

# Diffusion modelling of OIT depletion from HDPE geomembrane in landfill applications

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**ABSTRACT:** The results of a diffusion modelling study to evaluate experimental data on oxidative induction time (OIT) depletion from high-density polyethylene (HDPE) geomembrane (GM) in accelerated ageing tests are presented. The paper provides: (1) results of diffusion modelling of OIT depletion from a GM immersed in leachate and in a composite liner with leachate above the liner at different incubation temperatures; (2) a comparison of the results of the diffusion model and the conventional first-order (exponential) antioxidant depletion model; (3) estimates of diffusion and partitioning coefficients at typical landfill temperatures based on Arrhenius-type relationships; and (4) an application of the estimated parameters to model a composite liner with 30 cm thick sand layer. The antioxidant diffusion coefficients ranged from  $2.1 \times 10^{-15}$  (at 26°C) to  $1.6 \times 10^{-13}$  m<sup>2</sup>/s (at 85°C) and the partitioning coefficients ranged from 720 (at 26°C) to 4 (at 85°C). The antioxidant depletion time obtained using the first-order model was similar to that predicted using the diffusion model for tests where the OIT was depleted during the test period. However the first-order model gave smaller predictions of depletion time than the diffusion model in cases where there was only limited OIT depletion and in these cases the diffusion model is likely to give more accurate predictions. Arrhenius modelling provided a means of estimating diffusion and partitioning coefficients at field temperatures. At a typical landfill temperature of 35°C the calculated antioxidant depletion time for the geomembrane considered was about 130 years for a case where there was a 1.5 cm sand protection layer and 230 years for the case when 30 cm sand protection layer was used. Thus these results suggest that the use of a 30 cm sand protection layer in addition to the typical geotextile protection layer between the geomembrane and a coarser granular leachate drainage layer would provide potential benefits in terms of extending the geomembrane service life by reducing the rate of outward diffusion of antioxidants from the geomembrane (as well as providing good physical protection of the liner). This paper has also illustrated how diffusion modelling can be used for considering a range of situations different from those under which the basic experimental data was obtained.

**KEYWORDS:** Geosynthetics, Aging, Antioxidant, Diffusion, Geomembrane, Landfill, Liner, Temperature

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## 1. INTRODUCTION

High-density polyethylene (HDPE) geomembranes (GM) are frequently used in composite landfill liners due to their effectiveness in reducing outward advective and diffusive contaminant transport from the landfill (Rowe *et al.* 2004; Rowe 2005). Extensive research has recently been conducted into factors affecting both the leakage through geomembrane liners (Take *et al.*, 2007; El-Zein and Rowe 2008; Saidi *et al.*, 2008; Zhu *et al.*, 2009) and the source of tensions in the GM that could ultimately

cause stress cracking in these liners (Thusyanthan *et al.*, 2007; Brachman and Gudina, 2008a, b). HDPE GMs have excellent short-term high resistance to chemicals present in landfill leachate (Tisinger *et al.* 1991; Koerner 1998; Rowe *et al.* 2004). To protect GM from oxidative degradation antioxidants are added to the polymer matrix. The long-term performance of a GM not only depends on the chemical nature of the antioxidants but also on the physical loss of antioxidants during its lifetime. The service life of GM is initially controlled by the rate of

depletion of antioxidants. The process involves dissolution or consumption of antioxidants from the surface of GM and outward diffusion from the core to the surface due to a concentration gradient (Hsuan and Koerner 1998; Sangam and Rowe 2002). The depletion of antioxidants leaves the GM susceptible to oxidative degradation (Grassie and Scott 1985). Thus the first stage of degradation of GM is antioxidant depletion, the second stage is the induction time to the onset of polymer degradation, and the third stage is polymer degradation involving the decrease in a geomembrane property to a level often taken to be 50% of the original value (Hsuan and Koerner 1998). The aging of the geomembrane is a function of temperature and temperatures of 30–60°C have been reported for landfill liners (Rowe 2005; Koerner and Koerner, 2006; Rowe and Hoor 2009).

Antioxidant depletion has been examined in laboratory-accelerated ageing studies for GMs immersed in air, water, synthetic landfill leachate, acid mine drainage, and hydrocarbons (Hsuan and Koerner 1998; Sangam and Rowe 2002; Gulec *et al.* 2004; Rimal *et al.* 2004; Rowe and Rimal 2008a). In these studies results were analysed using a first-order antioxidant depletion model (Hsuan and Koerner 1998). This is adequate for predicting the depletion of antioxidants from GM for exposure conditions similar to (except of temperature) those examined in the original tests (e.g. data on a GM immersed in a fluid of interest at three or more temperatures could be used together with Arrhenius modelling to predict the likely performance of the GM immersed in the same fluid at a temperature different from the original test temperatures). However, the first-order antioxidant depletion model cannot be readily used to predict the performance of the GM in an environment different from that used to obtain the original data. Thus, for example, a first-order model with parameters obtained from leachate immersion tests will not provide a good prediction of the likely depletion rate in a composite liner in a landfill (Rowe and Rimal 2008a). Likewise, first-order antioxidant depletion parameters obtained from the tests reported by Rowe and Rimal (2008b) for a GM in a composite liner with a 1.5 cm thick sand protection layer cannot be directly used to predict the likely antioxidant depletion from a GM where there is a thicker (e.g. 30 cm thick) sand protection layer. To do so one would need to be able to model the diffusion from the GM into the adjacent porous media.

Although antioxidant depletion is controlled by diffusion of antioxidants from the GM, none of these prior studies analysed the antioxidant depletion data using diffusion modelling techniques. Furthermore, there has been no comparison of the results from diffusion modelling with those inferred from the first-order antioxidant depletion model. Rowe and Rimal (2008b) developed and applied a theoretical technique for modelling diffusion of antioxidants from a GM and used this to interpret the effect of various protection layers on the depletion of antioxidant from a GM. However, they only considered depletion at room temperature. The present study seeks to use similar diffusion modelling to evaluate the experimental data on antioxidant depletion from immersion and

composite liner simulation test at a range of incubation temperatures (85, 70, 55 and 40°C and room temperature). Thus this study had four objectives: (1) to analyse experimental data on OIT depletion from GM in leachate immersion tests and composite liner simulation tests at different incubation temperatures using a diffusion model; (2) to compare the results of the diffusion model and the first-order (exponential) antioxidant depletion model; (3) to establish Arrhenius-type relationships to estimate diffusion and partitioning coefficients at typical landfill temperatures; and (4) to use the estimated parameters to model OIT depletion from a GM in a composite liner with a 30 cm thick sand protection layer and hence assess the potential beneficial effect of the protection layer in reducing the depletion of antioxidants.

## 2. THEORETICAL CONSIDERATIONS

### 2.1. Outward migration of antioxidants

For all but thin polyethylene films (thickness < 0.1 mm) and high surface concentration of antioxidants (Möller and Gevert 1996; Haider and Karlsson 2000), the rate of loss of antioxidants depends on (a) the partitioning of the antioxidant between the GM surface and the adjacent fluid, and (b) the rate of diffusion of the antioxidants from core to surface of the GM. Consumption of antioxidants (e.g. hydrolysis of phosphite stabilizer and reaction of the antioxidant with oxygen, free radicals and alkyl peroxides) may occur at the surface of the GM and in an aqueous phase (Haider and Karlsson 2002; Grassie and Scott 1985). The loss of antioxidant from the GM at the surface is, in part, controlled by the affinity of the antioxidants for polyethylene relative to the surrounding media. This is usually related to the difference in solubility of the antioxidants in the two materials. When placed in a fluid, antioxidants will be released into the adjacent fluid until a final equilibrium is reached. At this point, the concentration of antioxidant in the GM,  $c_{gm}$  (ML<sup>-3</sup>), and in the adjacent fluid,  $c_f$  (ML<sup>-3</sup>), are related by Henry's law:

$$c_{gm} = c_f S_{gf} \quad (1)$$

where  $S_{gf}$  is a partitioning coefficient (–) between the GM and the fluid;  $S_{gf}$  is a constant for a given permeant, fluid, GM and temperature of interest. Equation 1 is valid at low concentrations or when the antioxidant does not interact with the polymer (Rogers 1985).

The diffusive flux of permeant through a GM is governed by Fick's first law of diffusion:

$$f = -D_{gm} \frac{\partial c_{gm}}{\partial z} \quad (2)$$

where  $f$  is mass flux or rate of transfer of diffusing substances through a unit area of the GM (ML<sup>-2</sup>T<sup>-1</sup>);  $D_{gm}$  is the diffusion coefficient in the GM (L<sup>2</sup>T<sup>-1</sup>);  $c_{gm}$  is the concentration of the diffusing substance in the geomembrane (ML<sup>-3</sup>); and  $z$  is the distance parallel to the direction of diffusion (L).

In the transient state, consideration of conservation of

mass gives the following governing differential equation (Fick's second law of diffusion):

$$\frac{\partial c_{gm}}{\partial t} = D_{gm} \frac{\partial^2 c_{gm}}{\partial z^2} \quad (3)$$

which must be solved for the appropriate initial and boundary conditions.

Temperature is a key factor influencing the diffusion of antioxidants. The temperature dependence of diffusion coefficient is mathematically described by Arrhenius-type relationship (Crank and Park 1968; Moisan 1985):

$$D_{gm} = D_0 \exp\left(-\frac{E_d}{R.T}\right) \quad (4)$$

In logarithmic form the above equation can be expressed as

$$\ln(D_{gm}) = \ln(D_0) - \left(\frac{E_d}{R}\right)\left(\frac{1}{T}\right) \quad (5)$$

where  $D_{gm}$  is the diffusion coefficient typically in  $m^2/s$ ;  $D_0$  is pre-exponential factor (a constant for a particular system independent of temperature) in  $m^2/s$ ;  $E_d$  is the activation energy of diffusion in  $kJ\ mol^{-1}$ ;  $R$  is the universal gas constant,  $8.31\ J\ mol^{-1}\ K^{-1}$ ; and  $T$  is the absolute temperature in K.

Other factors that affect the outward migration of antioxidants from the GM are solubility of antioxidant in the polymer, polymer structure (crystallinity and density), structure of the diffusant (molecular weight and shape) (Moisan 1980a, b; Billingham 1990). Moisan (1980b) demonstrated that the diffusion coefficient of an antioxidant decreased steadily with increasing density of polyethylene. This also implied a decrease in diffusion coefficient with increase in crystallinity of polyethylene. Experimental results of Roe *et al.* (1974) and Moisan (1980a) demonstrated that the diffusion coefficient decreased with increasing molecular weight of antioxidants. However, the shape of the molecules affected the correlation between diffusion coefficient and molecular weight. Billingham (1990) summarized the results on different studies on dependence of diffusion coefficient with molecular structure of antioxidants. It was concluded that, for a given molecular weight, the antioxidant with long flexible molecules diffused faster than the more rigid and compact molecules.

## 2.2. Exponential OIT depletion model, antioxidant depletion rate and time

OIT is a useful index of the amount of antioxidants in the GM. Depletion of OIT from GM follows a first-order (exponential) decay model (Hsuan and Koerner 1998; Sangam and Rowe 2002). The OIT representing the total amount of antioxidant remaining in the GM at time  $t$  is given by a kinetic equation of first-order.

$$OIT(t) = OIT_0 \cdot \exp(-st) \quad (6)$$

where  $OIT_0$  is the initial OIT (min);  $s$  is the antioxidant depletion rate ( $month^{-1}$ ); and  $t$  is the aging time (months).

In most previous studies, OIT depletion was modelled using Equation 6. The time taken for depletion of

antioxidants (Stage I of the GM service life) was calculated as the time taken for the reduction of OIT from the initial value of  $OIT_0$  to a final residual value of  $OIT_{(f)} = 0.5\ min$ . (Hsuan and Koerner 1998). On rearranging, Equation 6 gives:

$$t_d = \frac{\ln(OIT_0) - \ln(OIT_{(f)})}{s} \quad (7)$$

which can be used to calculate the antioxidant depletion time,  $t_d$ , for antioxidant depletion rate,  $s$  at a particular temperature.

## 2.3. Theoretical diffusion modelling and OIT depletion rates

The analytical solution to Equation 3 for outward diffusion of antioxidants from a polymer film (a GM in our case) placed in an infinite bath is given by Equations 8 and 9 (Crank 1975; Comyn 1985).

$$\frac{C - C_0}{C_1 - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left\{\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right\} \times \cos\left(\frac{(2n+1)\pi x}{2l}\right) \quad (8)$$

where  $C$  is the concentration at points within the GM;  $C_0$  is the initial concentration within the GM;  $2l$  is the GM thickness;  $n$  is the integer number;  $D$  is the diffusion coefficient;  $t$  is the time;  $x = 0$  at the centre of a GM of thickness  $2l$ ; and its faces being located at  $x = +l$  and  $-l$ . If the GM ( $-l < x < l$ ) has an initial antioxidant concentration  $C_0 = 1$  and the surfaces are kept at a constant concentration  $C_1 = 0$ , then the concentration  $C$  at points within the GM is given by:

$$C = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left\{\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right\} \times \cos\left(\frac{(2n+1)\pi x}{2l}\right) \quad (9)$$

The experimental results can be evaluated according to the solution given by Crank (1975) for mass.

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left\{\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right\} \quad (10)$$

where  $M_t$  denotes the mass of antioxidant which has left the GM at time  $t$ , and  $M_\infty$ , the corresponding quantity after infinite time (i.e. the initial mass of antioxidant in the GM). Thus the OIT value measured in the GM at time  $t$  can be represented by  $OIT = M_\infty - M_t$  and initially  $OIT_0 = M_\infty$ .

The normalized expression for OIT is given by

$$\frac{OIT}{OIT_0} = \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left\{\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right\} \quad (11)$$

The variation in the normalized  $OIT$  with time was calculated from Equation 11 for a GM with a typical thickness of 1.5 mm immersed in leachate for a diffusion coefficient  $D_{gm} = 2.1 \times 10^{-15} \text{ m}^2/\text{s}$  (Rowe and Rimal 2008b) as shown by the ‘analytical solution’ in Figure 1. Since the outward diffusion profile is symmetrical from the two sides of the GM, it is sufficient to model a half thickness (0.75 mm) of the GM with a zero constant concentration boundary condition at the surface and a zero flux boundary condition at the middle of the GM. This case also was modelled using the finite layer analysis program POLLUTE<sup>®</sup> v7.09, (Rowe and Booker 2004) and the concentration curve was integrated to obtain the mass of antioxidant in the GM at different times and these are shown as ‘model’ in Figure 1. The finite layer diffusion model results (Figure 1(a)) are in excellent agreement with the results evaluated using the analytical solution (Equation 11). The theoretical results were then plotted as  $\ln(OIT/OIT_0)$  versus time (Figure 1(b)) and a linear regression curve fitted to the normalized  $OIT$  values deduced from the diffusion model at different times was used to obtain the  $OIT$  depletion rate  $s$  (Equation 6). A visual inspection of Figure 1(b) reveals that while the regression line presents a very good fit, the data points do

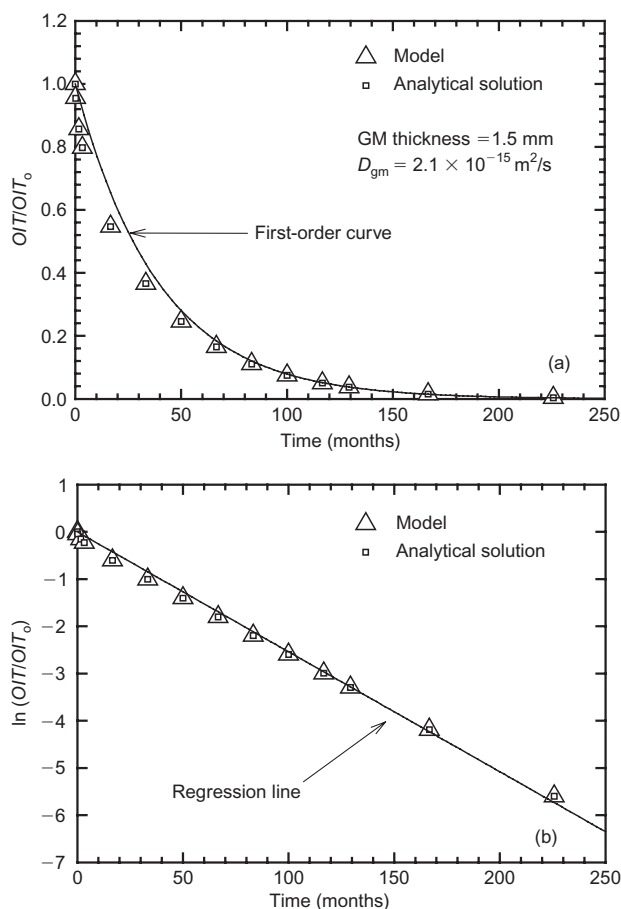


Figure 1. Normalized  $OIT$  depletion at different times based on diffusion theory (from both an analytical solution and a finite layer model) and a first-order regression fit to that data. The first-order curve in Figure 1(a) corresponds to the regression line in Figure 1(b)

not all fit on the straight line. This implies that the relationship given by Equation 6 is an approximation and inspection of Figure 1(b) suggests that the estimation of the depletion rate may vary depending on the time period over which the fit is applied. To quantify this observation, regression curves were fit to the ‘data’ from the analytical solution (i.e. any issues of ‘experimental error’ are excluded). A regression of the data from  $t = 0$  months (at  $OIT = OIT_0$ ) to  $t = 226$  months (corresponding to  $OIT = 0.5$  min. at complete depletion of antioxidants) from both the analytical solution and the finite layer model gave  $s = 0.0254 \text{ month}^{-1}$  (with  $R^2 = 1.0$ ). Regression of data at shorter time intervals gave, for example, (a)  $s = 0.0733 \text{ month}^{-1}$  ( $R^2 = 0.92$ ) for a fit from  $t = 0$  to 3.3 months, (b)  $s = 0.0318 \text{ month}^{-1}$  ( $R^2 = 0.95$ ) from  $t = 0$  to 33 months, (c)  $s = 0.0294 \text{ month}^{-1}$  ( $R^2 = 0.97$ ) from  $t = 0$  to 50 months, and (d)  $s = 0.0254 \text{ month}^{-1}$  (with  $R^2 = 1.0$ ) from  $t = 0$  to 226 months (full depletion as noted above). Based on these results it was found the evaluation of short-term theoretical data using the first-order kinetic equation (Equation 6) gave higher  $OIT$  depletion rates based on the short term data compared to those based on the long-term data at which the  $OIT$  had reached to 0.5 min. This arises from the fact that while the diffusion process can be reasonably approximated over a long-time period by the first-order relationship (Equation 6), diffusion gives relatively faster depletion at small times (when the concentration gradient is very high) and slower depletion at later times (when the concentration gradient is much lower). This also provides a theoretical basis for the fact that early time experimental data is often below the best fit line obtained in antioxidant depletions tests (e.g. Sangam and Rowe 2002; Rowe and Rimal 2008a; Rowe *et al.* 2009). Thus it can be concluded that it is important to analyse long term data (i.e. to depletion) to obtain accurate antioxidant depletion rates using a first-order approximation. Fitting to data over shorter time periods (as is often necessary at low temperatures due to the time it takes to deplete antioxidants at lower temperatures such as room temperature) will result in an over prediction of the depletion rate and consequently an underestimate of the time for antioxidant depletion.

### 3. MODELLING DIFFUSION OF OIT

A technique for modelling diffusion of  $OIT$  was developed to examine the application of the diffusion model to the  $OIT$  depletion data from leachate immersion and composite liner simulation tests. The authors have previously reported results of accelerated aging laboratory investigations on the  $OIT$  depletion and long-term performance of GM (Sangam and Rowe 2002; Rowe and Rimal 2008a, b; Rowe *et al.* 2009). A brief synopsis of these tests and material used will be presented below, followed by modelling procedures, parameters and results.

#### 3.1. Laboratory testing

##### 3.1.1. Immersion tests

Accelerated aging tests were conducted on 2.0 mm thick GM (GM-A, initial  $OIT = 133$  min., Table 1) immersed

in synthetic leachate and water (Sangam 2001; Sangam and Rowe 2002; Rowe *et al.* 2009). Coupons of the GM were placed in the incubation containers at 85, 70, 55, 40 and 22°C (room temperature). This study demonstrated that antioxidant depletion times were shorter for samples immersed in leachate than in water and longest in air.

### 3.1.2. Immersion versus composite liner tests

Aging tests were performed with a GM (GM-B, Table 1) in a simulated landfill liner system and were compared with results from conventional leachate immersion tests on the same GM (Rowe and Rimal 2008a). From top down, the composite liner cells (denoted as CL-T) comprised a 19 mm gravel layer (simulating the leachate collection layer), a 270 g/m<sup>2</sup> needle punched nonwoven geotextile protection layer, a 1.5 mm thick GM with initial OIT = 135 min., a hydrated geosynthetic clay liner (GCL), and compacted moist Ottawa silica sand. The gravel layer was saturated with leachate that was refreshed every 2 weeks. The composite liner cells were incubated at 85, 70, 55 and 26°C (room temperature). The leachate immersion test on the same GM was conducted simultaneously at the same temperatures. The GM in the simulated composite liner cells was removed at different times and tested for OIT (Rowe and Rimal 2008a). It was concluded that the length of antioxidant depletion time was considerably shorter in the leachate immersion tests than in the composite liner tests. Thus the results from simple immersion tests were confirmed to be conservative.

### 3.1.3. Composite liner tests with three different protection layers

The primary function of a protection layer above a GM in a barrier system is to protect the GM from physical

damage. However, it was hypothesized that the protection layer also may provide some protection to the GM from interaction with leachate and hence antioxidant depletion. If this were found to be the case, then the protection layer could be designed to improve the service life of the GM. To examine this concept, three protection layers were tested to examine their effect on antioxidant depletion from the GM (Rowe and Rimal 2008b). The first involved a typical GT protection layer above the GM (denoted as CL-T as described in the previous sub-section). The second consisted of GT and GCL above the GM (denoted as CL-TG). The third comprised a 1.5 cm thick sand layer contained between two GT layers (denoted as CL-TST). Rowe and Rimal (2008b) found that the time to antioxidant depletion time was best (longest) for the GM with protection layers of a GT and GCL (composite liner CL-TG) followed by GT-sand-GT (composite liner CL-TST) and shortest for GT alone (composite liner CL-T). The results suggested that the GM service life could be improved by using a GCL (in CL-TG) or 1.5 cm of sand plus a geotextile (CL-TST) above the GM. One might expect an even longer life with thicker sand layer but the work of Rowe and Rimal (2008b) did not address a greater thickness of sand.

## 3.2. Model parameters

Analysis of the composite liners explicitly modelled the gravel layer, protection layer, GCL and sand as porous media. The diffusion coefficient in GM was based on the OIT depletion data as described in the next section. A range of diffusion coefficients were modelled for the gravel, GT and sand layers to assess sensitivity over the range indicated in Table 2 for values at room temperature (with choice of values being guided by Rowe *et al.* 2004). Diffusions coefficients at other temperatures were related

**Table 1. Properties of HDPE GMs<sup>a</sup>**

Property	Method (ASTM)	GM-A		GM-B	
		Average	COV (%)	Average	COV (%)
Thickness (mm)	As received	2.0	1.4	1.5	–
Density (g/cm <sup>3</sup> )	D1505	0.940	–	0.944	2.43
Carbon black content (%)	D1603	2.54	–	2.43	–
OIT (min)	D3895	133	3.7	135	3.3
HP-OIT (min)	D5885	380	1.3	660	4.4
Crystallinity (%)	E794	44	1.2	49	6.1
MFI (g/10 min.)	D1238	0.42	1.5	0.49	3.2
Tensile properties (machine)	D6693				
Tensile-strength at yield (kN/m)		33.9	0.89	26.9	2.5
Tensile-strength at break (kN/m)		80.5	3.2	64.7	1
Tensile-strain at yield (%)		22	1.6	18.1	3.7
Tensile-strain at break (%)		1034	6.0	962	0.8
Tensile properties (cross machine)	D6693				
Tensile-strength at yield (kN/m)		34.0	2.2	27.1	2.5
Tensile-strength at break (kN/m)		79.6	3.9	59.9	8.1
Tensile-strain at yield (%)		23	0.69	18.1	1.4
Tensile-strain at break (%)		1012	6.7	898	8.4
Single point stress crack resistance (h)	D5397, Appendix	5220	3.0	> 400	–

COV, coefficient of variation.

<sup>a</sup>Modified from Rimal (2009).

to that at room temperature using an Arrhenius type model (e.g. Equation 4). The sensitivity analysis (Rimal 2009) showed that because of the many orders of magnitude difference in the diffusion coefficients in the GM and the porous media layers, the precise value of diffusion coefficient for these layers (over the likely range of uncertainty) only had a modest effect on the results with a maximum of 13% in the predicted antioxidant depletion time at room temperature and a minimum of 0% at 85°C. In the following analyses, the lower values for each range examined were adopted. The importance of the porous media layers arose from (a) the build-up in antioxidant in these layers as they diffuse out of the GM, and (b) the separation that they provide for the GM from direct contact with significant concentration of leachate constituents like surfactants.

At each test temperature, the diffusion coefficients in the GM were deduced by matching the predicted and observed immersion test results (described below). The partitioning coefficients were deduced from CL-T tests. To model the composite liner test at higher temperature the values of diffusion coefficients of antioxidants in other layers (GT, GCL, sand, gravel) were assumed to increase with temperature by the same ratio as that in the GM.

### 3.3. Diffusion modelling procedure

A linear relationship has been established between OIT and antioxidant concentration by Viebke and Gedde (1997) for an initial antioxidant concentration of between 0 to 0.3% by weight in polyethylene. Thus, it is assumed that the value of OIT measured at different time intervals can be taken to be representative of mass of antioxidant in the GM. The OIT test data at a particular incubation temperature were analysed following the methodology described below. The finite layer analysis program was used to solve the governing differential equations for appropriate boundary conditions.

As described by Rowe and Rimal (2008b), the outward diffusion of antioxidant from the initial concentration in the GM to the adjacent fluid was modelled for leachate immersion tests at room temperature. A thin layer (0.0001 m) was modelled at the surface of the GM to simulate the interface conditions between polyethylene GM and the fluid. The leachate was regularly refreshed in these tests thus it was assumed that there was no build-up of antioxidant in the adjacent fluid next to the GM surface. For a given GM diffusion coefficient the concen-

tration of antioxidant could be calculated at any time. The concentration curve (concentration plotted against depth) was integrated at each time OIT had been measured. As the mass of antioxidant is directly related to the OIT value, the calculated normalized antioxidant mass ratio  $m(t)/m_0 = OIT(t)/OIT_0$  from the model could be compared with the observed normalized ratio  $OIT(t)/OIT_0$ . The GM diffusion coefficient was adjusted as needed to get the best match between the calculated and observed OIT values. The leachate contains a surfactant that allowed full wettability of the interface (Rowe *et al.* 2008). Thus it was assumed that the properties of the thin interface layer in leachate immersion tests were the same as for the bulk GM. In the water immersion tests, the same diffusion coefficient was used for the bulk GM as that in the leachate immersion test. However, due to the reduced wettability, there was a difference in interface condition when the GM was exposed to water as opposed to leachate. The diffusion coefficient of the thin layer was adjusted to obtain the best match between the calculated and observed OIT data. The diffusion parameters deduced from the immersion tests were used to make predictions for the GM in the composite liners as described below.

In addition to the porous layers discussed earlier, for the composite liner (CL-T), the GM was divided into three layers (i.e. a top thin GM layer exposed to leachate, the GM layer, and the bottom thin GM layer exposed to water). These layers were adopted because in the CL-T test the top surface of the GM was in contact with leachate in the GT whereas the bottom surface was in contact with water in the GCL. For the results presented in this paper, the gravel and geotextile above the GM and the GCL and sand below the GM were modelled as porous media using diffusion parameters at the lower end of the range given in Table 2 at room temperature and the corresponding values given by an Arrhenius relationship at higher temperatures. The replacement of leachate at regular intervals with the consequent removal of mass of antioxidant from the gravel layer above the protection layer was modelled. The diffusion coefficients deduced from immersion tests were used for the GM while the GM partitioning coefficient was deduced from the CL-T test. In other composite liners CL-TG and CL-TST the protection layers were considered to inhibit the access of leachate to the GM. Therefore, in these composite liners, GM was modelled with a thin layer of GM exposed to water on both sides.

**Table 2. The parameters used for diffusion modelling of the composite liner cells at room temperature**

Layer	Diffusion coefficient (m <sup>2</sup> /s)	Matrix porosity
Gravel	6–10 × 10 <sup>-10</sup>	0.40
GT	6–10 × 10 <sup>-10</sup>	0.79
Sand	3–10 × 10 <sup>-10</sup>	0.41
GM	2.1 × 10 <sup>-15</sup>	N/A (1)
Thin GM interface layer exposed to leachate	2.1 × 10 <sup>-15</sup>	N/A (1)
Thin GM interface layer exposed to water	2.5 × 10 <sup>-16</sup>	N/A (1)
GCL	1–3 × 10 <sup>-10</sup>	0.80

## 4. RESULTS AND DISCUSSION

### 4.1. Results for immersion tests

The leachate immersion tests on 1.5 mm thick GM (49% crystallinity) were modelled and the illustrative results shown in Figures 2 to 4 correspond to temperatures of 85, 70 and 55°C, respectively (all results are given in Rimal (2009)). Each figure shows experimental data, the conventional first-order (exponential) best fit to the data, and the best fit results based on the diffusion modelling. It can be seen that the diffusion curve provided a better fit to the data than the exponential fit (although both are good). The deduced diffusion coefficients are presented in Table 3. The diffusion coefficients of the thin GM layer when exposed to water obtained by modelling water immersion test results and the partitioning coefficients at each test temperature are also given in Table 3. Similarly OIT depletion from a 2.0 mm thick GM (44% crystallinity) immersed in leachate also were modelled. The result for a test at 40°C is shown in Figure 5 (results at other

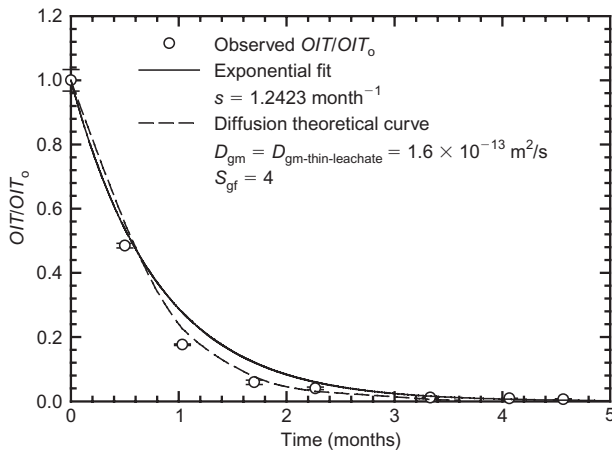


Figure 2. Normalized OIT depletion with time for 1.5 mm GM immersed in leachate at 85°C showing observed experimental data, the best first-order (exponential) fit to that data, and the diffusion model fit to the same data

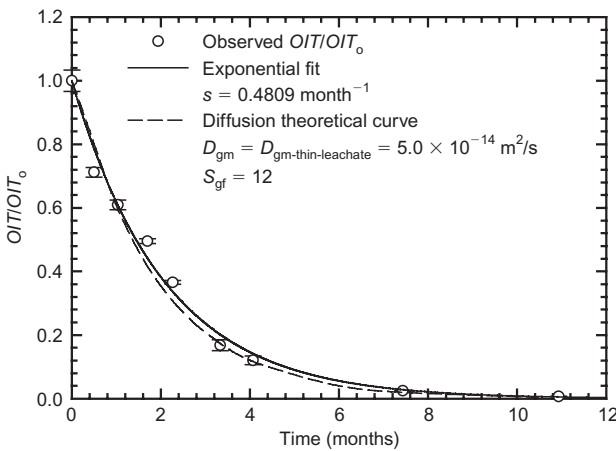


Figure 3. Normalized OIT depletion with time for 1.5 mm GM immersed in leachate at 70°C showing observed experimental data, the best first-order (exponential) fit to that data, and the diffusion model fit to the same data

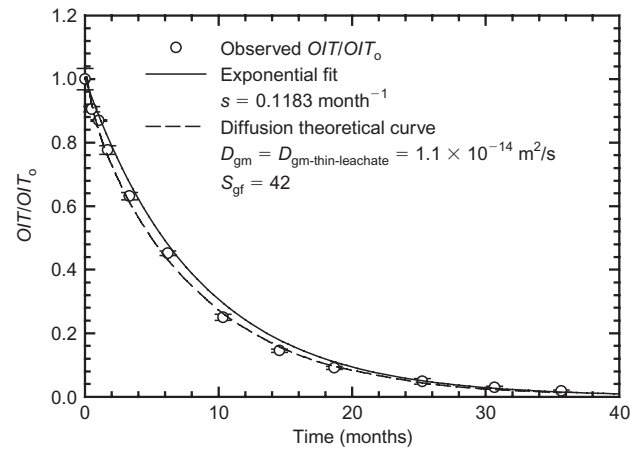


Figure 4. Normalized OIT depletion with time for 1.5 mm GM immersed in leachate at 55°C showing observed experimental data, the best first-order (exponential) fit to that data, and the diffusion model fit to the same data

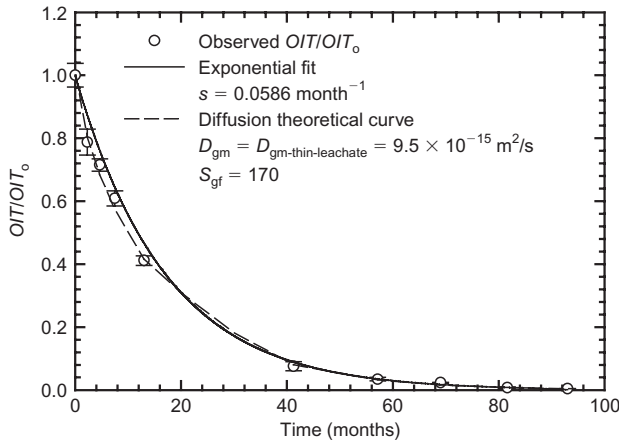
temperatures are given in Rimal (2009)). Diffusion coefficients  $D_{gm}$  deduced from analysing the data for 2 mm thick GM tests are given in Table 4 and they are fairly similar to those obtained for the 1.5 mm GM. The OIT depletion for the 2 mm GM could be well modelled using the same  $S_{gf}$  values as for the 1.5 mm GM. Thus at 85 and 55°C (the common temperatures for the two GMs) the same  $S_{gf}$  values were used for both GMs. The  $S_{gf}$  values for the 2 mm GM at 40°C and 22°C were obtained using the temperature-dependence relationship of partitioning coefficient developed for the 1.5 mm GM as described later in this paper.

The antioxidant depletion times to reach  $OIT = 0.5$  min. were derived using Equation 7 and a depletion rate,  $s$ , obtained from three different methods: (1) first-order (exponential) fit to the experimental data (denoted as  $S_1$ ), (2) first-order fit of the theoretical diffusion data generated upto the time that latest laboratory data was collected (denoted as  $S_2$ ), and (3) first-order fit of the theoretical diffusion data generated upto  $OIT = 0.5$  min. (denoted as  $S_3$ ). The values of  $S_1$ ,  $S_2$  and  $S_3$  are given in Table 5. The antioxidant depletion times  $T_1$ ,  $T_2$  and  $T_3$  obtained from Equation 7 using  $S_1$ ,  $S_2$  and  $S_3$ , respectively, are given in Table 6. The time when the diffusion curve itself reached  $OIT = 0.5$  min,  $T_4$ , is also given in Table 6.

For the 1.5 mm thick GM the depletion times  $T_1$ ,  $T_2$ ,  $T_3$ , and  $T_4$  were very similar at 85, 70 and 55°C with only 1–2 years difference between the predicted depletions times using the four different methods. This is not surprising since in each case the tests had been run long enough for the OIT to deplete and hence it was possible to get a -erm exponential fit to the data. Thus, as discussed in Section 2.3, one would expect good agreement. However at room temperature the OIT was far from being depleted to residual values. Hence there was significant difference in the predictions based on the period when data is available (i.e. short-term compared to the actual depletion time:  $T_1$  and  $T_2$ ) and those based on diffusion modelling to depletion ( $T_3$  and  $T_4$ ). This highlights the differences in predictions based on a first-order approximation using

**Table 3. Deduced diffusion and partitioning coefficients at different testing temperatures for 1.5 mm thick GM**

Temperature (°C)	$D_{gm}$ and $D_{gm-thin-leachate}$ (m <sup>2</sup> /s)	$D_{gm-thin-water}$ (m <sup>2</sup> /s)	$S_{gf}$ (-)
85	$1.6 \times 10^{-13}$	$1.1 \times 10^{-14}$	4
70	$5.0 \times 10^{-14}$	$6.6 \times 10^{-15}$	12
55	$1.1 \times 10^{-14}$	$2.6 \times 10^{-15}$	42
26	$2.1 \times 10^{-15}$	$2.5 \times 10^{-16}$	720



**Figure 5. Normalized OIT depletion with time for 2.0 mm GM immersed in leachate at 40°C showing observed experimental data, the best first-order (exponential) fit to that data, and the diffusion model fit to the same data**

**Table 4. Deduced diffusion and partitioning coefficient at different testing temperatures for 2.0 mm thick GM**

Temperature (°C)	$D_{gm}$ and $D_{gm-thin-leachate}$ (m <sup>2</sup> /s)	$S_{gf}$ (-)
85	$1.0 \times 10^{-13}$	4
55	$2.5 \times 10^{-14}$	42
40	$9.5 \times 10^{-15}$	172
22	$2.7 \times 10^{-15}$	1080

short- and long-term results. The predictions based on a first-order fit to data that is well short of the time to full depletion gave conservative (shorter) antioxidant depletion time than the diffusion model based on the available data

or the first-order fit to the diffusion results. Similar observations can be made for the 2 mm thick GM. The depletion times, as might be expected, are longer for the 2 mm GM than for the 1.5 mm GM.

**4.2. Results for simulated composite liner tests**

The composite liner tests were modelled at all temperatures using the GM properties deduced from the immersion tests as discussed earlier and typical results are illustrated in Figures 6 to 9. These plots show laboratory data and predicted depletion curves from the diffusion modelling of the composite system. The theoretical curves generated from the diffusion modelling provided good predictions of the laboratory results.

**4.3. Temperature dependence of diffusion and partitioning coefficients**

The results in Tables 3 and 4 can be used to obtain a relationship between logarithm of  $D_{gm}$  and inverse of the temperature as shown in Figure 10 for 1.5 mm thick GM and Figure 11 for 2.0 mm thick GM. Similar relationship have been obtained for various antioxidant in polymer/fluid in the literature (Moisan 1980a, 1985; Möller and Gevert 1994; Bertoldo *et al.* 2003). The activation energy of diffusion was deduced from the slope  $E_d/R$  of the regression curve. The Arrhenius equation and inferred activation energies are given in the figures. The calculated activation energy was 65.0 kJ/mol for 1.5 mm thick and 50.4 kJ/mol for 2.0 mm thick GM. Using the Arrhenius equations, diffusion coefficients were predicted for field temperatures ranging from 10 to 60°C (Table 7). A similar temperature dependence analysis (Figure 12; activation energy 58.5 kJ/mol) and prediction (Table 7) was carried

**Table 5. Antioxidant depletion rates obtained using three different methods**

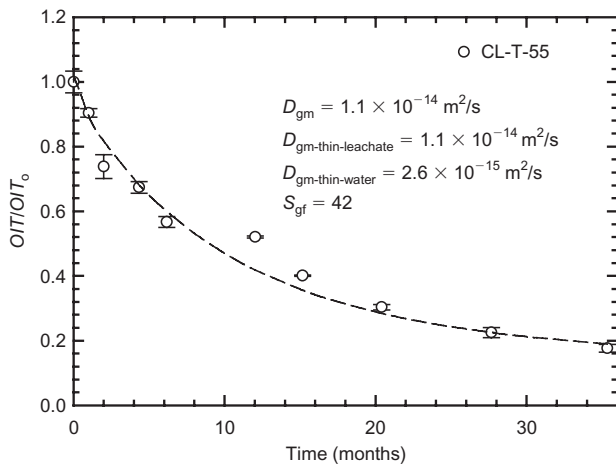
Antioxidant depletion rates (month <sup>-1</sup> ) for 1.5 mm thick leachate immersed GM (based on data from Rowe and Rimal 2008a)				Antioxidant depletion rates (month <sup>-1</sup> ) for 2 mm thick leachate immersed GM (based on data from Rowe <i>et al.</i> 2009)			
Temp.(°C)	$S_1$	$S_2$	$S_3$	Temp. (°C)	$S_1$	$S_2$	$S_3$
85	1.2423 (0.95)	1.5473 (1.00)	1.5386 (1.00)	85	0.4341 (0.96)	0.6237 (1.00)	0.6225 (1.00)
70	0.4809 (0.99)	0.5335 (1.00)	0.5325 (1.00)	55	0.1438 (0.98)	0.1578 (1.00)	0.1585 (1.00)
55	0.1183 (0.99)	0.1248 (1.00)	0.1241 (1.00)	40	0.0586 (0.99)	0.0602 (1.00)	0.0599 (1.00)
Room (26)	0.0253 (0.98)	0.0266 (0.98)	0.0224 (1.00)	Room (22)	0.0185 (0.98)	0.0179 (0.99)	0.0165 (1.00)

$S_1$  = Obtained by fitting laboratory data.  
 $S_2$  = Obtained by fitting the theoretical data generated upto the time that final laboratory data was collected.  
 $S_3$  = Obtained by fitting the theoretical data generated upto the time that OIT = 0.5 min.  
 Number in the parenthesis is coefficient of determination  $R^2$ .

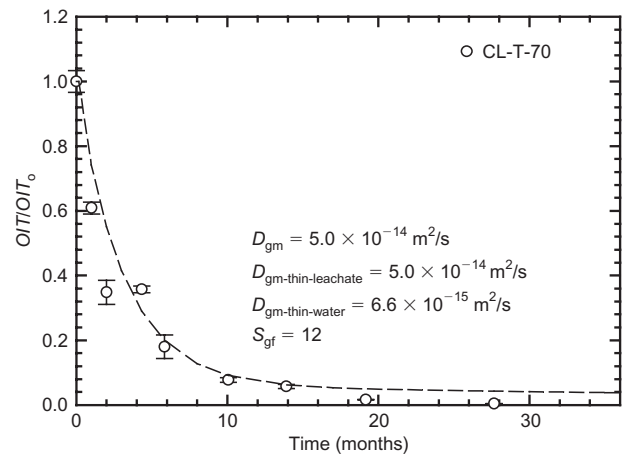
**Table 6. Calculated antioxidant depletion times using four different approaches**

Antioxidant depletion times (months) for 1.5 mm thick leachate immersed GM					Antioxidant depletion times (months) for 2 mm thick leachate immersed GM				
Temp. (°C)	T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>	T <sub>4</sub>	Temp. (°C)	T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>	T <sub>4</sub>
85	4.5	3.6	3.6	3.6	85	13	9.0	9.0	9.0
70	12	10	11	10	55	39	35	35	36
55	47	45	45	46	40	95	93	93	94
Room (26)	221	211	250	254	Room (22)	302	312	339	344

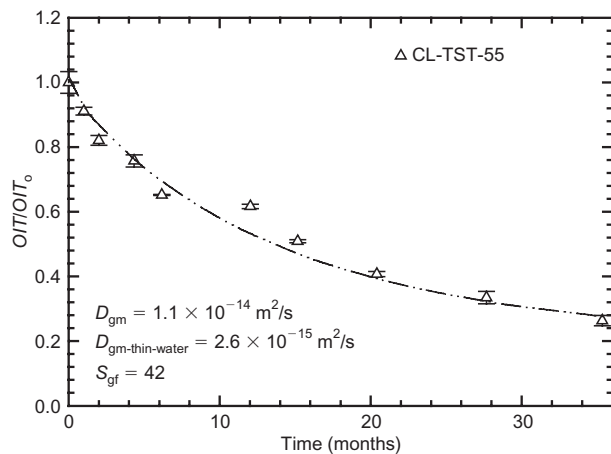
T<sub>1</sub> = Obtained using Equation 7 and S<sub>1</sub> from Table 5.  
 T<sub>2</sub> = Obtained using Equation 7 and S<sub>2</sub> from Table 5.  
 T<sub>3</sub> = Obtained using Equation 7 and S<sub>3</sub> from Table 5.  
 T<sub>4</sub> = Time when the diffusion modelling gives OIT = 0.5 min.



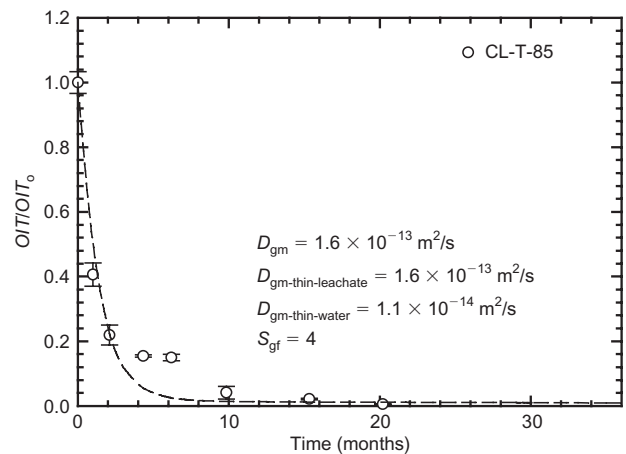
**Figure 6. Observed normalized OIT versus time and the predicted diffusion curve for a composite liner with a GT protection layer (test CL-T) at 55°C**



**Figure 8. Observed normalized OIT versus time and the predicted diffusion curve for a composite liner with a GT protection layer (test CL-T) at 70°C**



**Figure 7. Observed normalized OIT versus time and the predicted diffusion curve for a composite liner with a GT-1.5 cm sand-GT protection layer (test CL-TST) at 55°C**



**Figure 9. Observed normalized OIT versus time and the predicted diffusion curve for a composite liner with a GT protection layer (test CL-T) at 85°C**

out for the diffusion coefficient of thin GM layer when exposed to water.

The S<sub>gf</sub> values given in Table 3 were also plotted with respect to inverse of absolute temperature (Figure 13). There was a distinct decrease in S<sub>gf</sub> with the increase in

temperature and with activation energy of -78.5 kJ/mol. This indicates that the GM has a greater tendency to retain antioxidants at lower temperature than at higher temperature. Similarly, a decrease in S<sub>gf</sub> with increasing temperature was also obtained by Gandek *et al.* (1989b) for

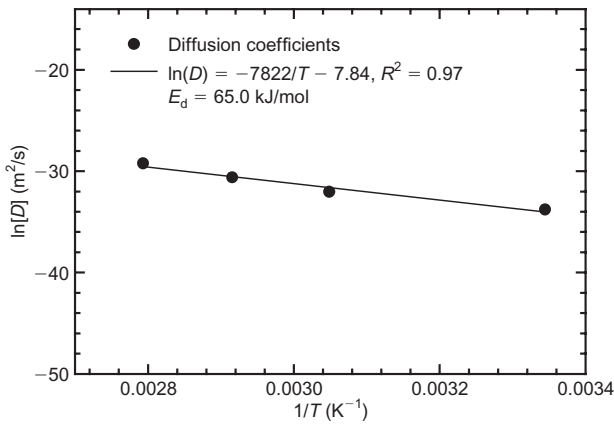


Figure 10. Arrhenius-type temperature dependence of diffusion coefficient of antioxidant for a 1.5 mm GM-B

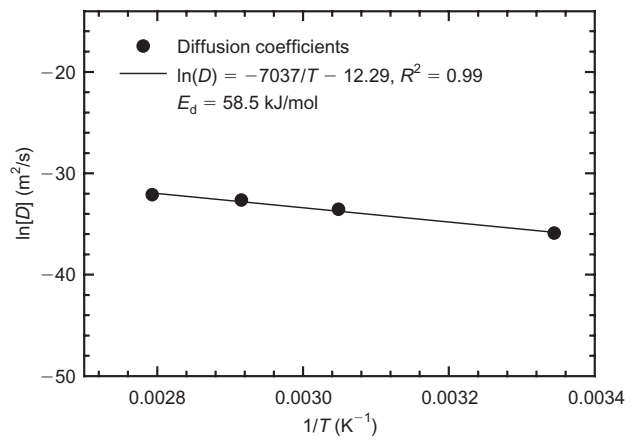


Figure 12. Arrhenius-type temperature dependence of diffusion coefficient in the thin GM layer exposed to water

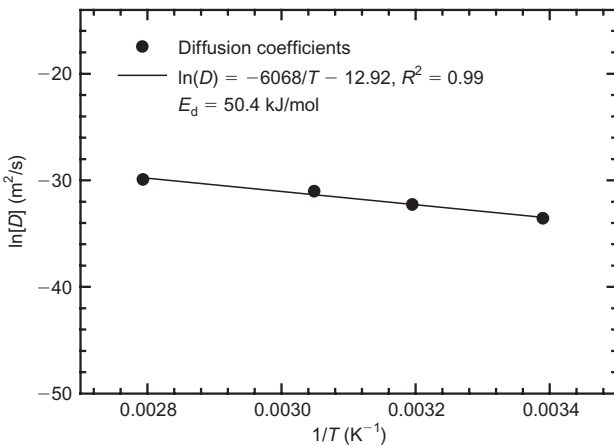


Figure 11. Arrhenius-type temperature dependence of diffusion coefficient of antioxidant for a 2.0 mm GM-A

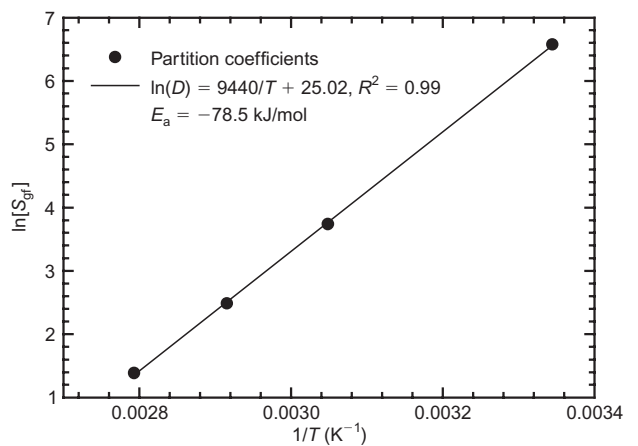


Figure 13. Temperature dependence of partitioning coefficient,  $S_{gr}$

phenolic antioxidant butylhydroxytoluene (BHT) in HDPE exposed to water. (It is noted that partitioning coefficient in Gandek *et al.* (1989a, b) was defined as migrant concentration in fluid divided by that in the solid and is, thus, the inverse of  $S_{gr}$ , as defined in this paper.) Using the relationship given in Figure 13,  $S_{gr}$  was predicted for field temperatures ranging from 10 to 60°C as given in Table 7.

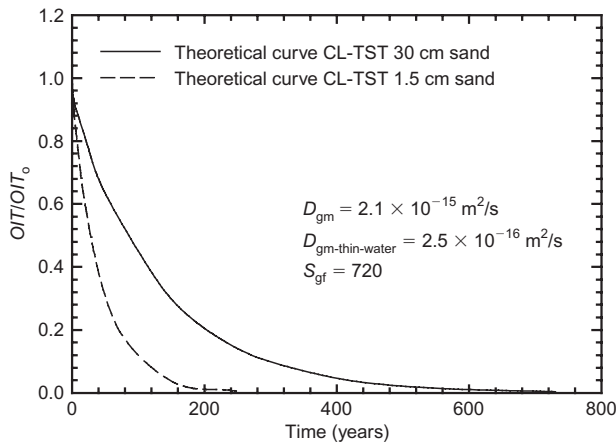
**4.4. Prediction for composite liner with protection layer involving 30 cm of sand**

Using the parameters at 26°C (laboratory temperature) an analysis was carried for a case involving composite liner

CL-TST with protection layer involving 30 cm thick sand layer sandwiched between two geotextile layers. The resulting theoretical curve is shown along with the theoretical curve for the test CL-TST with 1.5 cm thick sand layer at the room temperature in Figure 14. The OIT depletion rates and depletion time are given in Table 8. For the CL-TST with 1.5 cm of sand the OIT depletion times ( $T_1$ ,  $T_2$ ,  $T_3$  and  $T_4$ ) were predicted using techniques defined earlier in the paper. It was observed that predicted depletion time  $T_1$  and  $T_2$  were fairly similar. Both predictions were based on 35 months of data, but  $T_1$  was based on an exponential fit of the laboratory data and  $T_2$  was based on exponential fit to the diffusion modelling over a

Table 7. Predicted diffusion and partitioning coefficients at different service temperatures

Temperature (°C)	$D_{gm}$ (1.5 mm GM) (m²/s)	$D_{gm}$ (2 mm GM) (m²/s)	$D_{gm-thin-water}$ (m²/s)	$S_{gr}$ (-)
10	$3.9 \times 10^{-16}$	$1.2 \times 10^{-15}$	$7.3 \times 10^{-17}$	4197
20	$1.0 \times 10^{-15}$	$2.5 \times 10^{-15}$	$1.7 \times 10^{-16}$	1344
30	$2.4 \times 10^{-15}$	$4.9 \times 10^{-15}$	$3.8 \times 10^{-16}$	464
35	$3.7 \times 10^{-15}$	$6.8 \times 10^{-15}$	$5.5 \times 10^{-16}$	280
40	$5.5 \times 10^{-15}$	$9.3 \times 10^{-15}$	$8.0 \times 10^{-16}$	172
50	$1.2 \times 10^{-14}$	$1.7 \times 10^{-14}$	$1.6 \times 10^{-15}$	67
60	$2.5 \times 10^{-14}$	$3.0 \times 10^{-14}$	$3.1 \times 10^{-15}$	28



**Figure 14. Comparison between predicted antioxidant depletion for 1.5 and 30 cm of sand layer above the composite liner at room temperature**

35 month period. At 35 months OIT had only dropped by 12% (i.e.  $OIT/OIT_0 = 0.88$ ). Thus the period of 35 months could be considered as ‘short-term’ data at room temperature compared to the expected time period for depletion. Predicted depletion times  $T_3$  and  $T_4$  (both based on ‘long-term’ diffusion modelling to depletion) were fairly similar but were much longer than  $T_1$  and  $T_2$ . Thus it was found that the prediction based on a first-order fit to ‘short-term’ laboratory data or short-term diffusion modelling gave very conservative (on the low side) depletion times compared to those based on ‘long-term’ diffusion modelling. Thus it should be emphasized that prediction based on short-term (35 month) data in cases in which the antioxidant have only slightly depleted may lead to very conservative estimates of antioxidant depletion time.

The OIT depletion times  $T_3$  and  $T_4$  also were predicted for a 30 cm sand protection layer. The only difference between CL-TST (1.5 cm sand) and CL-TST (30 cm sand) is the thickness of the sand layer. Diffusion coefficients, interface layer between the GM and the adjacent media and boundary conditions of the system are the same. Thus the thickness of the sand layer is the only factor giving rise to the difference in results for CL-TST (1.5 cm sand) and CL-TST (30 cm sand) shown in Figure 14. At 26°C the value of predicted depletion time was significantly longer (by almost three times) when 30 cm thick sand layer was placed instead of 1.5 cm thick sand layer. Thus these results suggest that the use of a 30 cm sand

protection layer in addition to the typical geotextile protection layer between the geomembrane and a gravel leachate drainage layer would provide potential benefits in terms of extending the geomembrane service life by reducing the rate of outward diffusion of antioxidants from the geomembrane (as well as providing good physical protection of the liner).

It should be noted that although sand may provide an excellent protection layer, it is generally not good as part of a leachate collection system for municipal solid waste leachate due to the significant (many orders of magnitude) drop in hydraulic conductivity caused by biologically induced clogging (see Rowe *et al.* 2004; Rowe 2005; Cooke and Rowe 2008). For example, field exhumations (Reades *et al.* 1989; Barone *et al.* 1993) found that the upper portion of the sand protection layer over the liner at the Keele Valley Landfill became clogged within the first 4 years and did not contribute to the hydraulic performance of the leachate collection system. The lack of flow in the sand layer was evident from the presence of a clear diffusion profile for both chloride and several volatile organic compounds that started at the top of the sand layer. Thus the sand layer acted as part of the liner system in terms of a ‘diffusion barrier’ as opposed to part of the drainage system (Rowe 2005). This role as a diffusion barrier is good with respect to controlling both the outward diffusion of contaminants from the waste and, as demonstrated here, reducing the outward diffusion of antioxidants from the geomembrane.

Similar diffusion modelling predictions were made for 1.5 cm sand (test CL-TST) and a 30 cm thick sand protection layer at landfill liner temperatures of 26, 35 and 50°C. The predicted OIT depletion curves obtained from the diffusion model for a 30 cm sand protection layer are shown in Figure 15 and the depletion times are given in Table 9 for both 1.5 and 30 cm of sand as a protection layer. At a constant landfill liner temperature of 35°C the antioxidant depletion time ( $T_4$ ) was 130 and 230 years for a 1.5 and 30 cm sand protection layer above the GM, respectively.

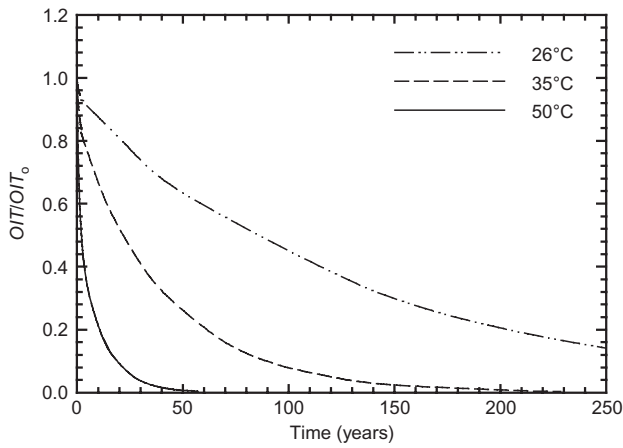
### 5. CONCLUSIONS

The findings of diffusion modelling of OIT depletion from HDPE GMs were presented. Based on the results the following specific conclusions were reached.

**Table 8. OIT depletion rates and depletion times for CL-TST with 1.5 cm of sand and 30 cm of sand at room temperature**

	1.5 cm sand	30 cm sand	Comparison (30 cm sand/1.5 cm sand)
$S_1$ (month <sup>-1</sup> )	0.0040	–	–
$T_1$ (months)	1400	–	–
$S_2$ (month <sup>-1</sup> )	0.0038 (0.95)	–	–
$T_2$ (months)	1473	–	–
$S_3$ (month <sup>-1</sup> )	0.0018 (1.0)	0.00064 (1.0)	0.36
$T_3$ (months)	3110	8748	2.8
$T_4$ (months)	3067	8767	2.9

Number in the parenthesis is coefficient of determination  $R^2$ .



**Figure 15. Predicted antioxidant depletion curves for a composite liner with a 30 cm sand protection layer above geomembrane GM-B at different temperatures**

1. Based on purely theoretical considerations it was shown that predictions of antioxidant depletion time based on Arrhenius modelling using antioxidant depletion rates obtained from a first-order approximation to short-term data (i.e. where there is still significant antioxidant remaining when the last data was collected) are conservative compared to predicted depletion time based on the diffusion modelling.
2. Experimental data on OIT depletion from a GM immersed in leachate and in a composite liner at different incubation temperatures were analyzed using a diffusion model and diffusion and partitioning coefficients were deduced. For 1.5 mm thick GM between 85°C and room temperature the diffusion coefficient ranged from  $2.1 \times 10^{-15} \text{ m}^2/\text{s}$  at 26°C to  $1.6 \times 10^{-13} \text{ m}^2/\text{s}$  at 85°C and partitioning coefficient ranged from 720 (at 26°C) to 4 (at 85°C).
3. The results of the diffusion model and the first-order antioxidant depletion model were compared. For both a 1.5 and 2 mm thick GM immersed in leachate long enough for the OIT to have been largely or totally removed (i.e. at 85, 70 and 55°C), the depletion time calculated using the first-order model was similar to that predicted using the diffusion model. However, at laboratory temperature where very little OIT had depleted during the study period there was a significant difference in the results obtained from a

first-order model and a diffusion model fitted to the available short-term data. Predictions based on a first-order fit to short-term data gave much smaller (conservative) antioxidant depletion times than a diffusion model based on the same data. This is consistent with the findings from purely theoretical consideration noted above. The predictions from the diffusion model are more likely to be correct.

4. Arrhenius-type relationships were established to estimate diffusion and partition coefficients of OIT at typical landfill temperatures. At the landfill temperature from 10–60°C the predicted diffusion coefficient ranged from  $3.9 \times 10^{-16}$  to  $2.5 \times 10^{-14} \text{ m}^2/\text{s}$  and partitioning coefficient ranged from 4200 to 28. For the 2.0 mm thick GM diffusion coefficient ranged from  $1.2 \times 10^{-15}$  to  $3.2 \times 10^{-14} \text{ m}^2/\text{s}$ .
5. The estimated diffusion and partitioning coefficients were used to model OIT depletion from a GM in a composite liner with 30 cm thick sand protection layer. At laboratory temperature of 26°C the predicted antioxidant depletion time based on theoretical diffusion model was approximately three times longer when 30 cm thick sand layer was placed instead of 1.5 cm thick sand layer. This highlighted the beneficial effect of using thicker sand protection layer. Using parameters based on Arrhenius modelling it was possible to model antioxidant depletion times at typical landfill temperatures. At a liner temperature of 35°C the antioxidant depletion time was about 130 years for the case with 1.5 cm sand layer and 230 years when 30 cm sand protection layer was used.
6. Although Arrhenius modelling using antioxidant depletion rates obtained from a first-order approximation to data can provide conservative predictions of antioxidant depletion time, the first-order antioxidant depletion model cannot be readily used to predict the performance of the GM in a system other than the original laboratory test configuration used to get the data. In contrast, diffusion parameters deduced from immersion tests could be used to get good predictions of the antioxidant depletion in various different liner systems and hence could be used for modelling a variety of other design scenarios not considered in this paper.

**Table 9. Predicted OIT depletion time ( $T_4$  to reach  $OIT_0 = 0.5 \text{ min.}$ ) for geomembrane GM-B with a 1.5 cm (CL-TST) and 30 cm sand protection layer at three landfill liner temperatures based on diffusion modelling (rounded to 2 significant digits)**

Temperature (°C)	OIT depletion time, $T_4$ (years)	
	1.5 cm of sand	30 cm of sand
26°C	260	730
35°C	130	230
50°C	47	57

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project is gratefully acknowledged. The value of discussion with G. Hsuan, R. Brachman and D.N. Arnepalli is also greatly appreciated.

## NOTATIONS

Basic SI units are given in parentheses.

$C$	concentration at points within the geomembrane ( $\text{kg}/\text{m}^3$ )
$C_0$	initial concentration at the surface of the geomembrane ( $\text{kg}/\text{m}^3$ )
$C_1$	concentration at the surface of the geomembrane ( $\text{kg}/\text{m}^3$ )
$c_f$	concentration of antioxidant in the adjacent fluid ( $\text{kg}/\text{m}^3$ )
$c_{\text{gm}}$	concentration of antioxidant in the geomembrane ( $\text{kg}/\text{m}^3$ )
$D$	diffusion coefficient ( $\text{m}^2/\text{s}$ )
$D_{\text{gm}}$	diffusion coefficient in the GM ( $\text{m}^2/\text{s}$ )
$D_0$	constant used in Equation 4 ( $\text{m}^2/\text{s}$ )
$E_d$	diffusion activation energy ( $\text{J}/(\text{mol K})$ )
$f$	mass flux or rate ( $\text{kg}/(\text{m}^2 \text{ s})$ )
$l$	geomembrane half-thickness (m)
$n$	integer number (dimensionless)
$m(t)$	mass of antioxidant at time $t$ (kg)
$m_0$	initial mass of antioxidant (kg)
$M_t$	mass of antioxidant which has left the geomembrane at time $t$ (kg)
$M_\infty$	mass of antioxidant in the geomembrane after infinite time (kg)
$OIT_0$	initial OIT (s)
$OIT_{(f)}$	final residual OIT value (s)
$OIT(t)$	OIT at time $t$ (s)
$R$	universal gas constant ( $8.314 \text{ J}/(\text{mol K})$ )
$S_{\text{gf}}$	a partitioning coefficient (dimensionless)
$s$	antioxidant depletion rate ( $\text{s}^{-1}$ )
$S_1$	antioxidant depletion rate obtained from first-order fit to data ( $\text{s}^{-1}$ )
$S_2$	antioxidant depletion rate obtained from first-order fit of the theoretical diffusion curve generated up to the final laboratory data ( $\text{s}^{-1}$ )
$S_3$	antioxidant depletion rate obtained from first-order fit of the theoretical diffusion curve generated up to $OIT = 0.5 \text{ min}$ ( $\text{s}^{-1}$ )
$T$	absolute temperature (K)
$T_1$	antioxidant depletion time derived from Equation 7 using $S_1$ (s)
$T_2$	antioxidant depletion time derived from Equation 7 using $S_2$ (s)
$T_3$	antioxidant depletion time derived from Equation 7 using $S_3$ (s)
$T_4$	antioxidant depletion time when diffusion curve itself reaches $OIT = 0.5 \text{ min}$ . (s)
$t$	time (s)
$t_d$	antioxidant depletion time (s)
$x$	the distance at the centre of the film (m)
$z$	the distance parallel to the direction of diffusion (m)

## ABBREVIATIONS

GCL	geosynthetic clay liner
GM	geomembrane
GT	geotextile
HDPE	high density polyethylene
HP-OIT	high pressure oxidative induction time
OIT	standard oxidative induction time

## REFERENCES

- Barone, F. S., Costa, J. M. A., King, K. S., Edelenbos, M. & Quigley, R. M. (1993). Chemical and mineralogical assessment of in situ clay liner Keele Valley Landfill, Maple, Ontario. In *Proceedings of Joint CSCE-ASCE National Conference on Environmental Engineering*, Montreal, Canadian Society for Civil Engineering, Montreal, Canada, pp. 1563–1572.
- Bertoldo, M., Ciardelli, F., Ferrara, G. & Scoconi, M. (2003). Effect of the structure of reactor poly(propylene-co-ethylene) blends on the diffusion coefficient and activation energy of a conventional antioxidant. *Macromolecular Chemistry and Physics*, **204**, No. 15, 1869–1875.
- Billingham, N. C. (1990). Physical phenomena in the oxidation and stabilization of polymers. In: *Oxidation Inhibition in Organic Materials*, Volume II, Pospisil, J. & Klemchuk, P. P., editors, CRC Press, Inc., Boca Raton, FL, pp. 249–297.
- Brachman, R. W. I. & Gudina, S. (2008a). Gravel contacts and geomembrane strains for a GM/CCL composite liner. *Geotextiles and Geomembranes*, **26**, No. 6, 448–459.
- Brachman, R. W. I. & Gudina, S. (2008b). Geomembrane strains from coarse gravel and wrinkles in a GM/GCL composite liner. *Geotextiles and Geomembranes*, **26**, No. 6, 488–497.
- Cooke, A. J. & Rowe, R. K. (2008). 2-D modelling of clogging in landfill leachate collection systems. *Canadian Geotechnical Journal*, **45**, No. 10, 1393–1409.
- Crank, J. (1975). *The Mathematics of Diffusion*, 2nd edition, Oxford University Press Inc. Oxford, 414 pp.
- Crank, J. & Park, G. S. (1968). *Diffusion in Polymer*, Academic Press, London, 452 pp.
- Comyn, J. (1985). Introduction to polymer permeability and the mathematics of diffusion. In *Polymer Permeability*, Comyn, J., editor, Elsevier Applied Science Publishers, London, UK, pp. 1–10.
- El-Zein, A. & Rowe, R. K. (2008). Impact on groundwater of concurrent leakage and diffusion of DCM through geomembranes in landfill liners. *Geosynthetics International*, **15**, No. 1, 55–71.
- Gandek, T. P., Hatton, T. A. & Reid, R. C. (1989a). Batch extraction with reaction: phenolic antioxidant migration from polyolefins to water. 1. theory. *Industrial and Engineering Chemistry Research*, **28**, No. 7, 1030–1036.
- Gandek, T. P., Hatton, T. A. & Reid, R. C. (1989b). Batch extraction with reaction: phenolic antioxidant migration from polyolefins to water. 2. experimental results and discussion. *Industrial and Engineering Chemistry Research*, **28**, 1036–1045.
- Grassie, N. & Scott, G. (1985). *Polymer Degradation and Stabilization*. Cambridge University Press, New York, USA. 222 pp.
- Gulec, S. B., Edil, T. B. & Benson, C. H. (2004). Effect of acidic mine drainage on the polymer properties of an HDPE geomembrane. *Geosynthetics International*, **11**, No. 2, 60–72.
- Haider, N. & Karlsson, S. (1999). Migration and release profile of chimassorb 994 from low-density polyethylene film (LDPE) in simulated landfills. *Polymer Degradation and Stability*, **64**, No. 2, 321–328.
- Haider, N. & Karlsson, S. (2000). Kinetics of migration of antioxidants from polyolefins in natural environments as a basis for bioconversion studies. *Biomacromolecules*, **1**, No. 3, 481–487.
- Haider, N. & Karlsson, S. (2002). Loss and transformation products of the aromatic antioxidants in MDPE film under long-term exposure to biotic and abiotic conditions. *Journal of Applied Polymer Science*, **85**, No. 5, 974–988.

- Hsuan, Y. G. & Koerner, R. M. (1998). Antioxidant depletion lifetime in high density polyethylene geomembranes. *Journal of Geotechnical and Geoenvironmental Engineering, ASCE*, **124**, No. 6, 552–541.
- Koerner, R. M. (1998). *Designing with Geosynthetics*, 4th edition. Prentice Hall, New Jersey, 761 pp.
- Koerner, G. R. & Koerner, R. M. (2006). Long term temperature monitoring of geomembranes at dry and wet landfills. *Geotextiles and Geomembranes*, **24**, No. 1, 72–77.
- Moisan, Y. L. (1980a). Diffusion Des Additifs Du Polyethylene-I, Influence De La Nature Du Diffusant. *European Polymer Journal*, **16**, No. 10, 979–987.
- Moisan, Y. L. (1980b). Diffusion Des Additifs Du Polyethylene-II, Influence De La Structure Du Polyethylene. *European Polymer Journal*, **16**, No. 10, 989–996.
- Moisan, Y. L. (1985). Effects of oxygen permeation and stabiliser migration on polymer degradation. In: *Polymer Permeability*, Comyn, J., editor, Elsevier Applied Science Publishers, London, UK, pp. 119–176.
- Möller, K. & Gevert, T. (1994). An FTIR solid-state analysis of the diffusion of hindered phenols in low-density polyethylene (LDPE): The effect of molecular size on diffusion coefficient. *Journal of Applied Polymer Science*, **51**, No. 5, 895–903.
- Möller, K. & Gevert, T. (1996). A solid-state investigation of the desorption/evaporation of hindered phenols from low density polyethylene using FTIR and UV spectroscopy with integrating sphere: The effect of molecular size on the desorption. *Journal of Applied Polymer Science*, **61**, No. 7, 1149–1162.
- Reades, D. W., King, K. S., Benda, E., Quigley, R. M., LeSarge, K. & Heathwood, C. (1989). The results of on-going monitoring of the performance of a low permeability clay liner, Keele Valley landfill, Maple, Ontario. In: *Focus Conference on Eastern Regional Ground Water Issues*. National Water Well Association, Kitchener, ON, pp. 79–91.
- Rogers, C. E. (1985). Permeation of gases and vapors in polymers. In *Polymer Permeability*, Comyn, J., editor, Elsevier Applied Science Publishers, London, UK, chapter 2, pp. 11–73.
- Rimal, S. (2009). *Aging of HDPE Geomembranes Used to Contain Landfill Leachate or Hydrocarbon Spills*, PhD Thesis, Department of Civil Engineering, Queen's University, Canada, 412 p.
- Rimal, S., Rowe, R. K. & Hansen, S. (2004). Durability of geomembrane exposed to jet fuel A-1. In: *Proceedings of 57th Canadian Geotechnical Conference*, Quebec City, October, BiTech Publishing Ltd, Richmond, British Columbia, Canada, CD-ROM, Section 5D, pp. 13–19.
- Roe, R. R., Bair, H. E., & Gieniewski, C. (1974). Solubility and diffusion coefficient of antioxidants in polyethylene. *Journal of Applied Polymer Science*, **18**, No. 3, 843–856.
- Rowe, R. K. (2005). Long-term performance of contaminant barrier systems. *Geotechnique*, **55**, No. 9, 631–678.
- Rowe, R. K. & Booker, J. R. (2004). *POLLUTE v.7 – 1-D Pollutant Migration Through a Non Homogenous Soil*, 983, 1994, 1997, 1999, 2004. Distributed by GAEA Technologies Ltd., www.gaea.ca.
- Rowe, R. K. & Hoor, A. (2009). Predicted temperatures and service lives of secondary geomembrane landfill liners. *Geosynthetics International*, **16**, No. 2, 71–82.
- Rowe, R. K., Quigley, R. M., Brachman, R. W. I., & Booker, J. R. (2004). *Barrier Systems for Waste Disposal Facilities*, 2nd Edition, Spon Press, London, 587 pp.
- Rowe, R. K. & Rimal, S. (2008a). Depletion of antioxidants from an HDPE geomembrane in a composite liner. *Journal of Geotechnical and Geoenvironmental Engineering, ASCE*, **134**, No. 1, 68–78.
- Rowe, R. K., & Rimal, S. (2008b). Aging of HDPE geomembrane in three composite landfill liner configurations. *Journal of Geotechnical and Geoenvironmental Engineering, ASCE*, **134**, No. 7, 906–916.
- Rowe, R. K., Islam, M. Z., & Hsuan, Y. G. (2008). Leachate chemical composition effects on OIT depletion in HDPE geomembranes. *Geosynthetics International*, **15**, No. 2, 136–151.
- Rowe, R. K., Rimal, S. & Sangam, H. P. (2009). Aging of HDPE geomembrane exposed to air, water and leachate at different temperatures. *Geotextiles and Geomembranes*, **27**, No. 2, 131–151.
- Saidi, F., Touze-Foltz, N. & Goblet, P. (2008). Numerical modelling of advective flow through composite liners in case of two interacting adjacent square defects in the geomembrane. *Geotextiles and Geomembranes*, **26**, No. 2, 196–204.
- Sangam, H. P. (2001). *Performance of HDPE Geomembrane Liners in Landfill Applications*. PhD Thesis, Department of Civil and Environmental Engineering, The University of Western Ontario, Ontario, Canada, 400 p.
- Sangam, H. P., & Rowe, R. K. (2002). Effects of exposure conditions on the depletion of antioxidants from high-density polyethylene (HDPE) geomembranes. *Canadian Geotechnical Journal*, **39**, No. 6, 1221–1230.
- Take, W. A., Chappel, M. J., Brachman R. W. I. & Rowe, R. K. (2007). Quantifying geomembrane wrinkles using aerial photography and digital image processing. *Geosynthetics International*, **14**, No. 4, 219–227.
- Tisinger, L. G., Peggs, I. D., & Haxo, H. E. (1991). Chemical compatibility testing of geomembranes. In: *Geomembranes Identification and Performance Testing*, Rollin, A. and Rigo, J. M., editors, Chapman and Hall, London, Rilem Report 4, 268–307.
- Thusyanthan, N. I., Madabhushi S. P. G. & Singh S. (2007). Tension in geomembranes on landfill slopes under static and earthquake loading—centrifuge study. *Geotextiles and Geomembranes*, **25**, No. 2, 78–95.
- Viebke, J. & Gedde, U. W. (1997). Antioxidant diffusion in polyethylene hot-water pipes. *Polymer Engineering and Science*, **37**, No. 5, 896–911.
- Zhu, B., Gao, D. & Chen, Y. M. (2009). Geomembrane tensions and strains resulting from differential settlement around rigid circular structures. *Geotextiles and Geomembranes*, **27**, No. 1, 53–62.

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