

Effect of Geomembrane Thickness on Diffusion of Toluene

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ABSTRACT

The effect of thickness (1.0 mm, 1.5 mm, 2.0 mm, and 2.4 mm) on the diffusion of toluene through four high density polyethylene (HDPE) geomembranes extruded from the same resin, antioxidant package, and carbon black is examined and the diffusion and permeation coefficients are reported. The implications are discussed.

1. INTRODUCTION

Geomembranes are a common barrier in municipal solid waste liner systems to prevent the leakage of landfill leachate. HDPE geomembranes are widely used in this application because they are excellent barriers to advective flow and the diffusive transport of inorganic contaminants present in the leachate (Rowe et al. 2004). However, geomembranes are susceptible to diffusive transport of volatile organic compounds, which are commonly found in landfill leachate as byproducts of the waste degradation (Kim et al. 1995). These contaminants are able to move through the HDPE geomembrane on a molecular level (Park and Nibras 1993; Prasad et al. 1994; Sangam and Rowe 2001, 2005; Edil 2003), resulting in potential contamination of surrounding soil and water.

Molecular transport through a geomembrane occurs in three steps: (1) adsorption of the contaminant onto the geomembrane, (2) diffusion through the geomembrane, (3) desorption from the geomembrane into the receptor fluid (Park and Nibras 1993; Prasad et al. 1994; Sangam and Rowe 2001, 2005). These processes are impacted by a variety of factors related to the geomembrane, test conditions, and contaminant types (Rowe 1998). For example, the diffusive flux through a geomembrane can change depending on properties of the geomembrane (crystallinity, degree of cross-linking, density, thickness, etc), permeant properties (molecular weight, polarity, initial concentration, etc.), and temperature (Michael and Bixler 1961, Rowe 1998, Sangam and Rowe 2001, 2005).

Ewais and Rowe (2014) studied the effects of the blown film process on the properties of geomembranes, and found that for different pulling speeds, there are differences in the mechanical and physical properties associated with blown-film geomembranes with exactly the same resin, but different thicknesses. Slight differences in crystallinity were reported for these geomembranes. Several studies (Michaels and Parker 1959: Michaels and Bixler 1961; Islam and Rowe 2009) have shown that increasing crystallinity of the geomembrane results in a decreased diffusion coefficient as diffusion occurs through the amorphous zone of the polymer. The objective of this study is to investigate the effect of geomembrane thickness in the diffusion process. The rate of diffusion should be inversely proportional to the square of the geomembrane thickness if the diffusion coefficient is constant (Cussler 1997).



2. MATERIALS AND METHODS

2.1 HDPE Geomembrane

The geomembranes used in this study were produced from the same resin and formed by blown-film extrusion. However, each geomembrane was pulled at a different speed from the dye, resulting in four different thicknesses. The properties of these geomembranes are shown in Table 1.

Table 1: Selected	properties ^a of	geomembranes	tested
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Property	Unit				
Thickness	mm	1.0	1.5	2.0	2.4
Density	g/cm ³	0.946	0.946	0.947	0.946
Crystallinity – 1 ^b	%	53.1 ± 1.2	50.5 ± 0.7	46.0 ± 2.0	41.0 ± 2.7
Crystallinity – 2 ^b	%	51.3 ± 4.7	48.5 ± 2.3	45.7 ± 2.5	41.7 ± 2.5
Crystallinity – 3 ^b	%	50.1 ± 1.8	41.6 ± 7.4	39.2 ± 4.0	39.8 ± 3.2
Crystallinity – 4 ^b	%	53.6 ± 1.8	48.0 ± 1.6	46.7 ± 0.9	48.4 ± 1.5

^aEwais and Rowe (2014)

^bASTM E793

2.2 Organic compounds

The contaminant used in this study was toluene (Table 2). Toluene is a chemical commonly found in landfill leachate, and has health risks associated with exposure above the recommended level (Rowe et al. 2004, USEPA 2009).

Property	Value		
Molecular weight	92.14	g/mol	
Density	0.8669	g/cm3	
Molar volume	106.28	cm3	
Aqueous solubility ^b	515	mg/L	
Log K ^c ow	2.79	-	

Table 2: Selected properties^a of toluene

^aMontgomery and Welcom (1990), Sangam and Rowe (2001)

[▶]At 20°C

^cn-octanol.water coefficient

2.3 Analytical Methods

Sample concentrations were analysed using Solid-Phase Micro Extraction gas chromatography with flame ionization detection. Each analysis used reference standards of known concentration to develop a calibration curve and sample concentrations were measured by comparison with the area under the curve for the test specimen with that for the standard.



2.4 Test Procedures

Diffusion tests were conducted using stainless steel cells (McWatters and Rowe 2009) at 21°C. A geomembrane separated the source and receptor of the cells. Volumes and initial concentration used are shown in Table 3 for each cell. The compartments were filled with deionized water and 1 ml of 5000 ppm BTEX in methanol was added to the source compartment.

The cells were sampled daily for the first week of the test and sampling frequency gradually decreased to once a month by 100 days into the test. When samples were taken, the same volume of deionized water replaced the volume extracted to ensure no air space developed in the cells.

Geomembrane	Source Volume	Receptor Volume	Co ^a
thickness (mm)	(mL)	(mL)	(ppm)
1.0	210	110	23.8
1.5	250	110	20.0
2.0	250	110	20.0
2.4	260	95	19.2

Table 3: Diffusion test cell volumes and initial concentrations

^aInitial concentration

The basic theory for diffusion through a geomembrane is summarized below, based on Sangam and Rowe (2001). The diffusive flux, f [ML⁻²T⁻¹], through a geomembrane can be calculated using Fick's first law.

$$[1] f = -D_g \frac{dc_g}{dz}$$

Where: D_g is the diffusion coefficient of the compound through the geomembrane (ML⁻²T⁻¹], c_g is the concentration of the compound in the geomembrane [ML⁻³], and z is the length of the path of diffusion or the thickness of the geomembrane [L]. At any point through the thickness of the geomembrane, the change in concentration with respect to time can be expressed using Fick's Second Law:

$$[2] \ \frac{\partial c_g}{\partial t} = D_g \frac{\partial^2 c_g}{\partial z^2}$$

At equilibrium, the concentration of a contaminant in the geomembrane, c_g , can be related to that in the adjacent aqueous solution, c_f , by a relationship analogous to Henry's Law, viz:

$$[3] c_g = S_{gf}c_f$$

where: S_{gf} is the partitioning coefficient [-], and c_f is the solution contaminant concentration [ML-³]. The diffusive flux through the geomembrane can be calculated using the fluid concentrations by substituting equation 3 into equation 1.



$$[4] f = -D_g \frac{dc_g}{dz} = -S_{gf} D_g \frac{dc_f}{dz} = -P_g \frac{dc_f}{dz}$$

Where: the product of the partitioning coefficient and the diffusion coefficient is expressed as P_g , the permeation coefficient [L²T].

Theoretical diffusion curves were calculated and fitted to the experimental results to infer the D_g and S_{gf} of the contaminants using the finite layer contaminant transport model POLLUTEV7 (Rowe and Booker 2004). These curves were calculated using the above diffusion equations with finite mass boundary conditions as described by Sangam and Rowe (2001).

3 RESULTS AND DISCUSSION

Figure 1 shows the calculated and experimental diffusion profile of toluene through the 1.0 mm and 1.5 mm geomembranes while Figure 2 shows the calculated and experimental profiles through the 2.0 mm and 2.4 mm geomembranes. The calculated profiles use S_{gf} and D_g (using POLLUTEv7) that best-fit the experimental data (Table 4).

The equilibrium concentrations of the contaminants in the 1.0 mm geomembrane tests were slightly higher than for the other thicknesses. The concentration of toluene at equilibrium was approximately 25% of the initial concentration for the 1.0 mm thickness diffusion test, which reached equilibrium in the shortest time. The equilibrium concentrations for the other three thicknesses were approximately 18% of the initial concentration. More time was required to reach equilibrium as the thickness increased, showing that increased thickness did provide a beneficial effect in reducing transient contaminant transport.

The diffusion coefficients varied with the change in thickness from 1 to 1.5 to 2.0 mm (there is no practical difference between the Dg results for 2 and 2.4 mm). When the calculated diffusion coefficients were related to the geomembrane crystallinities (Figure 3) there was a distinct downward trend. This was due to the less tortuous path and available with a larger amorphous zone corresponding to the lower crystallinity (Michaels and Parker 1959). The difference in crystallinity for each thickness was caused by different thermal and stress histories experienced by the geomembrane during the manufacturing process (Ewais and Rowe 2014).

The rate of transport through the geomembrane was controlled by Fick's second law (Eq.2). However, when comparing the transport of toluene through these geomembranes of different thickness both the thickness and diffusion coefficient were increasing (Table 4). Thus the expected benefit of slowing the rate of mass transfer for a thicker geomembrane in terms of a lower D_g/H^2 (Table 4) was somewhat smaller than would be expected for a constant D_g . For example, if the D_g was constant at the value for the 1mm geomembrane then for the 2.4 mm geomembrane D_g/H^2 would only be $3.3x10^{-6} \text{ s}^{-1}$ rather than the $5x10^{-6} \text{ s}^{-1}$ (i.e., 33% smaller).

The steady state flux through the geomembrane is given by Ficks first law (Eq. 4) which will be proportional to the permeation coefficient, P_g (Table 4), and inversely proportional to the geomembrane thickness for a given difference in concentration across the geomembrane. Thus, it will be proportional to the ratio of P_g/H . Because of the different stress and thermal histories of the geomembranes of different thicknesses tested, the ratio of P_g/H is similar for the 1 and 1.5

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mm thick geomembranes. Increased thickness beyond 1.5 mm resulted in a distinct decrease with increasing thickness and the lowest flux would be for the 2.4 mm thick geomembrane. However, again the benefit of increased thickness is smaller than if the geomembranes had the same diffusion coefficient. For example, if the D_g was constant at the value for the 1mm geomembrane then for the 2.4 mm geomembrane D_g/H would only be 1.2×10^{-8} m/s rather than 2×10^{-8} m/s (i.e., 40% smaller).

Thickness, H	S _{gf}	Dg	Dg/H ²	Pg	P _g /H
(mm)	(-)	(m²/s)	(S ⁻¹)	(m²/s)	(m/s)
1	150	1.9x10 ⁻¹³	19x10 ⁻⁶	2.9x10 ⁻¹¹	2.9x10 ⁻⁸
1.5	200	2.3x10 ⁻¹³	10x10 ⁻⁶	4.6x10 ⁻¹¹	3.1x10 ⁻⁸
2	190	2.8x10 ⁻¹³	7x10 ⁻⁶	5.3x10 ⁻¹¹	2.7x10 ⁸
2.4	180	2.7x10 ⁻¹³	5x10⁻ ⁶	4.9x10 ⁻¹¹	2.0x10 ⁻⁸

Table 4: Partitioning, diffusion, and permeation coefficients calculated using POLLUTEv7



Figure2 1 – Diffusion Plots for 1.0 mm and 1.5 mm thick geomembranes

Figure 1 – Diffusion plots for 2.0 mm and 2.4 mm thick geomembranes



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Figure 3 – Diffusion coefficient with respect to geomembrane crystallinity

4. CONCLUSION

This study examined the effects of the blown film process on migration of toluene through four different thicknesses of geomembranes produced with the same resin, but with different pulling speeds giving rise to the different thicknesses. Diffusion tests were conducted at room temperature (21°C) using stainless steel diffusion cells. S_{gf} and D_g were estimating using POLLUTEv7 to produce a theoretical diffusion curve that best fit the experimental data.

The diffusion coefficients of toluene through the four geomembranes showed a clear correlation with the crystallinities of the geomembrane; higher crystallinity corresponded to a lower diffusion coefficient. Although the four geomembranes had exactly the same resin, they did not have the same crystallinity because of the different stress and thermal histories (Ewais and Rowe 2014) and this resulted in change in the diffusion coefficient with changing thickness. Thus, the expected inverse relationship with thickness squared (H²) does not hold because the thicker geomembrane has a lower crystallinity and hence a higher diffusion coefficient than the thinner geomembrane. However, while the full H² effect was not realized, there was still a slower rate of diffusive mass transport (and a longer time to equilibrium) with increasing geomembrane thickness.

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