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Permeation of organic pollutants through a 14 year old field-exhumed HDPE geomembrane

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ABSTRACT: The permeation properties of pure organic chemicals through a 1.5 mm thick HDPE geomembrane after 14 years of use as liner for a landfill leachate lagoon were investigated. This geomembrane had a crystallinity of 66% which is considerably higher than the value of about 47% more typical of modern new HDPE geomembranes. Sorption tests conducted by immersing samples collected from different location in dichloromethane, trichloroethylene and toluene gave permeation coefficients of about 0.7 to 2.1×10^{-12} m^2/s, on average, one order of magnitude lower than those expected for a new unaged modern HDPE geomembrane. These results highlight the effects of high crystallinities in retarding the migration of the organic contaminants through HDPE geomembranes.

1. INTRODUCTION

Although HDPE geomembranes are frequently incorporated in engineering barrier system for modern landfills (Rowe 2001), there is a paucity of data relating to the long-term performance of these synthetic materials. Several laboratory and field investigations have been undertaken to address durability issues. For example, Rowe et al. (1998) described the decommissioning of an industrial and commercial landfill leachate lagoon after 14 years of service and the evaluation of a composite barrier system. The lagoon liner system consisted of a smooth 1.5 mm thick HDPE geomembrane overlying an approximately 3 m thick compacted clay liner. There was no protection layer above the geomembrane, which was directly exposed to the leachate and, above the leachate level, to the sunlight and atmosphere. The evaluation of the physical, chemical and mechanical properties of geomembrane samples collected from different locations on the lagoon liner suggested that some degradation had taken place. However, since the primary function of a geomembrane in landfills and other containment applications is to act as barrier to contaminant migration, it is important to assess the hydraulic or diffusive properties to complete the evaluation of the performance of the geomembrane liner.

This paper complements the previous paper by Rowe et al. (1998) by evaluating the permeation properties of a number of organic compounds through this 14 years old geomembrane.

2. DIFFUSION OF CONTAMINANTS THROUGH GEOMEMBRANES

The diffusion of contaminants through a geomembrane is a molecule-activated process that occurs by steps or jumps over a series of potential barriers, following the path of least resistance. The flux associated with one dimensional contaminant diffusion through a thin geomembrane can be described by Fick's first law:

$$J = -D_g \frac{dc_g}{dz} \tag{1}$$

where J is the flux or rate of contaminant transfer per unit area of section [$MT^{-1}L^{-2}$], c_g is the concentration of diffusing substance [ML^{-3}], z is the section thickness [L], and D_g is the diffusion coefficient [L^2T^{-1}]. For transient state conditions where the concentration gradient of the diffusing substance across the medium varies with time, the rate of the chemical concentration at any point is given by Fick's second law:

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

Although many laboratory methods and techniques are available (Haxo 1990, Rowe 1998) for estimating migration parameters, the immersion/sorption method has been commonly used for pure chemicals. In this method, also known as weight gain method, a coupon of geomembrane is immersed in contaminant solution and the geomembrane specimen periodically removed to measure the weight gained. The data are reported as fractional (relative) mass uptake (with respect to the equilibrium value) as function of time. For a constant diffusion coefficient, the solution of Fick's second law equation leads to (Crank 1975):

$$\frac{m_t}{m_{eq}} = 1 - \frac{8}{\pi^2}\sum_{n=1}^{n=\infty}\frac{(-1)^2}{(2n+1)^2}\,exp\left(\frac{-D_g(2n+1)^2\pi^2 t}{h_g^2}\right) \tag{3}$$

where m_t, m_{eq} represent the mass uptake at a given time[M], t, and at infinite time respectively [T], and h_g is the thickness of the geomembrane [L].

One of the simplest means of inferring the diffusion coefficient from sorption data is from the time $t_{½}$ when the amount sorbed has reached half of its equilibrium value as follows (Crank 1975):

$$D_g = 0.0492\frac{h_g^2}{t_{½}} \tag{4}$$

The value of $t_{½}$ can be deduced directly for m_t/m_{eq} = ½ by plotting sorption data against square root of time and D_g can be calculated using Eq. 4. This diffusion coefficient represents an average value that is not concentration dependant and is calculated assuming that the diffusion process is Fickian.

In general, the migration of organic molecules through a geomembrane is accompanied by sorption to the geomembrane sites and microvoids due to the affinity between the chemical and the geomembrane. The solubility coefficient of the chemical in the geomembrane, S_g [-], at saturation can be expressed as:

$$S_g = \frac{m_{eq}}{m_g} \tag{5}$$

where m_g is the initial mass (g) of the geomembrane. The associated permeation coefficient P_g [L^2T^{-1}] is:

$$P_g = S_g D_g \tag{6}$$

3. EXPERIMENTAL INVESTIGATION

3.1 Material

Three geomembrane samples were evaluated. The samples were collected from different locations on the lagoon and had experienced various exposure conditions: SNL (sunlight, no leachate), NSLS (no sunlight, leachate-slope), and NSLB (no sunlight, leachate and sludge at bottom). Typical properties of the samples as collected after 14 years of service are presented in Table 1.

Three organic chemicals (Table 2) commonly found in MSW landfill leachate (dichloromethane: DCM, trichloroethylene: TCE, and toluene: TOL) were examined. The chemicals were laboratory grade (99 +% purity) and were purchased from Sigma-Aldrich (Mississauga, Ontario, Canada).

Table 1. Properties of the 14 years old geomembrane samples investigated (modified from Rowe et al. 1998)

Property	ASTM	Sample		
		SNL	NSLS	NSLB
Density (g/cm^3)	D792	0.967	0.966	0.965
Crystallinity (%)	E794	67.5	65.5	65.7
Carbon Black Content (%)	D1638	2.64	2.73	2.2
Melt flow Index (g/10min.)	D1238	0.5	0.41	0.31
OIT (min)	D3895	1.8	6.3	5
Stress Crack Resistance (hrs.)	D5397	2.6	3.1	3
Tensile Properties	D638			
Yield–Strength (kN/m)		37	37	39
Yield-Strain (%)		11	11	10
Break-Strength (kN/m)		25	32	27
Break-Strain (%)		379	703	456

Table 2. Selected properties of chemicals tested†

Chemicals	MW (g/mol)	Density (g/cm^3)	MV‡ (cm^3)	logK$_{ow}$ (-)	DM (Debye)
Dichloromethane	84.93	1.3266	64.02	1.25	1.60
Trichloroethylene	131.39	1.4642	89.74	2.53	0.77
Toluene	92.14	0.8669	106.28	2.79	0.30

MW: Molar weight, MV: Molar Volume, DM: Dipole Moment
† From Montgomery & Welkom (1990)
‡ Calculated based on MW and density

3.2 Procedure

The immersion/sorption test method (Aminabhavi & Naik 1998, Sangam & Rowe 2001) was used in this study. After cleaning and drying the geomembrane to remove any residual moisture, samples cut in coupons were immersed in glass jars filled with each of the chemical being examined. At specific times, the coupons were retrieved from the bottles, gently wiped to remove any extra liquid chemical on the surface of the coupons and the weight measured using a high sensitivity (±0.0001g) electronic balance (Statorius, Model BP210S). This process took about 30 to 60 seconds and the coupons were immediately re-immersed in the bottles and then the experiment continued. Coupon weight was monitored with until equilibrium was reached. At any time t, the chemical mass uptake by the geomembrane sample was calculated as the difference of the measured weight at that time and the original mass. The temperature in the laboratory during the investigation was 23 ± 2ºC

4. RESULTS AND DISCUSSIONS

Figure 1 shows the typical variation of the total mass uptake by the geomembrane samples with time as the compounds are sorbed by the geomembrane. Since the equilibrium value may fluctuate due to experimental errors, it is difficult to obtain the exact equilibrium mass gained. Therefore, a maximum rise ($m_t = m_{eq}(1-e^{-bt})$) theoretical curve was fitted to the data. The theoretical curves fitted for sample NSLB are shown as lines in Figure 1 for the three compounds examined. As shown in Figure 2, there is no significant difference between the data obtained for the three samples for a given compound. As discussed later, this may be due to the fact there is only a slight difference between the fractions of the crystalline zone measured in terms of crystallinity.

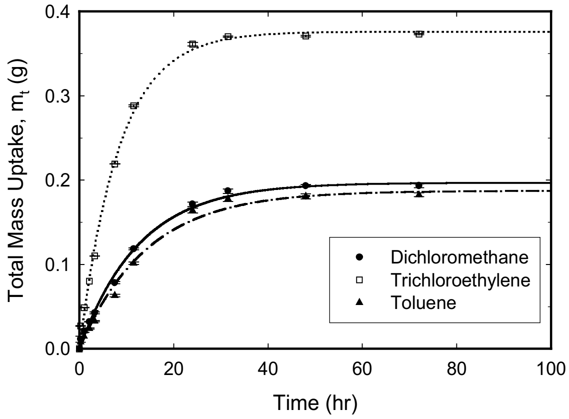

Figure 1. Contaminants mass uptake by sample NSLB during sorption tests

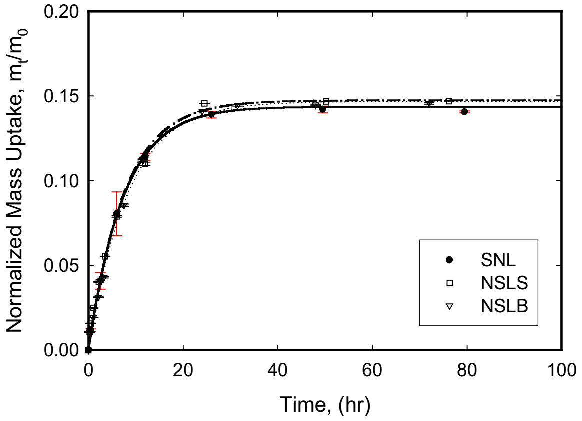

Figure 2. TCE mass uptake by the 14 years old geomembrane samples during immersion/sorption test

Table 3. Summary of inferred sorption (S_g), diffusion (D_g), and calculated permeation (P_g) coefficients

Chemical	SNL			NSLS			NSLB		
	S_g (-)	D_g 10^{-11}m^2/s	P_g 10^{-11}m^2/s	S_g (-)	D_g 10^{-11}m^2/s	P_g 10^{-11}m^2/s	S_g (-)	D_g 10^{-11}m^2/s	P_g 10^{-11}m^2/s
Dichloromethane	0.071	1.28	0.091	0.074	1.28	0.095	0.070	1.03	0.072
Trichloroethylene	0.144	1.44	0.207	0.147	1.44	0.212	0.146	1.28	0.187
Toluene	0.070	0.99	0.069	0.073	1.07	0.078	0.072	0.95	0.069

Based on the estimate of the masses at equilibrium, the sorption curves can be established by plotting m_t/m_{eq} vs. $t^{1/2}$ as shown in Figure 3 for sample NSLB. The initial portion of these curves is non-linear but typical for semi-crystalline polymers such as HDPE as reported by several investigators (Park & Nibras 1993, Aminabhavi & Naik 1998, Müller et al. 1998). The solubility, diffusion and permeation coefficients inferred from the tests using Eqs. 4, 5 and 6 respectively are shown in Table 3.

TCE exhibits the highest sorption, diffusion and permeation coefficients with values of 0.146, 1.28×10^{-11} m^2/s, and 0.187×10^{-11} m^2/s respectively for sample NSLB. Toluene and DCM have similar coefficients with DCM being slightly higher. As can be seen in Table 3, the coefficients for a given chemical are similar for the three samples examined and are generally lower than values reported for new modern HDPE geomembranes (Park & Nibras 1993, Aminabhavi & Naik 1998).

To appreciate the significance of aging on the inferred permeation coefficients, one should compare the measured data for the old geomembrane to values of the original material. However, since the diffusion parameters of the original material were not available, it is of some interest to compare the observed data to the typical values expected for a new modern geomembrane investigated by Sangam (2001). The new modern geomembrane was a 2.0 mm thick HDPE with a density of 0.940 g/cm^3 and a crystallinity of about 47% (See Sangam 2001 for the complete material datasheet). The sorption, diffusion and permeation coefficients inferred for that new unaged modern geomembrane using the same procedure as described above are shown in Table 4. It can be seen from Table 4 that the reduction factor (RF), calculated as the ratio of the permeation coefficients of the new unaged and old geomembranes, of the chemical examined ranged from 8 to 10, 10 to 12, and 9 to 10 for DCM, TCE, and Toluene respectively.

The observed differences in permeation coefficients of the old and modern geomembranes may be attributed to the relatively high crystallinity (65.5-67.5%) of the 14 years old samples compared to 47% for the new unaged modern geomembrane. As indicated by Naylor (1989) and Rogers (1985) the crystalline zones in semi-crystalline polymers like HDPE, act as relatively impermeable barriers to the migrating molecules by first, reducing the sorptive and diffusive region and second, restraining the mobility of the polymer molecules required for the accomplishment of the diffusive jump. As a consequence, the segmental mobility of the chains required to achieve migration is restrained and therefore the diffusion process becomes more dependent on the size and shape of the penetrant molecule (Naylor 1989, Rogers 1985).

Table 4. Comparison of inferred permeation coefficient of the old and the new unaged modern geomembranes

Chemical	Old GM	New GM¶			RF†
	P_g	S_g	D_g	P_g	
Dichloromethane	0.072-0.095	0.104	7.02	0.730	8-10
Trichloroethylene	0.187-0.212	0.225	9.71	2.185	10-12
Toluene	0.069-0.078	0.109	6.30	0.687	9-10

¶Density= 0.940g/cm^3, Crystallinity= 47%, OIT= 133 min.
†RF=P_g(New GM)/P_g(old GM)
S_g [-], D_g [10^{-11} m^2/s], P_g [10^{-11} m^2/s]

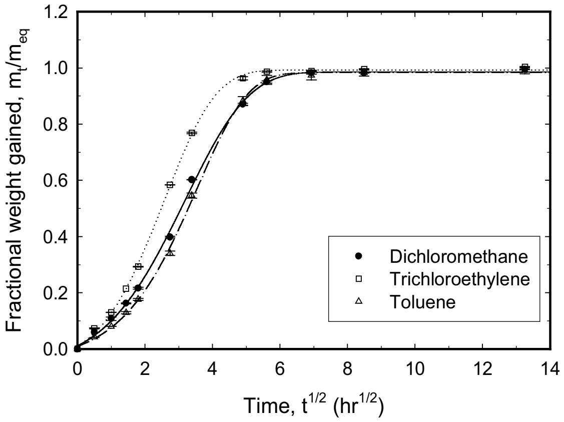

Figure 3. Observed sorption curves for samples NSLB immersed in different organic chemicals

To validate the above hypothesis, it is important to compare the sorption curves of the old and new geomembrane samples. Since the geomembranes (new and old) have different thicknesses and initial masses prior to the immersion test, it is essential to correct for these two factors by dividing the mass uptake by the geomembrane initial mass (m_g) and the square root of time by the thickness of the geomembrane. The resultant sorption curves presented in Figure 4 for TCE show that the new geomembrane sorbs more TCE and has a higher rate of TCE mass uptake compared to the 14 years old geomembrane suggesting significant influence of the crystallinity on the permeation process.

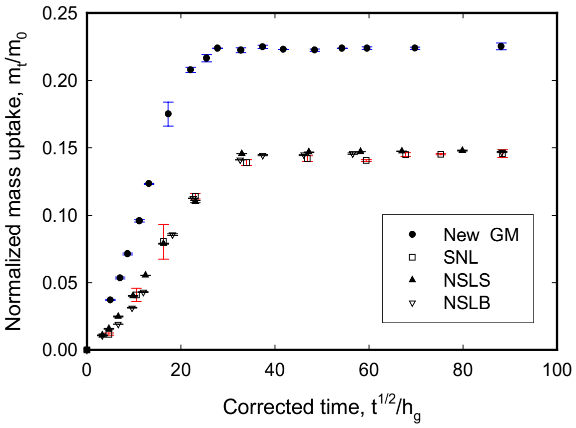

Figure 4. Comparison of sorption curves for the new and old geomembranes immersed in pure TCE

If the crystallinity of the geomembrane were the only key parameter as hypothesized, then correction of mass uptake by the percent of amorphous zone in which the sorption and the diffusion take place should yield sorption curves that coincide. This assumes that the diffusive migration including sorption and pure diffusion is limited to the amorphous zone. Considering the percent of the amorphous zone to be ($1-\chi$), where χ is the crystallinity, the generated curves are presented in Figure 5 and show similar equilibrium normalized mass uptake for all samples suggesting that sorption is governed by the available sorption sites defined by the amorphous zone. However, it can also be seen from the curves that the rising parts of the curves obtained for the old and new geomembranes do not coincide indicating different diffusion rates for the two set of geomembranes examined. This suggests that, in addition to the percent of the amorphous zone and hence the crystalline zone, other properties such as cross-linking and length of the polymer chains may affect the diffusion process by influencing the kinetics of the jumps required for the movement of the diffusing chemical.

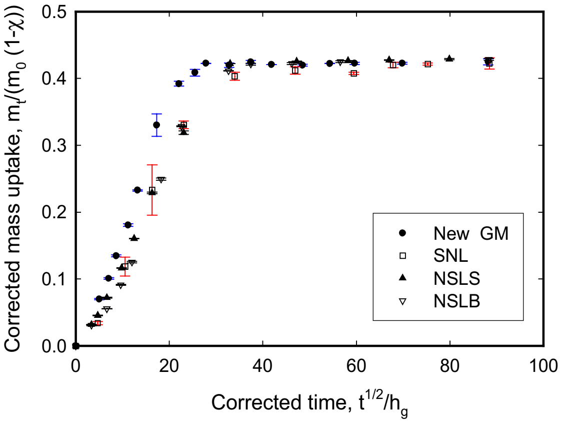

Figure 5. Corrected sorption curves with respect to sample crystallinity for the new and old geomembranes immersed in pure TCE

5. SUMMARY AND CONCLUSIONS

An investigation onto the permeation properties of pure organic pollutants into a 14 year old HDPE geomembrane has been presented. The results from immersion tests indicated that the organic chemicals examined permeate through this old geomembrane at rates of about one order of magnitude slower than expected for a typical new unaged modern geomembrane. Since the HDPE geomembranes crystallinity appears to increase with ageing (Sangam 2001), these results suggest that diffusion in an intact geomembrane may decrease as the geomembrane ages.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

Aminabhavi T.M. & Naik H.G. 1998. Chemical compatibility testing of geomembranes- Sorption/Desorption, Diffusion and Swelling phenomena, *Geotextiles & Geomembranes*, 16(6): 333-354.

Crank J. 1975. *The mathematics of diffusion*. 2nd Edition, Oxford: Clarenderon Press.

Haxo H.E. Jr. 1990. Determining the transport through geomembranes of various permeants in different applications. In R.M. Koerner (ed.), *Geosynthetic Testing for Waste Containment Applications*, ASTM SPT 1081:75-94.

Montgomery J.H. and Welkom L.M. 1990. *Groundwater chemicals desk reference*. Lewis Publishers Inc., Chelsea, Michigan.

Müller W., Jakob I., Tatzky G.R. & August H. 1998. Solubilities, Diffusion and Partitioning Coefficients of Organic Pollutants in HDPE Geomembranes: Experimental Results and Calculations. *Proceedings of 6th International Conference on Geosynthetics*, Atlanta, IFAI, 239-248.

Naylor T. deV. 1989. Permeation properties. In Colin Booth & Colin Price (eds.), *Comprehensive Polymer Science,* 2, Pergamon Press, Oxford, 643-668.

Park J.K. & Nibras M. 1993. Mass flux of organic chemicals through polyethylene geomembranes. *Water Environment Research*, 65: 227-237.

Rogers C.E. 1985. Permeation of gases and vapors in polymers. In J. Comyn (ed.), *Polymer Permeability*, Elsevier Applied Science Publishers, London, UK, 11-73.

Rowe R.K. 1998. Geosynthetics and the minimization of contaminant migration through barrier systems beneath solid waste, *Proceedings of the 6th International Conference on Geosynthetics*, Atlanta, IFAI, 1: 27-103.

Rowe R.K. 2001. Liner Systems. In Rowe R.K. (ed.), *Geotechnical and Geoenvironmental Engineering Handbook*, Kluwer Academic Publishing, Norwell, U.S.A., 739-788.

Rowe, R.K., Hsuan, Y.G., Lake, C.B., Sangam, P. & Usher, S. 1998. Evaluation of a composite (geomembrane/clay) liner for a lagoon after 14 years of use. *Proceedings of the 6th International Conference on Geosynthetics*, Atlanta, IFAI, 1: 191-196.

Sangam H.P. 2001. *Performance of HDPE Geomembrane Liners in Landfill Applications*. PhD Dissertation, The University of Western Ontario, 394p.

Sangam H.P. and Rowe R.K. 2001. Migration of dilute aqueous organic pollutants through HDPE geomembranes. *Geotextiles & Geomembranes* 19(6): 329-357.