diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Diffusion Barriers

E.L. Cussler

Department of Chemical Engineering and Materials Science
University of Minnesota
Minneapolis, MN 55455
U.S.A.

1. Introduction

Diffusion is interesting because it is slow. As a result, many studies of diffusion seek ways to make the process fast and selective. For example, most membrane separations use thin polymer films to recover particular chemicals. Nitrogen is separated from air, and water is purified by ultrafiltration. This is an active and important area of diffusion research.

However, in other cases, we may seek to slow diffusion rather than to accelerate it. We may want protection from acids or oxygen. Paints and packaging are examples with this goal. In these cases we are seeking not to make diffusion fast and selective but to make it as slow as possible.

The obvious way to retard diffusion is to use thicker layers of less permeable polymers. However, as the data in Figure 1 show, this may often be difficult: a polymer which is highly impermeable to water may be highly permeable to oxygen. Even when we can achieve low permeabilities of many solutes, we almost always want still thinner coatings of still less permeable materials. In some cases, we want to reduce the permeability by a factor of 10,000. This is the goal for this research: how can we reduce the permeability of any diffusion barrier by a factor of 10,000?

In this paper, we discuss two possible routes for this reduction. The first is to incorporate immobile reactive groups into the diffusion barrier. These groups react with particular diffusing solutes and hence retard permeation of those solutes. Alternatively, we can use as diffusion barriers composite materials containing aligned impermeable flakes. The flakes force a tortuous path across the barrier. The first of these methods, reactive solutes, can reduce the unsteady state permeation by factor of 1000. The incorporation of aligned flakes can reduce both unsteady and steady state permeation by a factor of as much as 100. By combining these two methods, we can approach by our target of 10,000. The details of how this is accomplished are given in the remainder of this paper.

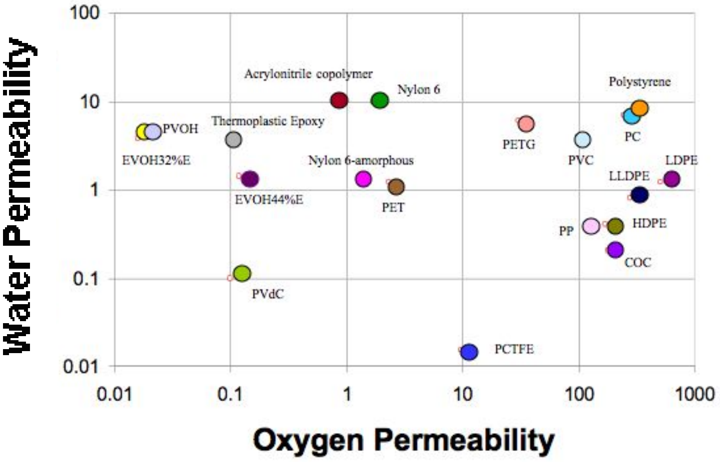

Figure 1. Oxygen vs Water Permeability for Various Polymers

2. Slowing Diffusion with Reactive Barriers

To facilitate our discussion, we will focus on a particular experiment in a diffusion cell like that shown in Figure 2. This cell consists of two well-stirred volumes separated by a thin diffusion barrier. One of the volumes contains a high concentration of the solute of interest, but the other volume initially contains only solvent. By measuring the rate at which solute goes from the volume at high concentration to the volume which is initially solute free, we can evaluate the success of any diffusion barrier. While the apparatus in Figure 2 is specific to gases whose concentrations are measured by pressure or by gas chromatography, we can make a similar experiment for liquids where the concentration is measured by changes in pH or light absorption.

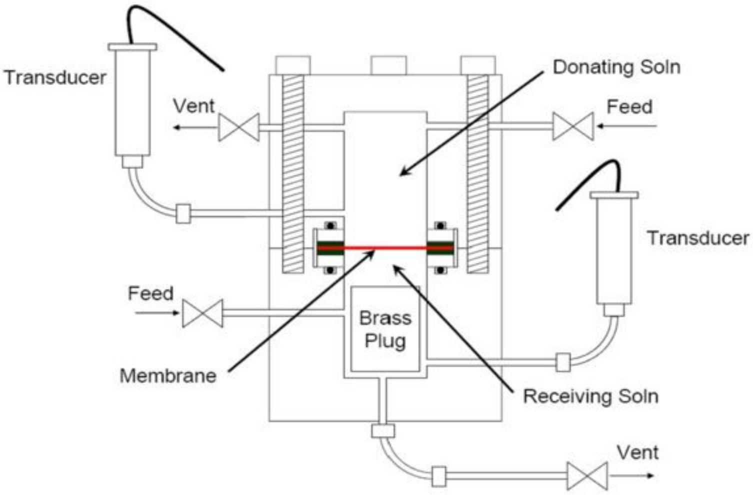

Figure 2. Basic Experiment Gases

The key equation describing the concentration c_1 in the initially solvent-free volume is

$$\frac{c_1}{c_{10}} = \frac{PA}{V\ell}\left(t - \frac{\ell^2}{6D}\right) \tag{1}$$

where c_{10} is the high concentration in one volume, P is the permeability of the diffusion barrier, A is its cross-sectional area, ℓ is its thickness, V is the volume of the originally solvent-free volume, t is the time, and D is the diffusion coefficient. Note that this equation predicts that after a lag, the concentration will rise linearly with time. This rise or leak rate is proportional to the permeability P and is essentially a steady state value. The permeability is, of course, the product of a diffusion coefficient D and a partition coefficient H, which is the equilibrium solubility in the barrier divided that in the adjacent solution. Thus, the leak rate depends on the permeability.

This linear region exists only after an initial time lag given by $(\ell^2/6D)$. This lag represents the time it takes for the solute to initially breach the diffusion barrier and approach its steady state leak rate. As Eq. 1 shows, the lag is not proportional to the permeability P, but to the diffusion coefficient D. Thus this basic experiment is characterized by two quantities, a steady state leak rate proportional to the permeability and an unsteady state time lag proportional to the diffusion coefficient.

We now turn from this simplest reaction-free case to the case where there is a chemical reaction with a second immobile solute in the film. For simplicity, we consider only the case where the reaction is fast and irreversible, like an acid-base reaction. In this case, the concentration in the initially solute-free volume is given by

$$\frac{c_1}{c_{10}} = \frac{PA}{V\ell}\left(t - \frac{\nu\ell^2 c_{20}}{2Pc_{10}}\right) \tag{2}$$

The new parameters in this equation are c_{20}, the concentration of the immobile reactive species, and ν, which is a stoichiometric coefficient. As before, this equation suggests that at larger times, the concentration will rise linearly with the time. The slope of this leak rate is again proportional to the permeability P and is unchanged by the presence of the reagent. Thus the leak rate is the same in the nonreactive case and in the case of rapid irreversible chemical reaction.

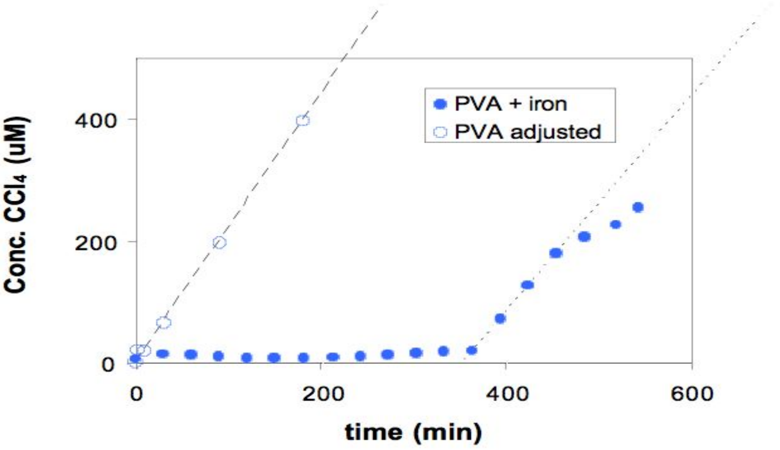

Figure 3. Carbon Tetrachloride in Landfills

However, the lag in the reactive case is dramatically different. It still depends on the square of the membrane thickness ℓ, but it now also depends on the concentration of the reagent species. Interestingly, it depends inversely not on the diffusion coefficient D, but on the permeability P. In practice, this new lag $(\nu l^2 c_{20}/2Pc_{10})$ is much larger than in the nonreactive case. As we will show below, it is often possible to make the lag 100 or 1000 times larger than in the nonreactive case. However, this better barrier exists only in unsteady state. Once the diffusion barrier is breached, it leaks just the way it did before.

We can illustrate these features by three examples. The first example is the escape of carbon tetracholoride from landfills lined with a barrier, which is sometimes called a "geotextile." As Figure 3 shows, carbon tetrachloride quickly penetrates a thin polyvinylalcohol barrier, as shown by the open circles. However, when nanoparticles of iron are added to this same membrane, the lag is increased dramatically by over 200 times, as shown by the filled circles. Similar results are obtained with other polymers like polyethylene, but the experiments are much, much longer. Thus, if the geotextile without iron is a good barrier for a month, it will be a good barrier for 15 years when nanoparticles of iron are blended into the polymer.

As a second example, we consider the containment of Cs-137, a radioactive isotope made in the manufacture of atomic weapons. This isotope is unusually dangerous because it is water soluble. It is currently stored in steel tanks which are nearing the end of their design life. If these tanks were to rupture, they could cause catastrophe in any communities which use water from the watershed around the radioactive storage.

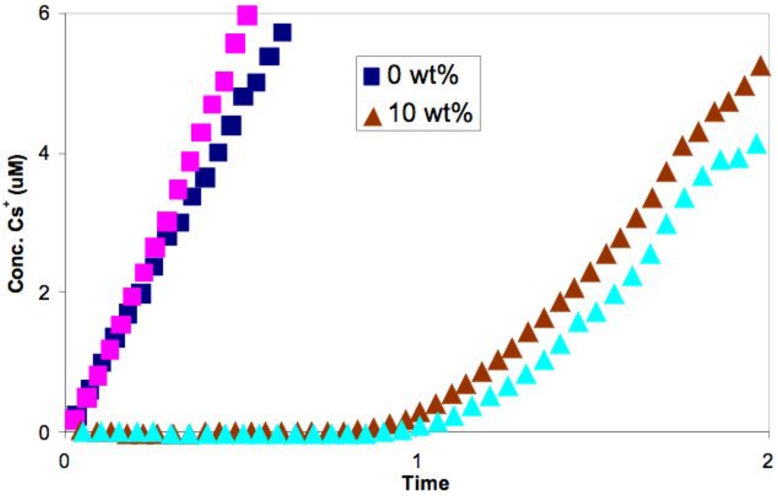

Figure 4. Cesium-137 Containment

As shown in Figure 4, the cesium escape can be retarded by adding crystalline silicon titanate or “CST” to a polymer film which surrounds the radioactive storage. If there is no CST in the polymer film, this cesium gets across the film quickly. However, if the film contains 10 wt% CST, the cesium escape is retarded by a factor 80. Remember that this retardation is an unsteady state effect, and the cesium eventually does breach the film. While the rate at which it leaks is somewhat lower than the rate of the CST-free film, it does eventually leak. (We are not sure why this leak, once it occurs, is not the same rate as the leak in the absence of CST).

We can test this analysis more completely by looking at the simple system of zinc oxide incorporated into a polyvinylalcohol membrane and challenged by solutions of hydrochloric acid. In this case, we measure the lag as a change of pH. We then can compare this lag with the value calculated from Eq. 2. This comparison is given in Figure 5. The ordinate shows the measured lag time and the abscissa is its calculated value. The solid line, which is the theoretical result calculated from Eq. 2, has no adjustable parameters. The agreement between theory and experiment is good.

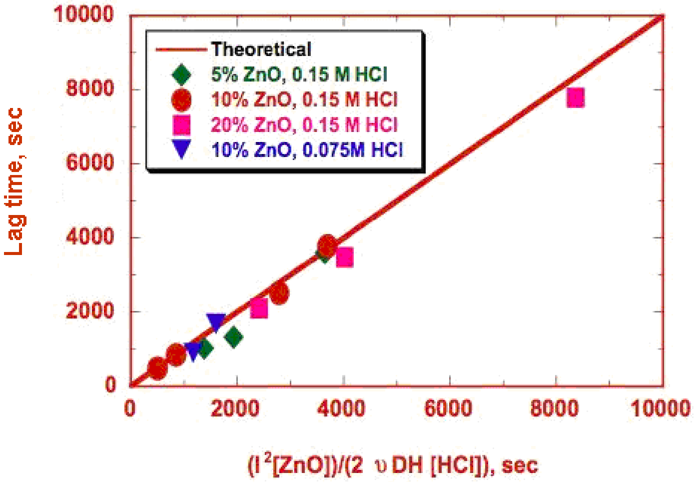

Figure 5. Predicted Lag equals Experimental Lag

We must again emphasize that the lag in these cases is an unsteady-state effect. While we can increase the lag by 1000 times or more, the barrier will eventually fail. The saving grace is that if our barrier previously worked for a week, the factor of 1000 means that our new barrier will work for almost 20 years.

3. Barriers with Aligned Flakes

We now turn to the case of thin polymer film containing aligned flakes of still less permeable material. One example which is convenient to study is a polymer like polyethylene filled with flakes of mica. In many cases, we will have a film which is still quite flexible. Thus we have the promise of having the mechanical properties of the original polymer but the diffusion properties of the crystalline, inorganic mica.

In this case, we are interested in how the permeability changes with the volume fraction of flakes ϕ and the aspect ratio of the flakes α. This aspect ratio is defined as the intermediate dimension divided by the smallest dimension. Thus, for example, for ribbon-shaped flakes which are very long, the aspect ratio α is the width divided by the thickness of the ribbon.

We are interested in two special cases, both of which involve dilute flakes, that is, cases where the volume fraction ϕ is much less than one. In the first of these cases, often called the dilute limit, the product of concentration and shape $\phi\alpha$ is also less than one. In this case, the permeability does not change much. In a second, more interesting case called the semi-dilute limit, ϕ is much less than one but $\alpha\phi$ is much greater than one. In this case, the permeability of the barrier is dramatically changed.

How the permeability is changed in this semi-dilute case is best seen by referring to the same key experiment shown in Figure 2, and described for nonreactive films by Eq. 1, and for reactive films by Eq. 2. The corresponding result for flake-filled films is

$$\frac{c_1}{c_{10}} = \frac{PA}{v\ell}\left\{\frac{1}{1+\dfrac{\alpha^2\phi^2}{1-\phi}}\right\}\left(t - \frac{\ell^2}{6D}\left[\alpha^2\phi^2 + 1\right]\right) \tag{3}$$

This differs from Eq. 1 because of the factors in braces and square brackets. The factor in the braces gives the reduction in the leak rate caused by the presence of the flakes. The factor in the square brackets gives the change in the lag time caused by the flakes. Thus, unlike the case of chemically reactive barriers, the flakes both reduce the steady state leak rate and increase the unsteady lag.

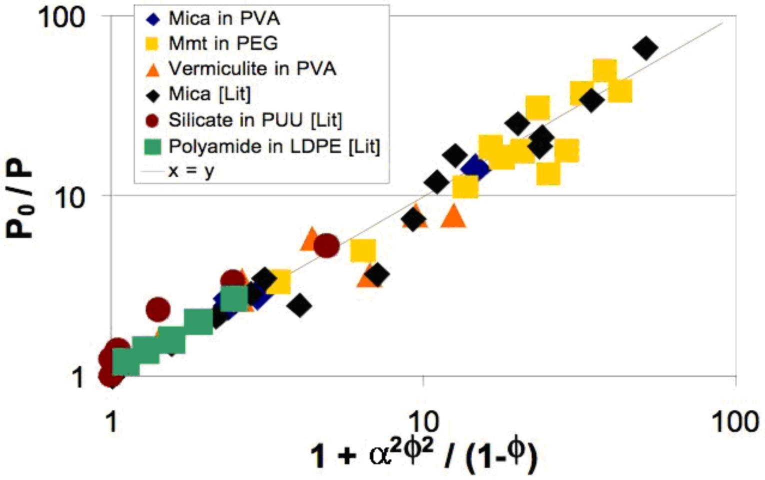

Figure 6. Permeability of Various Flake-Filled Films

Some of the results obtained with membranes containing aligned flakes are shown in Figure 6. In this figure, the ordinate gives the permeability without flakes P_0 divided the permeability with flakes P. Large values of this ratio are evidence of effective barriers. The abscissa gives the factor in braces in Equation 3, which measures the steady-state effect of the aligned flakes. The experimental permeability shown on the ordinate correlates well with the function of flake shape and concentration shown on the abscissa. This is true for a wide variety of materials: mica in polyvinylalcohol, montmorillanite in polyethylene glycol, vermiculite in polyethylene glycol, silicate flakes in polyurethanes and polyamide flakes in low-density polyethylene. In every case, the correlation between theory and experiment is strong.

I must stress that the function in braces in Eq. 3 is controversial, challenged by many competing arguments. To expand on this controversy, we discuss two additional kinds of experiments. First, we made 100 µm flakes of titanium in a polydimethylsiloxane matrix using the techniques of photolithography. An example of these materials is shown at the right of Figure 7. At the left of Figure 7, we show that it takes three layers of square flakes to completely obscure the underlying surface. Thus we would expect that one layer of flakes would not cause a tortuous diffusion path, but rather would function primarily by solute being forced to neck down into a smaller area. Two layers would still leave gaps. Only three layers will begin to cause tortuousity.

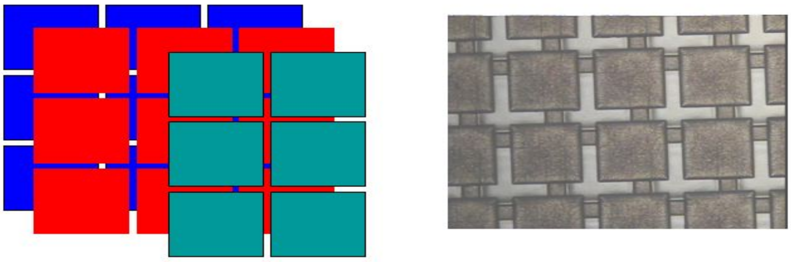

Figure 7. Lithographically-Made Flakes

These results are supported by the gas permeation experiments in an apparatus like that in Figure 2 and shown in Figure 8. On the ordinate of this graph is the concentration difference of helium divided by the initial concentration. These concentrations are measured as partial pressure differences. On the abscissa is the time divided by the membrane thickness. Putting in one layer of flakes retards the diffusion; putting in three or five layers retards it by more but by the same amount. This is consistent with Eq. 3.

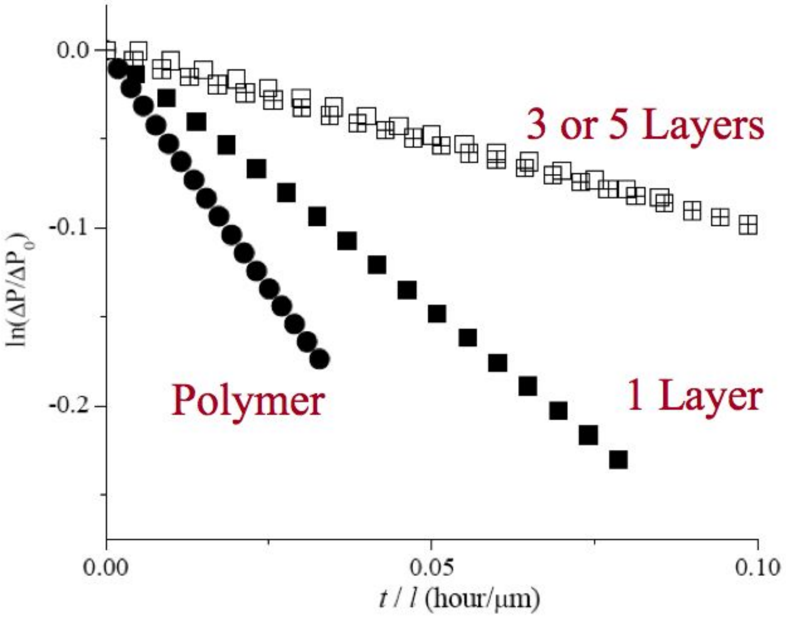

Figure 8. Self-Assembled Flakes of Block Copolymers

As a second example, we show the permeability across a block copolymer of polystyrene (PS) and polylactic acid (PLA). Polystyrene is a glass and polylactic acid is a rubber. Under most circumstances, the permeability would be dominated by that of the more permeable polymer, that is, by the polylactic acid. In this particular case, however, the block copolymer is chosen so that it self-assembles into a layered structure rather like the structure of the mica flakes. If we measure the helium concentration as a function of time, we obtain different permeabilities *B,* in the rubber P_{PLA}, the glass P_s, and the composite *P*, as shown in Figure 9. The data show that the rubber is highly permeable, and that the glass is considerably less permeable. The composite is intermediate but is consistent with a permeability calculated as resistances in series:

$$\frac{1}{P} = \frac{1-\phi}{P_{PLA}} + \frac{\phi}{P_{PS}} \tag{4}$$

Again, we have a permeability of a composite structure which is in agreement with what we would expect from diffusion theory.

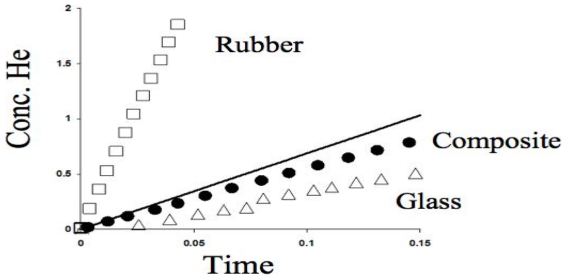

Figure 9. Results with Self-Assembled Flakes

4. Barriers with Reactions and Flakes

Finally, we might ask whether the effects of reaction, which produce an unsteady state result of a factor of 1000 or more, can be combined with the presence of flakes, which produce steady state permeability changes up to a factor of 50. That these two effects can be combined is shown by the data in Figure 10. The ordinate gives the measured experimental lag, and the abscissa reports the predicted lag. We see good agreement for systems that contain mica, zinc oxide challenged by hydrochloric acid, and a combination of mica and zinc oxide. Thus we believe that these two effects can be effectively combined. We should stress, however, that this is true only for the unsteady state case where both reactions and flakes are effective. In the steady state case, we would expect the reactions to have relatively little effect.

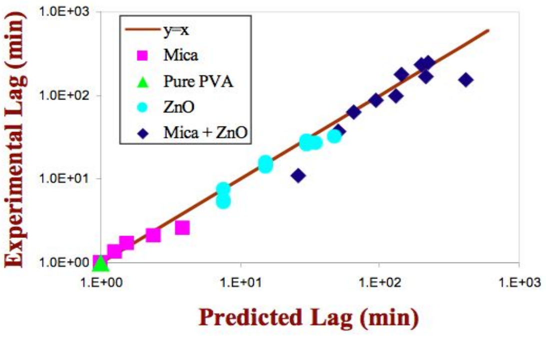

Figure 10. Lags Caused by Reactions and Flakes

5. Conclusions

In this paper, we present a strategy for improving the barrier properties of any polymer. We can use reactive membranes to increase the lag time by a factor of 1000. We can use flake-filled membranes to increase the lag time by a factor of 50 and reduce the steady-state leak rate by a similar factor. We can even get orientation from self-assembly of block copolymers, although the permeation may be significantly faster than what can be expected with inorganic flakes. In any case, we can get close to our original objective of reducing the permeability of any material by a factor of 10,000.

Further Reading

Brydges, W.T., S.T. Gulate, G. Baum, "Permeability of glass ribbon-reinforced composites," *J. Mater. Sci.,* **10** 2044-2049 (1975).

Cussler, E.L., "Membranes Containing Selective Flakes," *J. Memb. Sci.* **52**, 275-288 (1990).

Cussler, E.L., S.E. Hughes, W.J. Ward, and R. Aris, "Barrier Membranes," *J. Memb. Sci.* **38** 161-174 (1988).

De Rocher, J.P., B.T. Gettlefinger, J. Wang, E.E. Nuxoll, and E.L. Cussler, "Barrier membranes with different sizes of aligned flakes," *J. Memb. Sci.* **254**, 21-30 (2005).

Eitzman, D.M., R.R. Melkote and E.L. Cussler, "Barrier Membranes with Tipped Impermeable Flakes", *AIChE J.* **42**, 2-9 (1996).

Fredrickson, G.H., J. Bicerano, "Barrier properties of oriented disc composites," *J. Chem. Phys*., **110** 2181-2188(1999).

Lape, N. K., Chuanfang Yang, and E. L. Cussler, "Flake-Filled Reactive Membranes," *J. Memb. Sci.* **209**, 271-282 (2002).

Lape, N.M., H. Mao, D. Camper, M.A. Hillmyer, and E.L. Cussler, "Barrier Membranes of Self-Assembled Lamellar Poly(Lactide-Isoprene-Lactide) Triblock Copolymers," *J. Memb. Sci.* **259**, 1-9 (2005).

Moggridge, G. D., N. K. Lape, C. Yang, W. H. Smyrl, and E. L. Cussler, "Barrier Films Using Flakes and Reactive Additives," *Prog. in Organic Coatings*, **46**, 231-240 (2003).

Nielsen, L.E., "Models for the permeability of filled polymer systems," *J. Macromol. Sci. Chem. A,* **1** 929-942 (1967).

Nuxoll, E.E., and E.L. Cussler, "The Third Parameter in Reactive Barrier Films," *AIChE J.,* **51***,* 456-463 (2005).

Shimotori, T., E.E. Nuxoll, E.L. Cussler, and W.A. Arnold, "Polymer Membranes Containing Fe^O as a Containment Barrier," *Environ. Sci. Tech.* **38** 2264-2270 (2004).

Shimotori, T., E.L. Cussler and W.A. Arnold, "High Density Polyethylene Membrane Containing Fe^o as a Containment Barrier," *J. Environ. Engng* (accepted).

Swannack, C., C. Cox, A. Liakos, D. Hirt, “Three-dimensional simulation of barrier properties of nanocomposite films,” *J. Membr. Sci.,* **263** 47-56 (2005).

Warta, A.M., W.A. Arnold, and E.L. Cussler, “Membranes containing crystalline silicotitanate as a barrier for cesium ion,” *Environ Sci Tech*, **39**(24), 9738-9743 (2005).

Yang, C. F., E .E. Nuxoll and E. L. Cussler, "Reactive Barrier Films," *AIChE J.*, **47**, 295-302 (2001).