure PVA membrane. The theory does predict increases in lag times of 100 or more times, which are observed. The increases measured, however, are less than predicted. The ratio of the predicted lag time to the corresponding experimental value is smallest for Cu^{2+} ($\cong 2$), larger for carbon tetrachloride, nitrobenzene, and 4-nitroacetophenone ($\cong 6$), and largest for CrO_4^{2-} ($\cong 13$).

We believe that theory and experiment disagree because not all of the reactive material in the membrane is consumed by the contaminant. In particular, only 44.7 % of the iron (based on the dry membrane prior to hydration) is used for the reaction with Cu^{2+} before the breakthrough and 19.0 % for carbon tetrachloride. The same analysis show that 24.5 %, 16.7 %, and 6.0 % of the iron is available for nitrobenzene, 4-nitroacetophenone, and CrO_4^{2-}, respectively. These numbers do not account for iron loss during hydration of the PVA membrane (~50%). Thus, of the iron remaining in the membrane after hydration, 89% is used by Cu^{2+} and 38% by carbon tetrachloride. We hypothesize that the remaining iron is still contained within the membrane and coated with an iron hydroxide which slows the reaction to a point where contaminants can diffuse across the film before they react with the reactive particles.

We also recognize that use of the Fe^0/PVA membranes as a model barrier has two disadvantages. The iron reacts with water, and it is susceptible to oxidation in air. Water and air are present due to large free volume in the PVA matrix. The hydrated PVA membrane is 50 % water by volume, which makes PVA highly permeable to dissolved species. In engineering applications using less permeable materials such as HDPE, which can contain less than 0.03 wt% water, such problems will be much less significant. As a result, Fe^0 will be mainly used for reaction with contaminants, and we expect the barrier membrane life will be much longer.

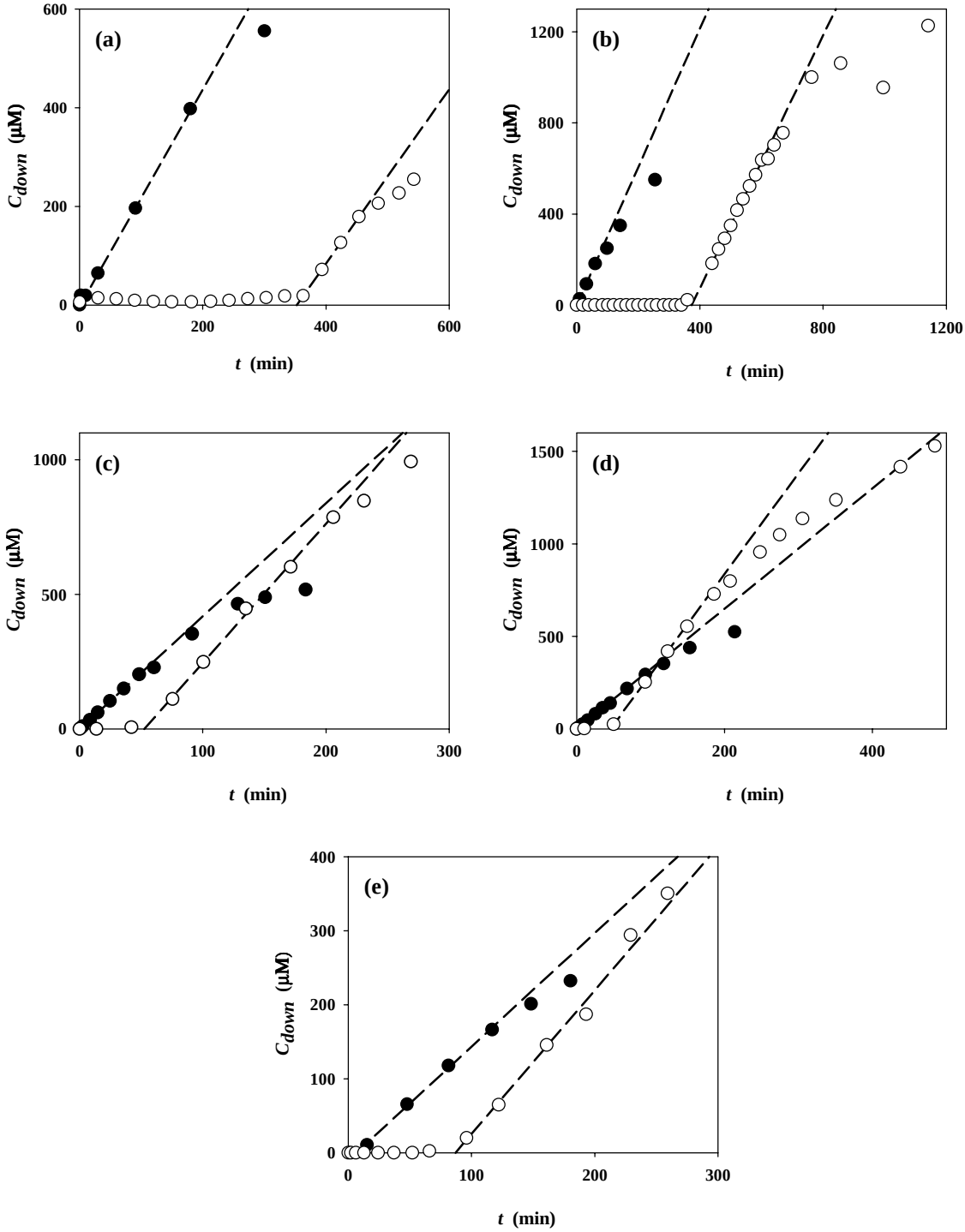

Figure 1. The breakthrough curves through PVA (●) and Fe^0/PVA (○) membranes: (a) carbon tetrachloride, (b) Cu^{2+}, (c) nitrobenzene, (d) 4-nitroacetophenone, and (e) CrO_4^{2-}. The dashed lines are related to the steady-state flux.

Modeling

A numerical model for a system of spherical, uniformly distributed reactive particles within a barrier membrane was also developed. It is assumed that the particles shrink uniformly as the reaction occurs. The key parameters are the ratio of reaction rate versus diffusion rate (the Damköhler number), particle loading, and membrane thickness. The coupled, non-linear partial differential equations are solved using a centered finite difference method in space and the explicit Euler method in time. The model suggests 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.

Planned Activities

In the next 12 months, planned activities include: 1) testing matrix effects on the Fe^0/PVA membrane by performing experiments with uncontaminated groundwater obtained from the Hanford site; 2) synthesizing and testing HDPE membranes containing Fe^0; 3) synthesizing and testing CST/PVA membranes as a model cesium and strontium barrier; and 4) continuing to develop analytical and numerical models for reactive barrier membrane design.

Information Access

Papers were presented at the American Institute of Chemical Engineering (AIChE) Annual Meeting (Nov. 2002) and the American Chemical Society (ACS) National Meeting (March 2003). A manuscript reporting our efforts with the Fe^0/PVA membranes will be submitted in June 2003.