Waste Management & Research (1994) **12**, 61–71

DIFFUSION COEFFICIENTS OF ORGANICS IN HIGH DENSITY POLYETHYLENE (HDPE)[1]

T. V. Prasad, K. W. Brown* and J. C. Thomas

Texas A&M University, Soil and Crop Science Department, College Station, TX 77843-2474, U.S.A.

(*Received 3 November 1992, accepted 22 April 1993*)

Only limited data are available on the diffusion of volatile organic solvents through flexible membrane liners (FMLs) used for lining impoundments and landfills. To expand this database, a rapid, inexpensive method is needed to measure the diffusion coefficients of volatile organic solvents through FML materials. An absorption method has been developed to determine the diffusion coefficients of volatile organic solvents through FML materials. The method is based on the depletion of an organic compound from an aqueous solution due to absorption by a submerged sample of FML. A numerical solution of Fick's second law of diffusion was used to develop a graph which can be used to determine the diffusion coefficient from the time dependent concentration data. The diffusion coefficients obtained from the absorption tests were validated by comparing them with coefficients determined using a two chamber diffusion cell. The diffusion coefficients determined for toluene and xylene in high density polyethylene (HDPE) were 5.1×10^{-9} cm^{2}s^{-1} and 1.0×10^{-9} cm^{2}s^{-1} by the two methods, respectively. The data indicate that the coefficient of distribution (K_d) between the FML and the organic solution, a value which is needed to calculate the diffusion coefficient from the data, can be estimated from the log of the octanol-water partition coefficient (K_{ow}), a commonly measured and reported value for many chemicals.

Key Words—Landfill, liner, solvents, leachate, leakage, mechanism, Fick's law, partitioning.

1. Introduction

Multiple liners are now utilized for surface impoundments and landfills used for hazardous waste containment. Liners typically consist of an upper flexible membrane liner (FML) over a leachate collection and removal system which, in turn, both overlie a composite bottom liner consisting of a second FML over a compacted clay liner. The use of FMLs as landfill liners has been widely accepted because, given proper installation, they are almost impermeable to the mass flow of liquids. While studies have been conducted to document the loss of liquids through flaws in FMLs (Brown & Thomas 1988, Jayawickrama *et al.* 1988) little attention has been given to the diffusion of volatile organic compounds through FMLs.

Diffusion through FMLs may be measured using techniques of vapour transmission, radioactive tracer transmission, water absorption, or water vapour absorption (Lord *et al.* 1985). Carpenter & Fisher (1981) used sequential chemical absorption techniques

---

[1] Contribution of the Texas Agricultural Experiment Station, Texas A&M University System, College Station, TX 77843. This work was supported in part through Award 89-06445 from the United States EPA Hazardous Substance Research Center for Region Pair 4-6 (Award R815718) in Raleigh, N.C.

* Author to whom correspondence should be addressed.

(modification of ASTM D-471 test) to determine permeation and diffusion properties of elastomers. The diffusion coefficient was estimated from the following expression,

$$D = 0.212\, l^2/t \qquad [1]$$

where, t is the time for the FML to reach 90% of the equilibrium concentration, l is the thickness, and D is the diffusion coefficient. Because this expression was derived without considering the effect of the coefficient of distribution between the FML and the organic solution, it is applicable only when a sheet of the FML is suspended in a solution of constant concentration.

Haxo & Lahey (1988) have shown that even at low concentrations, some volatile organics are highly absorbed by polymeric films. In their study, samples of FMLs were placed in cells filled with a series of aqueous solutions saturated with a single organic. They reported that the amount of organics absorbed by FMLs from the saturated solutions approached the amounts the FML absorbed when immersed in neat organics. Haxo (1989) explained these findings as being anomalous and that it may have occurred due to water acting as a permeable medium between the FML and the reservoir of excess organics which allowed the organics to be absorbed by the FML until saturation of the FML was reached. Haxo (1989) conducted experimental work in which volatile organic chemicals were partitioned between dilute aqueous solutions and FML materials. Again, the results indicated that the organics were strongly partitioned into the FML materials but no attempt was made to utilize the data to determine the diffusion coefficients.

Zobel (1982) designed an apparatus to measure diffusion coefficients of packaging films to odiforous compounds. Steady state organic vapour permeability was measured for different gradients at low concentrations and the diffusion coefficient was calculated using an empirically derived equation:

$$D = l^2/7.2\sqrt{t} \qquad [2]$$

where, t is the time for saturation. Similar steady state methods were utilized by Pasternak *et al* (1970) and Smith & Adam (1981) for estimating the value of D.

Haxo *et al* (1984) used the ASTM D1434 procedure for determination of gas permeability of FMLs, the ASTM E96 procedure to determine water vapour permeability of polymeric membranes, and a modification of the ASTM E96 procedure to determine solvent vapour permeability. The permeation rates of organic vapours determined by these methods varied by 5 orders-of-magnitude, depending upon the type and thickness of the FML and the type of organic.

August & Tatzky (1984) measured and reported permeability values for various types of FMLs and organics using a specially designed permeation cell in which the fluid above the FML was kept at a constant concentration C and the space beneath the FML was kept at a constant concentration $C = O$ through the use of a partial vacuum. Permeability values obtained from the studies of Haxo *et al.* (1984) and August & Tatzky (1984) for the same type of FML and chemical differed considerably. For example, the permeation rate reported by Haxo *et al.* (1984) for xylene through a 0.97 mm thick HDPE FML was 220 g m^{-2} d^{-1} while the permeation rate reported by August & Tatzky, (1984) for a 1 mm thick HDPE FML was 32 g m^{-2} d^{-1}. These differences may be due to differences between the FML materials or may have been due to different concentration gradients.

TABLE 1

Physical and chemical properties of the organic chemicals used in the absorption tests

Organic chemical	Molecular weight	Density at 20°C (g cm^{-3})	Solubility in water (mg l^{-1})	Log of the octanol-water Partition Coefficient
Acetone	58.1	0.788	–	–
Benzene	78.0	0.877	1,150	2.12
Cyclohexane	84.2	0.778	45	3.44
1,2-Dichloroethane	99.0	1.255	8,500	1.48
Toluene	92.1	0.866	515	2.73
Trichloroethylene	131.4	1.338	1,100	2.36
Xylene	106.2	0.870	200	3.26

Haxo & Lahey (1988) conducted experiments in a three-chambered laboratory vessel designed to simulate a landfill. Their data show that organics in dilute aqueous solutions are rapidly absorbed by the FML materials, diffuse through them, and are rapidly transferred to the air or water on the other side of the membrane. Unfortunately, due to the complexity of the experimental setup it is not possible to calculate diffusion coefficients from the data.

Diffusion coefficients of volatile organic compounds through FMLs are needed to assess leakage rates, to set pretreatment standards for land disposal and to facilitate the optimum design and configuration of landfill liner systems. Since diffusion tests are expensive and time consuming, a rapid test which can be conducted in readily available laboratory equipment needs to be developed. Therefore, this study was undertaken to develop a rapid and inexpensive method of using absorption test data to determine the diffusion coefficients of organics through FMLs.

2. Materials and methods

Seven organic chemicals representative of chlorinated hydrocarbons (1, 2-dichloroethane and trichloroethylene), aromatic hydrocarbons (cyclohexane, benzene, toluene, and xylene), and oxygenated hydrocarbons (acetone) were selected for this study. Pertinent physical and chemical properties of these chemicals are given in Table 1. The FML used was 1 mm (40 mil) thick high density polyethylene (HDPE). Table 2 shows some of the relevant properties of this FML.

Absorption tests were carried out in 400 ml jars sealed with teflon lined caps equipped with swagelock fittings which allowed the solution to be sampled. FMLs were cut into 50.2 by 76.2 mm pieces and placed in a jar containing 350 ml of aqueous organic solution of known concentration. The solutions were prepared by saturating the water with organic solvents, except for acetone which was prepared at a concentration of 50 000 mg/l. Sodium azide was added at a concentration of 50 mg/l to inhibit biodegradation. Each mixture was stirred for several hours. Subsamples were then analysed by a

TABLE 2
Relevant properties of the HDPE material used in this study

Property	Method	HDPE
Thickness (mil)	ASTM D751	40
Density (g cm^{-3})	ASTM D1505	0.944
Water absorption (% change in weight)	ASTM D570	0.0079
Moisture vapour transmission (g m^{-2} d^{-1})	ASTM E96	<0.001

HDPE – High Density Polyethylene

Tracor model 540 gas chromatograph (GC) equipped with a DB5 megabore column (fused silica type, cross bonded phase, 0.53 mm diameter, 30 m long, 1.5 µm film thickness, manufactured by J&W Scientific), and a Flame Ionization Detector (FID). While stirring continued, subsamples were analysed hourly until two successive analyses showed no difference, at which point the solution was assumed to be saturated. These solutions were then used as stock solutions for absorption tests and calibrating the GC. Concentrations were 1 150, 45, 8 500, 515, 1 100, and 200 mg/l for benzene, cyclohexane, 1,2-dichloroethane, toluene, trichloroethylene, and xylene respectively. The jars containing the solutions were kept at a constant temperature of 25°C. Samples were withdrawn periodically (more frequently at the start of each test) and analysed by GC. Additionally, absorption tests were also conducted by weighing samples of FML before and after immersion in pure organic solvents to determine the partition coefficients.

Permeation tests were conducted in an apparatus patterned after that of Haxo & Lahey (1988). The apparatus was modified to include only two chambers, each equipped with a sampling port, and separated by a FML with no exposed edges. A solution of known concentration was added to one chamber, while distilled water was added to the other chamber. Samples were withdrawn from these chambers periodically and analysed by GC.

3. Theoretical considerations

3.1 Absorption

When a known volume and mass of FML is submersed in a solution of known concentration of a volatile organic in a vapour tight jar, the concentration of the organic in the solution will change over time depending upon the interaction between the organic and the FML. If we assume that: 1) the diffusion coefficient in the FML is a constant; 2) equilibration of the organic in the solution phase with the absorbed phase on the surface of the FML is achieved instantaneously; and 3) the diffusion of the organic through edges of the thin FML is negligible, then the change in concentration in the solution with time can be described by the following equations:

$$\frac{\partial C_f}{\partial t} = D\frac{\partial^2 C_f}{\partial x^2}$$

$$C_f(x,t) = 0,\ t = 0,\ 0 < x < l$$

$$C_{s(t)} = C_{so},\ t = 0 \qquad [3]$$

$$C_{f(0,t)} = C_{f(l,t)} = K_d C_s \text{ for all } t$$

$$\partial C_f/\partial x = 0,\ x = l/2, \text{ for all } t$$

$$\partial C_s/\partial t = D(\partial C_f/\partial x)_{x=0} A/V_s$$

where: A=the area of the FML exposed in the diffusion chamber, (cm^2); C_f=concentration of the organic in the FML at any given time t, (g cm^{-3}); C_s=concentration of the organic in solution at any time t, (g cm^{-3}); C_{so}=concentration of the organic in the solution at time $t=0$, (g cm^{-3}); D=diffusion coefficient, (cm^2 s^{-1}); K_d=coefficient of distribution between the solution phase and the FML; l = the thickness of the FML, (cm); t=time, (s); V_s=the volume of the solution in the jar, (cm^3); x=one-half of the thickness of the FML.

Since equation 3 does not have an analytical solution, a numerical solution procedure was used. The following equation represents the discretized form of equation 3.

$$U_{i+1,j} = U_{i,j} + D\frac{\Delta t}{(\Delta x)^2}(U_{i,j+1} - 2U_{i,j} + U_{i,j-1}) \qquad [4]$$

Where: U=the concentration at different points of time, and i,j = time increments.

A FORTRAN code was written to estimate the change in concentration of the organic in solution with time for assumed values of D. A family of curves representing the concentration of the organic in the solution versus time was generated for various assumed values of D. The experimental data of the time dependent concentration in the solution containing the sample of FML was then compared to the curves generated by the simulation to estimate the actual value of D.

3.2 Diffusion

Using the same assumptions listed above, the following mathematical formulation was used to describe the permeation of the organic to the other chamber through the FML separating the chambers of a two-chamber diffusion cell.

$$\frac{\partial C_f}{\partial t} = D\frac{\partial^2 C_f}{\partial x^2}$$

$$C_T = C_{TO}\ \&\ C_B = 0,\ t = 0 \qquad [5]$$

$$C_{f(1,0)} = K_d C_{TO},\ C_f(0 \leqslant x < 1,0) = 0$$

TABLE 3

Calculated partition coefficients of organics between aqueous solutions and FMLs

Organic	Solubility in FML ($mg\ kg^{-1}$)	Partition Coefficient K_d*
Acetone	1.25×10^4	0.2
Benzene	6.58×10^4	57.2
Cyclohexane	1.07×10^5	2 377.7
1,2-Dichloroethane	6.13×10^4	7.2
Toluene	9.88×10^4	191.8
Trichloroethylene	1.48×10^5	134.5
Xylene	9.97×10^4	498.5

* Partition coefficient is calculated as solubility of organic in FML divided by solubility of the organic in water. For acetone, a value of 0.2 has been assumed.

$$C_{f(0,t)} = K_d C_B\,(t) \;\&\; C_{f(1,t)} = K_d C_T\,(t),\ t > 0$$

$$\partial C_B / \partial t = D(\partial C_f / \partial x)_{x=0}\, A / V_B$$

$$\partial C_T / \partial t = D(\partial C_f / \partial x)_{x=1}\, A / V_T$$

where: C_B = concentration of the organic in the bottom chamber of the permeation apparatus at any time t, (g cm^{-3}); C_T = concentration of the organic in the top chamber of the permeation apparatus at any time t, (g cm^{-3}); C_{TO} = concentration of the organic in the top chamber of the permeation apparatus at $t = 0$, (g cm^{-3}); V_B = volume of the bottom chamber, (cm^3); V_T = volume of the top chamber, (cm^3).

This problem was solved numerically in a manner similar to that described for the previous problem.

4. Results and discussion

4.1 Absorption

Partition coefficients (K_d) between aqueous solutions and FMLs for the various organics used in this study were calculated from the data obtained from absorption tests using pure solvents and are presented in Table 3. The data indicate that of the chemicals tested, cyclohexane has the greatest partition coefficient while the acetone has the least. When listed in decreasing order of partition coefficients, the chemicals tested are cyclohexane, xylene, toluene, trichloroethylene, benzene, 1,2-dichloroethane, and acetone. The partition coefficients are inversely related to the solubility of the organic in water and directly related to the octanol-water partition coefficient. A plot of the log of the octanol-water

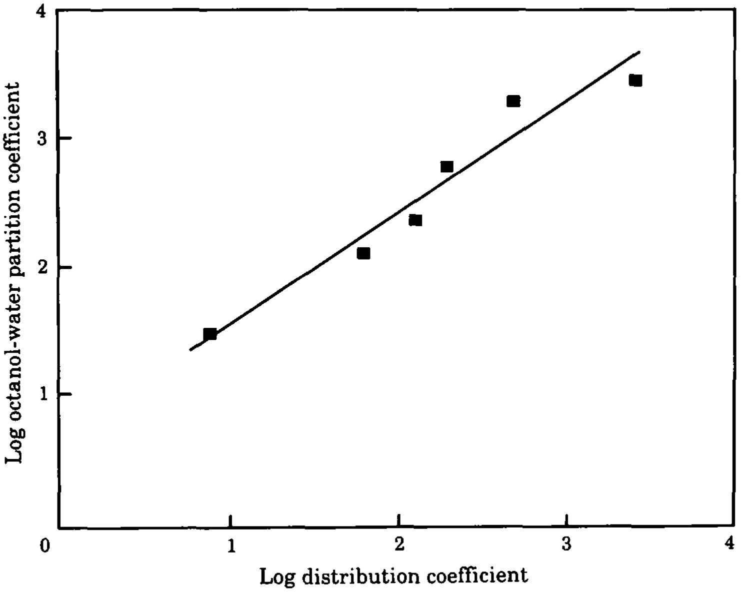

Fig. 1. Relationship between the log of the octanol-water partition coefficient and the log of the distribution coefficient. $y = 0.84x + 0.73$, $r^2 = 0.95$

partition coefficient versus the log of the partition coefficient (Fig. 1) yielded a straight line relationship with an r^2 of 0.95. Thus, these data suggest that it may be possible to

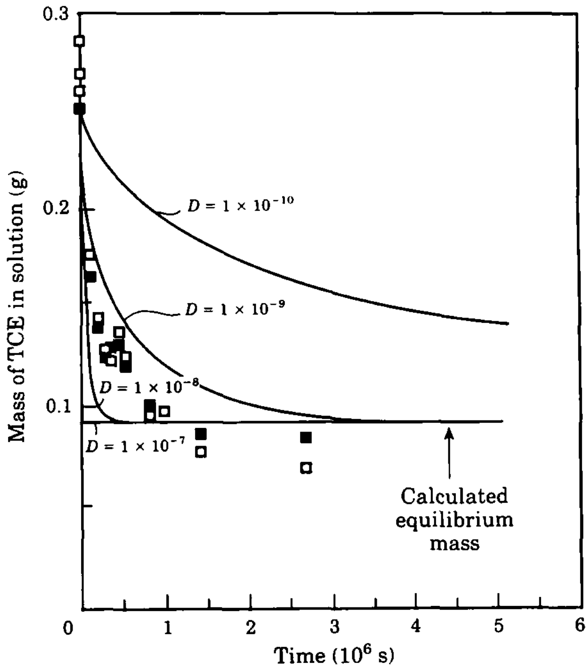

Fig. 2. Mass of TCE remaining in the 350 ml of solution versus time for absorption tests with 1 mm thick HDPE sample. (■), rep. 1; (□), rep. 2.

estimate partition coefficients for other organic solvents from the K_{OW} values reported in the literature.

The measured partition coefficients were used with equation 5 to predict the amounts of organics remaining in solution as a function of time. Figure 2 shows the measured mass of TCE (trichloroethylene) remaining in solution versus time in an absorption test with 1 mm thick HDPE as compared to the computer generated curves for four assumed values of D ranging from 1×10^{-7} to 1×10^{-10} $cm^2\ s^{-1}$. The data indicate that the diffusion coefficient for TCE in the 1 mm HDPE is about 5×10^{-9} $cm^2\ s^{-1}$. The complete list of diffusion coefficients determined for the 1 mm HDPE to all seven organics in aqueous solutions used in this study is given in Table 4.

4.2 Diffusion

Plots of the experimental data and calculated data for the two chamber permeation cells show the estimated diffusion coefficients are 5×10^{-9} $cm^2\ s^{-1}$ and 1×10^{-9} $cm^2\ s^{-1}$ for TCE and xylene, respectively (Figs 3 and 4). These data are in close agreement with the diffusion data obtained from the absorption test and indicate that the use of absorption tests is a valid technique for determination of diffusion coefficients. One permeation test was carried out in solutions containing a mixture of TCE and toluene to test for interactive effects between the chemicals on their diffusion coefficients. The results shown in Fig. 3 indicated that toluene and TCE do not exhibit any interactions and diffuse through the FML at the same rates as they did in tests conducted with individual aqueous solutions. However, August & Tatzky (1984) and Morel *et al.* (1979) have

TABLE 4

Diffusion coefficients for 1 mm HDPE calculated from the absorption and diffusion test data

Organic Chemical	Diffusion Coefficient ($cm^2\ s^{-1}$) Measured in absorption tests	 Measured in diffusion chamber	 Calculated from data of August & Tatzky (1984)
Acetone	$< 1.0 \times 10^{-12}$		
Benzene	3.7×10^{-10}		
Cyclohexane	1.2×10^{-10}		
1,2-Dichloroethane	6.8×10^{-8}		
Toluene	5.1×10^{-9}		2.3×10^{-9}
Trichloroethylene	5.2×10^{-9}	5.0×10^{-9}	6.9×10^{-9}
Xylene	1.0×10^{-9}	1.0×10^{-9}	1.8×10^{-9}

* Permeability coefficients were calculated as the product of diffusion coefficient and solubility of the organic in the FML.

shown experimental evidence that interactive effects on permeability of some organics through FMLs do exist. Further research is required to determine how the combination of solvents affects the diffusion process.

Implications of these data are that the organic solvents in landfill leachates will be partitioned into and diffuse through the FML. Since equilibrium concentrations between chambers on either side of the FML are reached rather quickly, concentrations of soluble organic contaminants measured in the landfill leachate may be nearly the same as the concentrations immediately beneath the FML. Thus, it is possible that significant amounts of organics may diffuse through FMLs.

5. Conclusions

Absorption tests have been shown to be useful as a low cost, rapid means of estimating diffusion coefficients of organics in FMLs. Procedures for calculating these coefficients from simple absorption tests with minimal instrumentation have been developed. However, care must be taken to make sure that processes other than absorption of the chemical by the test FML, such as biodegradation, volatilization and photodegradation, are prevented by proper selection of experimental conditions and equipment. Diffusion coefficients may vary by several orders-of-magnitude due to inherent differences in the FML materials and generalizations between materials and manufacturers must be made with extreme caution. Partition coefficients needed for calculating diffusion coefficients may be estimated from the log of the octanol-water partition coefficients. The data show the potential for organic contaminants to diffuse through FMLs and contaminate the underlying soil and water resources.

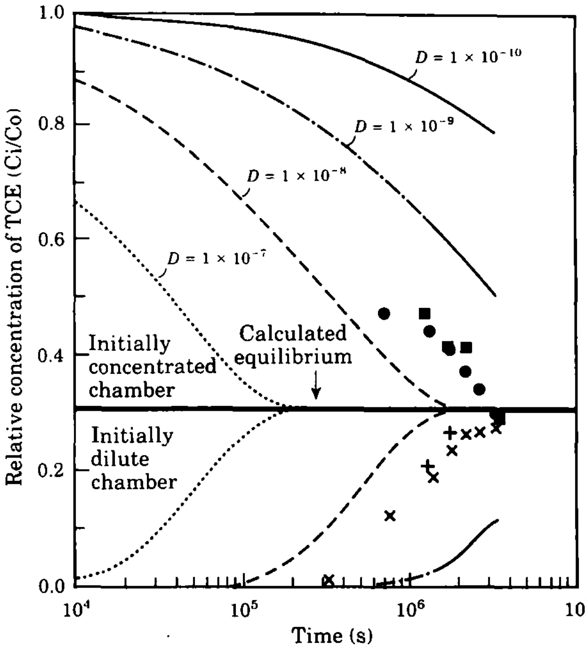

Fig. 3. Modeled and experimental values of relative concentration of TCE versus time in seconds [(■) and (+): test data with 1100 mg l^{-1} TCE. (●) and (×): test data with 125 mg l^{-1} toluene and 400 mg l^{-1} TCE].

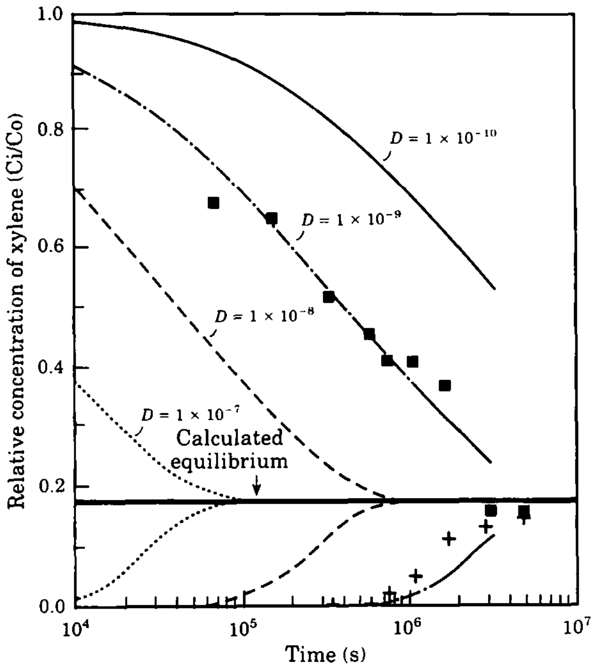

Fig. 4. Modeled and experimental data of relative concentration of xylene versus time in seconds [(■) and (+): test data from initially concentrated and dilute chamber, respectively] separated by a 1 mm thick HDPE.

References

August, H., & Tatzky, R. (1984). Permeabilities of commercially available polymeric liners for hazardous landfill leachate organic constitutents. In: *International Conference on Geomembranes*, June 20–24, Denver. Co. Vol I. Industrial Fabrics Association International, St. Paul, U.S.A. 1984. pp 163–168

Brown, K. W. & Thomas J. C. (1988). Leak rates into drainage systems underlying lined retention facilities. *Journal of Hazardous Materials* **18**, 179–188.

Carpenter, C. N. & Fisher, A. O. (1981). Sequential chemical absorption techniques for evaluating elastomers. *Materials Performance* **20**, 40–45.

Haxo, H.E. (1989). Compatibility of flexible membrane liners and municipal solid waste leachates. In: *15th Annual Research Symposium Remedial Action, Treatment and Disposal of Hazardous Waste*, April 10–12, Cincinnati, U.S.A.

Haxo, H. E., Miedema J. A. & Nelson N. A. (1984). Permeability of polymeric membrane lining materials. In: *International Conference on Geomembranes* June 20–24, Denver, CO. Vol I. Industrial Fabrics Association International, St. Paul, U.S.A. 1984. pp 151–156.

Haxo, H. E. & Lahey, T. P. (1988). Transport of dissolved organics from dilute aqueous solutions through flexible membrane liners. *Hazardous Waste & Hazardous Materials*. **5**, 275–294.

Jayawickrama, P. W., Brown, K. W., Thomas, J. C. & Lytton, R. L. (1988). Leakage Rates through Flaws in Membrane Liners. ASCE, *Journal Environmental Engineering Division* **114**, 1401–1420.

Lord, A. E., Koerner R. M. & Lindhult, E. C. (1985). Chemical mass transport measurements to determine flexible membrane liner (FML) lifetime. In: *Land Disposal of Hazardous Waste*. Proceedings of the Eleventh Annual Research Symposium, EPA/600/9-85/013, US Environmental Protection Agency, April, 1985.

Morel, G., Jozefonvicz, J. & Aptel, P. (1979). Pervaporation membranes prepared by radiochemical grafting of N-vinylpyrrolidone onto films. *Journal of Applied Polymer Science* **23**, 1833–1849.

Pasternak, R. A., Schimscheimer J. F. & Heller, J. (1970). A dynamic approach to diffusion and permeation measurements. *Journal of Polymer Science*, **(A–2)** 467–479.

Smith, T. L. & Adam, R. E. (1981). Effect of tensile deformations on gas transport in glassy polymer films. *Polymer* **22**, 299–304.

Zobel, M. G. R. (1982). Measurement of odour permeability of polypropylene packaging films at low odourant levels. *Polymer Testing* **3**, 133–142.