DISPOSAL BARRIERS THAT RELEASE CONTAMINANTS ONLY BY MOLECULAR DIFFUSION

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ABSTRACT. Engineered barriers can slow the movement of pollutants out of land disposal facilities in several ways. If the advective velocity is low, release will be primarily by molecular diffusion. Attenuation processes also work to slow the transport of many contaminants. Barriers that cause pollutants to be released almost entirely by molecular diffusion represent the best barriers achievable. Use of thick barrier materials will maximize the breakthrough time of contaminants that diffuse through the barrier. Thin barriers with exceedingly low permeabilities will not necessarily outperform thicker, more permeable liners. In fact, if diffusion is the dominant mechanism of release, the thicker, more permeable barrier may actually outperform the thinner barrier with lower permeability.

INTRODUCTION

Engineered barriers that retard the release of contaminants from land disposal facilities have traditionally been designed solely on the permeability of the material. However, even barriers with a permeability of zero will not stop the release of contaminants because flow will still occur from molecular diffusion of contaminants across the barrier. Many investigators have ignored the release of contaminants via molecular diffusion either out of lack of knowledge of this transport process or in the belief that rates of release would be insignificant. However, with increasing concern over the effects of groundwater contamination and improved techniques for detecting minute concentrations of pollutants in groundwater, there is heightened realization that all transport processes, including molecular diffusion, must be considered.

A barrier which allows escape of pollutants only by molecular diffusion is the best that can be built. There are several ways to make a barrier essentially a diffusion barrier, including the use of extremely low-permeability materials and inward hydraulic gradients. The analysis of release rates associated with diffusion is relatively straightforward because the diffusion coefficient is known fairly accurately for many materials. The uncertainty in the diffusion coefficient is much less than the typical uncertainty in perme-

ability. Thus, not only are barriers that release contaminants only by molecular diffusion the best engineered barriers possible, but their performance is also more predictable than barriers designed solely upon permeability.

TYPES OF BARRIERS

Up until about a decade ago, uncontrolled dumping of waste in landfills and lagoons was not uncommon. In recent years, attempts have been made to minimize groundwater contamination near waste disposal sites by installing engineered barriers around and beneath the waste. The barriers have usually involved liners or cutoff walls (Fig. 1). Most liners are constructed of earth, plastic, rubber, asphalt, or concrete. Cutoff walls may be formed by grouting or driving steel sheet piling, but more commonly the walls are formed by excavating a trench and backfilling it with low-permeability materials such as soil or a soil-cement mix (e.g., slurry walls).

With such barriers, the design has almost always been based on the permeability, or hydraulic conductivity, of the barrier material. However, the permeability of barrier materials is very difficult to predict or determine accurately. As a result, predictions about the probable performance of engineered barriers are fraught with considerable uncertainty.

MOLECULAR DIFFUSION

Diffusion is a process in which solutes in a solution flow in response to a gradient in concentration. The
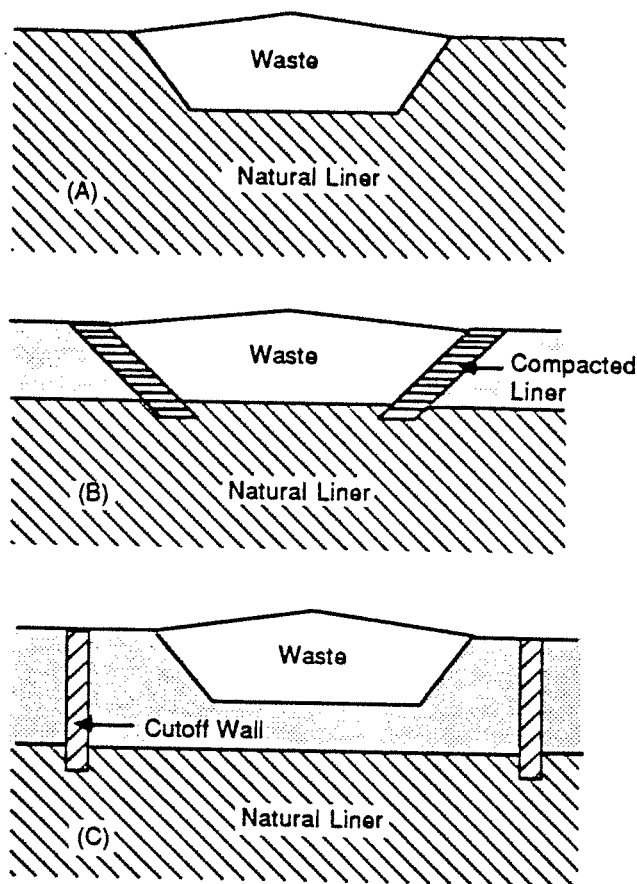
FIGURE 1. Examples of engineered barriers.

solution itself need not flow for diffusive transport to occur. An example of solute transported purely by molecular diffusion is given in Fig. 2. In this case, there is no advective flow because the hydraulic gradient is zero. However, since there is a gradient in solute concentration, there will be solute transport via molecular diffusion.

The process of diffusion is usually assumed to occur in accord with Fick's first and second laws. For free solutions (i.e., no porous matrix), Fick's first law states that one-dimensional diffusion occurs as follows:

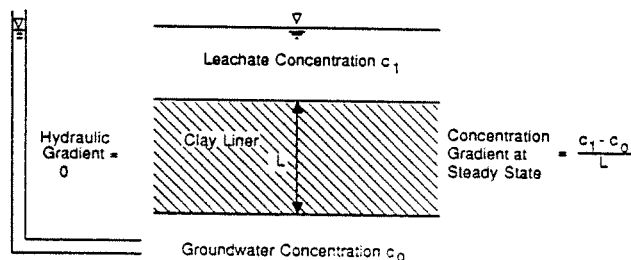$$J_d = -D_o \frac{\partial c}{\partial x} \qquad [1]$$

FIGURE 2. Example of a clay liner system in which molecular diffusion is the transport mechanism.

where J_d is the diffusional mass flux (mass transported per unit area perpendicular to the direction of transport, per unit time), D_o is the free-solution diffusion coefficient, c is the concentration of a solute, and x is the direction in which the diffusion is occurring.

The driving force for diffusion of individual ions or molecules is the gradient in chemical potential. Also, the limiting velocity of a particle may be defined as the product of the absolute mobility of the particle and its driving force. When these relations are combined with the definition of mass flux, the following expression results:

$$J_d = \frac{-uRT}{N} \frac{\partial c}{\partial x}. \qquad [2]$$

The expression for the free-solution diffusion coefficient at infinite dilution is:

$$D_o = \frac{uRT}{N} \qquad [3]$$

where R is the universal gas constant (8.134 J $mol^{-1}K^{-1}$), T is the absolute temperature (°K), N is Avogadro's number (6.022×10^{23} mol^{-1}) and u is the absolute mobility of a particle. This expression is known as the Nernst-Einstein equation (1). By combining Eq. 3 with expressions relating the absolute mobility to the limiting ionic equivalent conductivity (2) and to the viscous resistance of the solvent molecules, i.e., Stokes' Law (3), two additional expressions for D_o result:

$$D_o = \frac{RT\lambda^\circ}{F^2|z|} \qquad [4]$$

and

$$D_o = \frac{RT}{6\pi N \eta r} \qquad [5]$$

where F is the Faraday (96,490 Coulombs), $|z|$ is the absolute value of the ionic valence, λ° is the limiting ionic equivalent conductivity, η is the absolute viscosity of the solution, and r is the molecular or hydrated ionic radius. Equations 4 and 5 are the well-known Nernst and Einstein-Stokes equations, respectively. Although the above equations apply only to ideal conditions (i.e., infinite dilution and the assumptions inherent therein) they do provide an indication of some of the factors affecting D_o.

The usefulness of Eq. 4 is that limiting values of D_o (known as self-diffusion coefficients) can be calculated provided the associated λ° values are known. These calculations have been made for a number of ions using λ° values from Appendix 6.2 of Robinson

and Stokes (2) and the results are indicated in Table 1. A similar table has been provided by Quigley et al. (4).

The values of D_o reported in Table 1 should be considered to be the maximum values attainable under ideal conditions (i.e., microscopic scale, infinite dilution, etc.). Under nonideal conditions (e.g., macroscopic scale, concentrated solutions), a number of effects, negligible for ideal conditions, become important. A good example of one of these effects is given by Robinson and Stokes (2). When two oppositely charged ions are diffusing in solution, a microscopic charge separation or electrical potential gradient is set up between the ions due to their different mobilities. The effect of this charge separation is to speed up the slower moving ion and to slow down the faster moving ion. Since, on a macroscopic scale, electroneutrality must be satisfied, the resultant speeds of both ions must be equal. This electrical potential effect is responsible, in part, for the differences between the simple electrolyte diffusion values, shown in Table 2, and their respective component self-diffusion coefficients given in Table 1. Other effects responsible for the difference in D_o values under nonideal conditions include solute-solute and solute-solvent interactions.

Solutes will not diffuse as quickly in soil as they will in free solutions. For soil, Eq. 1 becomes

$$J_d = -(\tau D_o)\, \theta \frac{\partial c}{\partial x} \qquad [6]$$

or

$$J_d = -D^* \, \theta \frac{\partial c}{\partial x} \qquad [7]$$

where τ is a tortuosity factor (dimensionless), θ is

TABLE 1
Calculated Self-Diffusion Coefficients for Representative Ions at Infinite Dilution in Water at 25°C

Anions	$D_o \times 10^{10}$ m²/s	Cations	$D_o \times 10^{10}$ m²/s
OH⁻	52.76	H⁺	93.07
F⁻	14.74	Li⁺	10.27
Cl⁻	20.31	Na⁺	13.33
Br⁻	20.79	K⁺	19.56
I⁻	20.43	Rb⁺	20.70
HCO₃⁻	11.84	Cs⁺	20.54
Acetate	10.88	Be²⁺	5.98
SO₄²⁻	10.64	Mg²⁺	7.05
CO₃²⁻	9.22	Ca²⁺	7.92
		Sr²⁺	7.90
		Ba²⁺	8.46
		Pb²⁺	9.245
		Cu²⁺	7.13
		Zn²⁺	7.02

Note: D_o values calculated from the Nernst equation.

TABLE 2
Representative Values of Free-Solution Diffusion Coefficients (CRC Handbook of Chemistry and Physics, 66th Edition, 1985–86)

Solute	Concentration	$D_o \times 10^{9}$, m²/s
HCl	0.1 M	3.1
LiCl	0.1 M	1.3
NaCl	0.1 M	1.5
CaCl₂	0.1 M	1.1
Glucose	0.4%	0.7
Citric Acid	0.1 M	0.7

the volumetric moisture content of the soil (dimensionless), and D^* is the effective diffusion coefficient. It should be noted that some researchers include θ in the tortuosity factor. The volumetric moisture content is equal to the product of the porosity, n, and the degree of saturation, S_r.

In general, the tortuosity factor is considered to account for the increased distance of flow and the more tortuous pathways experienced by solutes diffusing through soil. The tortuosity factor is expressed as

$$\tau = (x/x_e)^2 \qquad [8]$$

where x is the straight-line distance between two points defining the flow path, and x_e is the actual, effective distance of flow through the soil between the same two points. Since $x_e > x$, $\tau < 1$. Typical values of τ reported in the literature are provided in Table 3. Many of the values of τ in Table 3 are based on results of diffusion tests performed with unsaturated soils.

In reality, there may be other effects associated with the tortuosity factor. For example, Olsen et al.

TABLE 3
Representative Tortuosity Factors Taken from the Literature

τ Values	Soil	Tracer	Reference
0.08–0.12	50% Sand/Bentonite	³⁶Cl	[16]
0.04–0.49	0,10,25,50,75% Bentonite/Sand	³⁶Cl	[17]
0.01–0.22	"	³H	"
0.59–0.84	0,5,10,15,25,50,100% Bentonite/Sand	³⁶Cl	[18]
0.33–0.70	"	³H	"
0.20–0.33	Silty Clay Loam, Clay	Br	[19]
0.08–0.31	Silty Clay Loam, Sandy Loam	Br	[20]
0.033–0.539	6 Natural Soils	⁶⁵Zn	[21]
0.01–0.58	5 Natural Soils	³⁶Cl	[22]
0.0032–0.023	Loam	⁸⁶Rb	[23]
0.027–0.31*	Loam, Silty Clay Loam, Clay	Cl	[24]
0.04–0.45	75μ and 200μ Glass Beads	⁸⁶Rb	[25]

*Transmission Factors

(5) considered two other effects, the variation in the viscosity of the solvent within the pore space, represented by the factor, α, and the negative adsorption (i.e., exclusion) of ions, represented by the factor, γ. They combined all these effects (including the volumetric moisture content) into one factor and termed it the "transmission factor," or

$$\tau = \alpha\gamma(x/x_e)^2\theta. \qquad [9]$$

While these and other effects may be present in many situations, it is neither possible nor feasible in most cases to separate them. In short, the tortuosity factors reported in the literature may account for more than just the pore geometry of the porous matrix.

Fick's first law describes steady-state flux of solutes. For unsteady (transient) transport, Fick's second law applies:

$$\frac{\partial c}{\partial t} = D^* \frac{\partial^2 c}{\partial x^2}. \qquad [10]$$
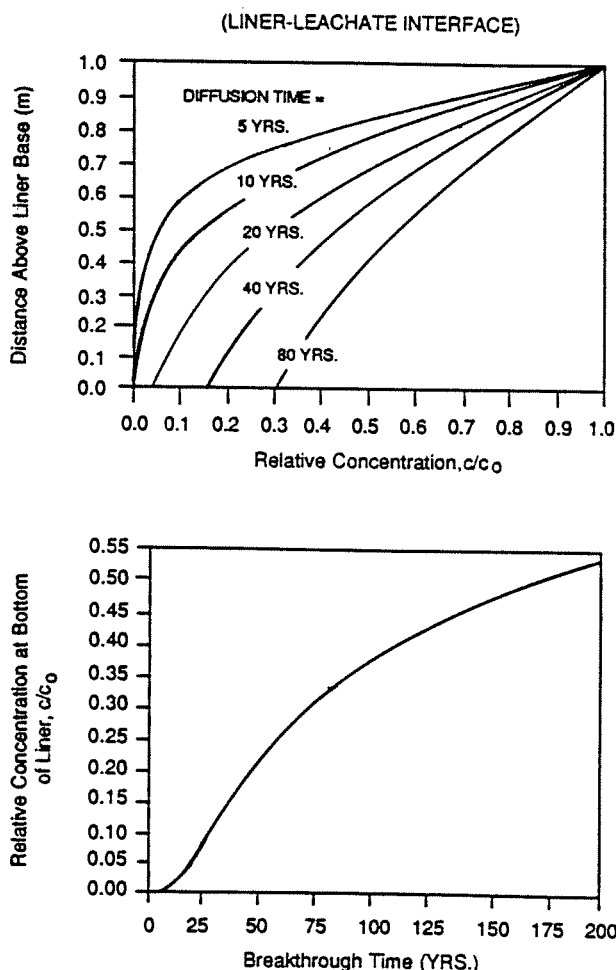
Equation 10 is integrated for appropriate initial and

boundary conditions to obtain a description of the solute concentration changes with respect to time and space. Complex error functions facilitate the integration.

An example of the application of Fick's second law is as follows. A 1 m thick clay liner retains leachate containing a particular solute at a concentration of 10,000 mg/L. The underlying ground water is completely free of this solute. The effective diffusion coefficient is 2×10^{-10} m^2/s. The resulting distribution of solute in and at the bottom of the liner as a function of time solely due to diffusional transport is illustrated in Fig. 3. The solute distribution was determined from the following solution to Eq. 10 (6) which assumes the leachate concentration is constant with time:

$$\frac{c}{c_o} = \text{erfc}\left(\frac{x}{2\sqrt{D^*t}}\right) \qquad [11]$$

where erfc is the complementary error function. The concentrations of solute reaching the base of the liner at 10, 20, 40, and 80 years are approximately 50, 460, 1600, and 3200 mg/L, respectively. Since, in some cases, these concentrations exceed allowable values, it is apparent that diffusion of chemicals through fine-grained materials can be an important transport mechanism even over relatively short (20–30 years) periods.

ADVECTIVE TRANSPORT

Advective transport of contaminants through porous materials is generally assumed to occur in accordance with Darcy's law in which

$$v = ki = -k\frac{\partial h}{\partial x} \qquad [12]$$

where v is the Darcian velocity, k is the hydraulic conductivity, i is the dimensionless hydraulic gradient, h is the total hydraulic head, and x is the distance along the path of flow. The advective flux, J_a, is given by:

$$J_a = vc = n_e v_s c \qquad [13]$$

where v_s is the seepage velocity, or average linear velocity along the path of flow, and n_e is the effective porosity (i.e., the volume of pore fluid that is effective in conducting flow divided by the total volume). A comparison of Eqs. 12 and 13 reveals that the seepage velocity is given by:

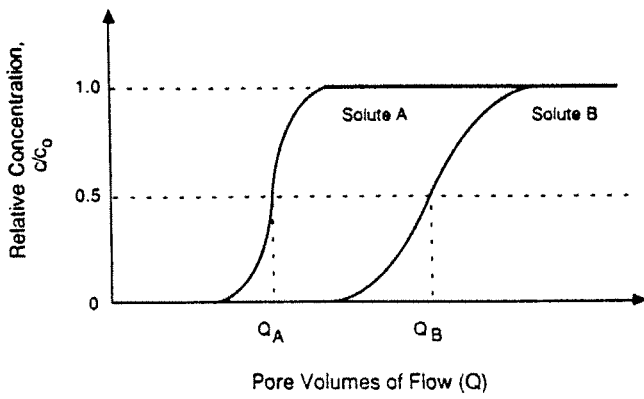$$v_s = \frac{v}{n_e} = \frac{ki}{n_e} = -\frac{k}{n_e}\frac{\partial h}{\partial x}. \qquad [14]$$

FIGURE 3. Concentration profiles for 1 m thick clay liner and $D^* = 2 \times 10^{-10}$ m^2/s.

FIGURE 4. Breakthrough curves for retarded (B) and unretarded (A) solutes.

Considerable controversy exists over typical values of n_e for relatively impermeable soils. Some have suggested that n_e is more-or-less equal to the total porosity of the soil, n, whereas others suggest that $n_e < n$ because most of the flow occurs through macropores, cracks, fractures, or other features. In clays, dead-end pores, exceedingly small pores, and soil-water sorbed onto the surfaces of clay particles may occupy a significant percentage of the total pore space, but contribute very little to flow.

Even more controversy exists over the hydraulic conductivity of relatively impermeable soils. Daniel (7), Day and Daniel (8), and Daniel (9) report data showing how difficult it is to predict the hydraulic conductivity of clayey soils. Other investigators have observed similar problems. As a result, it is very difficult to make accurate predictions of seepage velocities caused by advective flow.

ATTENUATION OF CONTAMINANTS

Contaminants (solutes) may migrate slower than the transporting solution (solvent) for a variety of reasons. Some of the causes of contaminant attenuation in soil include ion exchange, precipitation, biological reactions, and radioactive decay.

Suppose a solution contains two solutes, A and B. Solute A is conservative, viz., is not attenuated by soil; solute B is attenuated. A column test in which there is negligible diffusive flow (just advective flow) is performed and effluent analyses yield the results shown in Fig. 4. The "retardation coefficient," R, is defined as follows:

$$R = \frac{Q_B}{Q_A} \qquad [15]$$

where Q_A and Q_B are the pore volumes of flow for solutes A and B, respectively, at a relative concentration, c/c_o, of 0.5. Since $Q_B > Q_A$, $R > 1.0$ for a retarded solute.

The retardation coefficient may also be calculated independently by the following relationship:

$$R = 1 + \frac{\rho_d}{\theta} K_p \qquad [16]$$

where ρ_d is the dry bulk density of the soil and K_p is the partition coefficient. The partition coefficient relates mass of solute sorbed per mass of soil, q, to the concentration of solute in solution, c, at equilibrium. Batch adsorption tests are often used to determine the relationship between q and c over an appropriate range of concentrations. When the q vs. c relationship is constant (i.e., linear isotherm), the partition coefficient is given a specific name (i.e., the distribution coefficient, K_d). Unfortunately, K_p is often dependent upon the equilibrium concentration of the solution (Fig. 5). Nonetheless, it is usually convenient to assume a linear relationship for the purpose of calculating retardation procedures for performing batch isotherm tests and the factors affecting those procedures are discussed extensively in U.S. EPA (10).

The sorption of hydrophobic organic pollutants also can be described adequately by Eq. 16 provided the distribution coefficient is defined as follows:

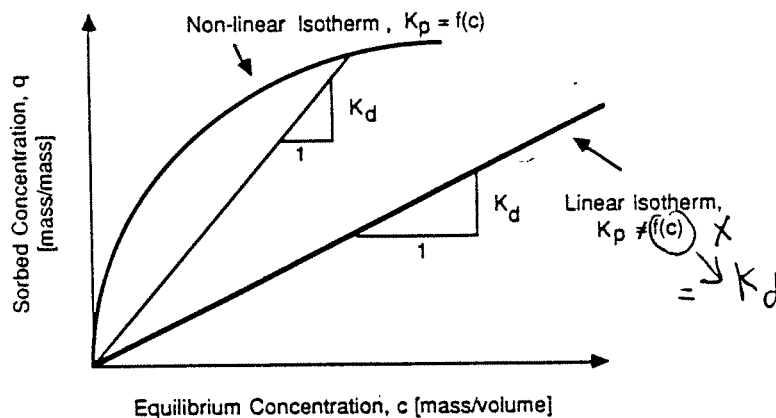$$K_d = f_{oc} \cdot K_{oc} \qquad [17]$$

FIGURE 5. Typical adsorption relationships for reactive solutes.

wher f_{oc} is the fraction of organic-carbon in the soil (dimensionless) and K_{oc} is the organic carbon partition coefficient (11). The organic-carbon partition coefficient has been empirically correlated with a number of parameters, especially the octanol-water partition coefficient, K_{ow}. These empirical correlations are covered in detail by Griffin and Roy (12).

EXAMPLE: COMPARISON OF CLAYS AND GEOMEMBRANES

Clay and geomembrane liners are both used to line landfills and lagoons. Both types of liners have their advantages and disadvantages. Geomembranes have lower hydraulic conductivity and can be constructed to more exacting standards than earthen liners. However, geomembranes are very thin, can be torn or punctured, do not tend to self-heal, and have ill-defined longevity. Earthen liners are much thicker, may undergo some self-healing if damaged, can attenuate many contaminants, and should last for millennia. On the negative side, clay liners are much more permeable than geomembranes, require a local source of soil, occupy more volume than geomembranes, and are more difficult to construct to precise standards. However, because geomembranes have much lower hydraulic conductivity than clay, geomembranes are considered by many to be superior to clay. But are they really better when we also consider diffusion?

An interesting question is how the performance of geomembrane liners compares to clay liners. Some calculations may help to answer this question. For example, consider two liners, a geomembrane and a compacted-clay liner, each with the following properties:

Property	Geomembrane	Clay
porosity	0.10	0.50
hydraulic conductivity, k (m/s)	1.0×10^{-14}	1.0×10^{-9}
diffusion coefficient, D^* (m²/s)	3.0×10^{-14}	2.0×10^{-10}
thickness (m)	.00152 (60 mils)	0.91436 (3 feet)
hydraulic gradient, i	100	1.16

These values are assumed, and some discussion of their magnitudes is warranted. The hydraulic conductivity and thickness of the clay are the maximum and minimum values, respectively, currently being allowed by the U.S. EPA for double-liner systems. The clay porosity is a representative, average value, and the diffusion coefficient for the clay is representative of values currently being measured at the University of Texas. Although geomembranes are nonporous, a porosity of 0.1 was used for computational convenience. The thickness of the geomembrane is typical of current U.S. practice. The
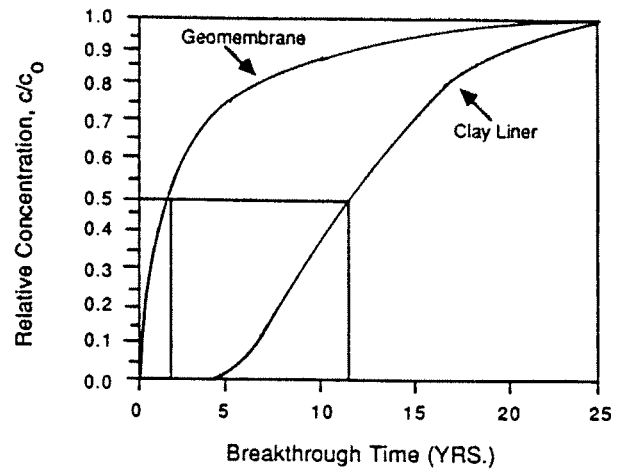

FIGURE 6. Solute breakthrough curve for geomembranes and clay liners.

diffusion coefficient for the geomembrane is about the same as a value reported by Lord and Koerner (13) based on water adsorption tests. This diffusion coefficient for the geomembrane is from two to four orders of magnitude less than other reported values which were measured using radioactive tracers (13,14). Also, the hydraulic conductivity for the geomembrane is thought to be conservative. Finally, the hydraulic gradient in each case represents 0.152 m (0.5 ft) of ponded leachate assuming atmospheric pressure at the base of the liner and no suction within the liner.

If the values stated above are utilized in conjunction with the well known Ogata (15) solution to the differential equation describing solute transport, breakthrough curves may be calculated and compared. This calculation has been performed and the results are presented in Fig. 6. Note that the breakthrough time (at $c/c_o = 0.5$) for the geomembrane is exceedingly fast, about 1.7 years, especially when compared with the breakthrough of 11.5 years for the clay liner. This difference results even though the geomembrane has a hydraulic conductivity which is 5 orders of magnitude less than the clay and an effective diffusion coefficient which is about 4 orders of magnitude less. The reason for this difference is the relative thickness of the two liners and rapid diffusional transport across a very short distance through the geomembrane.

BARRIERS DESIGNED AS DIFFUSION BARRIERS

The total flux, J, of contaminants breaching a barrier is the sum of the advective and diffusional fluxes given by Eqs. 13 and 7, respectively, or:

$$J = J_a + J_d = vc - D^*\theta \frac{\partial c}{\partial x}. \qquad [18]$$

A barrier will release contaminants almost exclusively via molecular diffusion if the advective flux is much less than the diffusional flux. The desirability

of designing a barrier to release contaminants only by diffusion should now be clear; the question is how to effect such a design.

One way to make a diffusion barrier is to utilize materials having exceedingly low hydraulic conductivity. Geomembranes, asphaltic materials, and clay soils may meet such requirements. Our experience indicates that for hydraulic gradients on the order of 1, materials with hydraulic conductivities less than roughly $1 - 10^{-8}$ cm/s release contaminants primarily by molecular diffusion. Thus, it is desirable to design barriers to have this magnitude of hydraulic conductivity. For barriers that release contaminants only by molecular diffusion, the hydraulic conductivity has no bearing on the rate of release. Accordingly, it is a waste of time and money to try to achieve a lower hydraulic conductivity once the conductivity is low enough so that release of contaminants is primarily via diffusion.

The advective component of flow may also be minimized by reducing the hydraulic gradient. For cutoff walls, this may be accomplished by pumping ground water and producing a gradient toward the source of groundwater contamination. For landfills, leachate removal will minimize the gradient. For lagoons, an intermediate barrier underlain by a drainage system may be needed.

One factor that many designers fail to recognize is the importance of the thickness of the barrier. Thick barriers reduce the concentration gradient and increase the time required for contaminants to diffuse through the barrier. This was illustrated in the earlier example where a geomembrane was compared to a clay liner.

CONCLUSIONS

Molecular diffusion is an important mechanism of contaminant migration in soils with low hydraulic conductivity. The best barriers for minimizing contaminant release are those which allow almost no advective transport such that the only mechanism of contaminant migration is molecular diffusion. Barriers that release contaminants only by molecular diffusion may be constructed from low-hydraulic-conductivity materials or by controlling the hydraulic gradient across the barrier to keep the advective flux negligible.

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