

Aging of HDPE Geomembrane in Three Composite Landfill Liner Configurations

R. Kerry Rowe, F.ASCE¹; and S. Rimal²

Abstract: Laboratory-accelerated aging experiments conducted to examine the depletion of antioxidant from a geomembrane (GM) underlain by a geosynthetic clay liner (GCL) are described. Three different “protection” layers between the GM and overlying gravel and leachate are examined: (1) A traditional nonwoven geotextile (GT); (2) a GT-GCL; and (3) a GT-sand-GT layer. The GT-GCL protection layer gives an antioxidant depletion rate 0.59 to 0.66 times slower than the GT layer alone. The GT-sand-GT layer gives depletion rates 0.72–0.75 times that of the conventional GT alone. Based on Arrhenius modeling, the time required for depletion of antioxidants at 35°C is estimated to be 65 years for a GM with a GT-GCL protection layer, 50 years for a GT-sand-GT layer, and 40 years for a conventional GT protection layer. These times are all significantly greater than the depletion time for GM immersed in leachate (10 years) for the geomembrane tested.

DOI: 10.1061/(ASCE)1090-0241(2008)134:7(906)

CE Database subject headings: Durability; Geomembranes; Landfills; Liners; Service life; Temperature.

Introduction

High density polyethylene (HDPE) geomembrane (GM) liners are widely used in municipal solid waste (MSW) landfills as a part of a barrier system on the base of a landfill. For a landfill with a single liner, the barrier system typically involves a gravel leachate drainage layer, a protection layer, and a composite liner comprised of an HDPE geomembrane and either a geosynthetic clay liner (GCL) or a compacted clay liner (CCL). The composite liner provides the primary barrier to the migration of leachate to surface or groundwater. There has been considerable recent research related to the leakage of fluids and gases through composite liners (Barroso et al. 2006; Touze-Foltz et al. 2006; Bouazza and Vangpaisal 2006). However, these studies assume an effective GM with only a few holes. To ensure that long-term contamination does not occur, it is important that the durability of GM is maintained over the contaminating lifespan of the landfill (Rowe et al. 2004).

The protection layer is most commonly a needle-punched geotextile (GT) with a mass per unit area exceeding 250 g/m². However, other protection layers (e.g., sand) may be even more effective (Dickinson and Brachman 2006; Brachman and Gudina 2008). This layer is intended to protect the geomembrane from physical damage. However, it can also be anticipated that it will

provide some protection to the GM from interaction with leachate and the depletion of antioxidants. If that is the case, then this layer may be designed to improve the service life of the GM.

Accelerated aging tests are commonly used to assess the service life of GMs (Hsuan and Koerner 1998; Sangam and Rowe 2002; Müller and Jakob 2003; Gulec et al. 2004). Most commonly, the accelerated aging involves immersing the GM in a fluid of interest (typically air, water, or leachate) and incubating the sample at elevated temperatures. The material properties are then evaluated as a function of incubation time. The test data can be utilized to establish the Arrhenius relationship between degradation rate as a function of temperature (Koerner et al. 1992). This relationship can be employed to extrapolate the degradation rates obtained in the laboratory to any other temperature. The service life (or stages in service life) can then be estimated based on the degradation rate.

Antioxidants are added in the GM to retard oxidation and prolong their service life. The amount of antioxidant and stabilizers added to the GM is typically 0.5–1% (Hsuan and Koerner 1995). Conceptually, the chemical aging process for a GM can be considered to have three distinct stages (Viebke et al. 1994; Hsuan and Koerner 1998): (1) Antioxidant depletion; (2) induction to the onset of polymer degradation; and (3) polymer degradation involving the decrease in GM property to an arbitrary level (e.g., to 50% of the initial value). The service life of the GM is the sum of the three stages. Prior accelerated aging studies have mostly focused on estimating the length of the antioxidant depletion time of the GMs (Hsuan and Koerner 1998; Sangam and Rowe 2002; Müller and Jakob 2003; Rimal et al. 2004; Gulec et al. 2004). Most of these investigations employed simple immersion of GM coupons in different media (e.g., water, air, leachate, acid mine drainage, etc.). The results from these tests have shown that there is a significant difference in antioxidant depletion time depending upon the type of exposure condition. The results obtained from immersion in leachate are considered to be approximate and likely conservative for the tested GM (Sangam and Rowe 2002). Hsuan and Koerner (1998) examined a case with water saturated sand above and dry sand below the GM. These tests were de-

¹Professor, Geo Engineering Centre at Queen's – RMC, Queen's Univ., Kingston, Ontario, Canada, K7L 3N6 (corresponding author). E-mail: kerry@civil.queensu.ca

²Ph.D. Student, Geo Engineering Centre at Queen's – RMC, Queen's Univ., Kingston, Ontario, Canada, K7L 3N6.

Note. Discussion open until December 1, 2008. Separate discussions must be submitted for individual papers. To extend the closing date by one month, a written request must be filed with the ASCE Managing Editor. The manuscript for this paper was submitted for review and possible publication on June 27, 2007; approved on October 26, 2007. This paper is part of the *Journal of Geotechnical and Geoenvironmental Engineering*, Vol. 134, No. 7, July 1, 2008. ©ASCE, ISSN 1090-0241/2008/7-906–916/\$25.00.

signed to simulate the site conditions, but may not be conservative since there was no contact between leachate and the GM. The need to examine the antioxidant depletion time of the GM under more realistic field exposure conditions than simple immersion tests can be addressed by performing accelerated aging tests on simulated composite liners exposed to leachate (Rowe and Rimal 2008).

This paper focuses on examining the antioxidant depletion time for GMs in simulated composite liners. The objective of the study is to identify the potential effect of different protection layers above the GM on the depletion of antioxidants from the GM. Three different protection layers will be examined as described in the following section.

Experimental Investigation

Composite Liner Configurations

For the purpose of this study, the simulated composite liner consisted of GM over a GCL and compacted moist sand as a foundation layer. Three protection layers above the GM were considered as illustrated in Fig. 1. The first involved a 270 g/m² needle punched nonwoven GT protection layer above the GM [denoted as scenario CL-T, Fig. 1(a)]. The second type consisted of GT and GCL above the GM [denoted as CL-TG, Fig. 1(b)]. The third consisted of a 1.5 cm thick sand layer contained between two GT layers [denoted as CL-TST, Fig. 1(c)]. In the following discussion, these three liner systems will be referred to as CL-T, CL-TG, and CL-TST (CL=composite liner, T=GT, G=GCL, S=sand) for simplicity of presentation.

Previous research has suggested that surfactants and trace metals commonly found in leachate can increase the depletion of antioxidants and aging of GM. The surfactants increase the wettability of the GM, thereby, increasing the potential for both outward diffusion of antioxidants (Islam and Rowe 2007) and contact with trace metals has been reported to increase the consumption of antioxidants in anoxic conditions (Osawa and Saito 1978; Wisse et al. 1990). Thus, in the second case (CL-TG), a GCL was placed on top of the GT layer to examine its effectiveness in protecting the GM from leachate and influencing antioxidant depletion from the GM. Although this configuration is not typically used in landfills, it is examined in this study because GCLs have been found to attenuate metals such as Al, Fe, Mn, Ni, Pb, Cd, Cu, and Zn that are typically present in the MSW leachate (Lange et al. 2005). Furthermore, surfactants are known to get adsorbed in clay (Beigel et al. 1998). Thus, it was hypothesized that the GCL above the GM may provide chemical protection to the GM by partially reducing the contact between surfactants and trace metals and the GM.

GT and sand may be used for GM protection against physical damage (Koerner et al. 1996; Tognon et al. 1999; Qian et al. 2002; Rowe et al. 2004). Thus, the third protection layer, (i.e., CL-TST) involved a thin (1.5 cm) layer of sand sandwiched between an upper and lower GT layer. Although the GT and sand is permeable, it can be anticipated that with the absence of significant flow in this layer [as may be anticipated when the sand clogs (Rowe 2005)], it will act as a diffusion barrier, even if there is not much potential for attenuation of surfactants and metals. Thus, this configuration was selected to allow an assessment of its effectiveness in providing chemical protection to the GM.

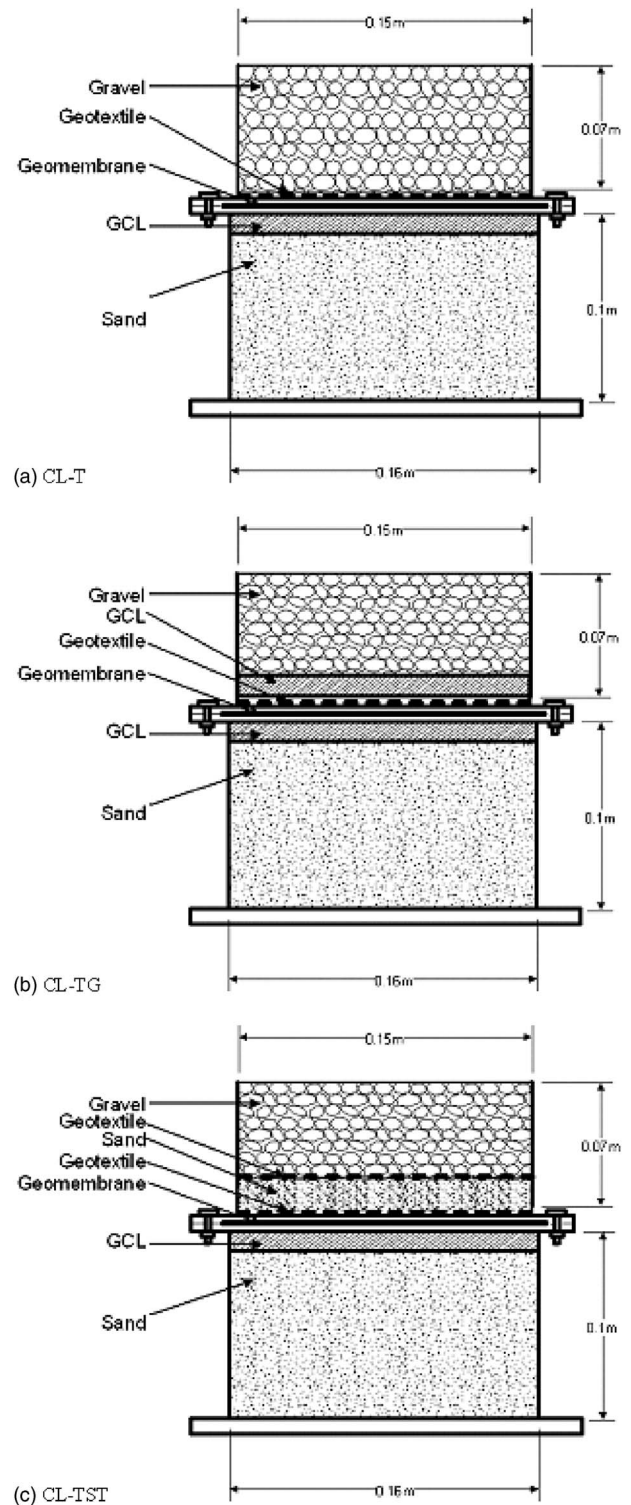


Fig. 1. Schematic of composite liner cells: (a) CL-T: GT protection layer; (b) CL-TG: GCL-GT protection layer; and (c) CL-TST: GT-sand-GT protection layer

Materials and Procedure

The composite liner cells (Fig. 1) were constructed from stainless steel to withstand long-term tests at temperatures up to 85°C and exposure to the chemical used in synthetic leachate. A brief description of materials and procedure used is provided in the following paragraphs.

Table 1. Properties of the GCL

Property	Method (ASTM)	Average
Staple fiber nonwoven cover geotextile Mass per unit area ^a	D 5261 (ASTM 2006m)	200 g/m ²
Scrim reinforced carrier geotextile Mass per unit area ^a	D 5261 (ASTM 2006m)	200 g/m ²
Bentonite mass per unit area ^a	D 5993 (ASTM 2006l)	3.66 kg/m ²
Hydraulic conductivity	D 5084 (ASTM 2006k)	5×10^{-11} m/s
Internal shear strength	D 6243 (ASTM 2006e)	24 kPa Typical

^aMinimum average roll value.

Grade 24 Ottawa silica sand was used as a foundation layer for all three configurations. It was clean sand without dust, clay, or iron compounds. The sand had relative density of 2.65. The sand had grain size distribution (ASTM D6913) (ASTM 2006q) with a mean grain size (D_{50}) of 0.5 mm, a coefficient of uniformity (Cu) of 3, and coefficient of curvature (Cc) of 1.0. Based on Standard Proctor test (ASTM D698) (ASTM 2006j), the optimum moisture content was 13.7% at a dry unit weight of 15.7 kN/m³.

The sand was placed at 14% moisture content and compacted in the bottom portion of the cell in three equal increments using a similar approach and compaction energy per unit volume as used in the Standard Proctor test (ASTM D698) (ASTM 2006j). After compaction, the sand had mean porosity of 0.41, void ration of 0.71, dry density of 1.55 g/cm³, and a degree of saturation of 52%.

A GCL was placed on top of the foundation sand. The properties of the thermally locked GCL are summarized in Table 1. Prior to placing the GCL on the underlying sand, about 200–210 ml of water was added to the top of the sand to provide sufficient moisture to hydrate the GCL without significantly changing the moisture content of the sand from the compacted value after hydration. This was done to ensure that (a) excessive water was not added to alter the compacted state of the sand; (b) there was sufficient water to hydrate the GCL within a reasonable time period; and (c) the moisture content of GCL and sand was consistent in each composite liner cell. To assess the hydration of the GCL, a number of control cells were prepared and left at laboratory temperature for hydration. These cells were opened periodically and the moisture content of GCL and sand layers were measured to obtain the moisture content profile. Three days were required for the GCL to reach a gravimetric water content of 95%, 19 days to reach 120%, and 30 days to reach 138%. At 30 days, the GCL had a bulk void ratio of 4.4, bentonite porosity of 0.80, and a degree of saturation of 92%. The GCL used in the protection layer was hydrated by adding water to the top portion of the composite liner cell and the moisture content was monitored with time using control cells.

The 1.5 mm thick HDPE GM tested had the properties given in Table 2. The property most relevant to this paper was the initial standard oxidative induction time (OIT) of 135 min. The GM was placed on top of the GCL. The upper portion of the stainless steel cell was installed on top of the GM and connected to the bottom portion.

The GT protection layer placed over the GM in all three cases had properties as given in Table 3. Crushed coarse 19 mm limestone gravel was placed over the protection layer to simulate the leachate collection layer.

The CL-TG and CL-TST configurations were similar to that described above except that for the CL-TG configuration [Fig.

Table 2. Properties of the HDPE Geomembrane, COV=Coefficient of Variation

Property	Method (ASTM)	Average	COV (%)
Thickness (mm)	As received	1.5	—
Density (g/cm ³)	D1505 (ASTM 2006b)	0.944	2.43
Carbon black content (%)	D1603 (ASTM 2006a)	2.43	—
OIT (min)	D3895 (ASTM 2006p)	135	3.3
HP-OIT (min)	D5885 (ASTM 2006o)	660	4.4
Crystallinity (%)	E794 (ASTM 2006n)	49	6.1
MFI (g/10 min)	D1238 (ASTM 2006h)	0.553	0.4
Tensile properties (machine direction)	D6693 (ASTM 2006f)		
Tensile strength at yield (kN/m)		26.9	2.5
Tensile strength at break (kN/m)		64.7	1
Tensile strain at yield (%)		18.1	3.7
Tensile strain at break (%)		962	0.8
Tensile properties (cross-machine direction)	D6693 (ASTM 2006f)		
Tensile strength at yield (kN/m)		27.1	2.5
Tensile strength at break (kN/m)		59.9	8.1
Tensile strain at yield (%)		18.1	1.4
Tensile strain at break (%)		898	8.4
Single point stress crack resistance (hrs)	D5397 (ASTM 2006g), Appendix	>400	

1(b)] a GCL, with properties as given in Table 1, was placed above the GT layer. The GCL was allowed to hydrate using an adequate volume of distilled water. Gravel was then placed over the GCL. For the CL-TST configuration [Fig. 1(c)], a 1.5 cm layer of Ottawa sand at 14% moisture content was placed over the GT protection layer. Another layer of GT was then placed over the sand layer. The gravel was placed over the second GT.

Accelerated Aging Baths and Exposure Conditions

The assembled composite liner cells were placed in four 117 cm × 86 cm × 40 cm (length × width × height) insulated stainless steel incubation baths. One each of the baths was maintained at a temperature of 85, 70, 55, and 26 °C (room). An

Table 3. Properties of the Geotextile

Property	Method (ASTM)	Average
Mass per unit area (g/m ²)	D 5261 (ASTM 2006m)	270
Thickness ^a	D 5199 (ASTM 2006d)	2 mm (80 mil)
Grab tensile strength (N) ^a	D 4632 (ASTM 2006i)	975
Grab elongation % ^a	D 4632 (ASTM 2006i)	50
Hydraulic conductivity	D 4491 (ASTM 2006r)	3×10^{-3} m/s
Apparent opening size (mm) ^b	D 4751 (ASTM 2006c)	0.180 mm (sieve No. 80)

^aMinimum average roll value.

^bMaximum average roll value.

Omega CN1A series temperature control system was used to maintain the bath temperature at $\pm 1^\circ\text{C}$ of the specified value. A pump was used to provide fluid circulation.

The incubation bath temperatures were selected to be high enough to accelerate the aging process in a reasonable time period. They were also selected such that they would not modify the nature of materials (e.g., below the melting point of the GM: 131°C and such that they would not destroy the antioxidants in the GM). The temperature was kept below 95°C because prior studies have suggested that for some GMs, volatilization of antioxidants may be important for temperatures above 95°C (Karls-son et al. 1992; Smith et al. 1992; Hsuan and Guan 1998).

The gravel portion of the composite liner cells were saturated with synthetic leachate allowing the GM to be exposed to the synthetic leachate from the top. The synthetic leachate was prepared in the laboratory with a composition based on leachate from Keele Valley MSW landfill (Hrapovic 2001; Sangam and Rowe 2002). The synthetic leachate ($\text{pH} \sim 6$) contained volatile fatty acids, inorganic salts, trace metals, and surfactant. Details regarding leachate components and concentration are provided in Rowe and Rimal (2008). The leachate was refreshed with new leachate at two week intervals. Studies by Rowe et al. (2008) have demonstrated that a two week replacement of leachate is sufficient to prevent a buildup on antioxidant in the leachate that would impact on the results. The GM was exposed to synthetic leachate for up to 3 years.

Periodic Testing

Incubated samples were retrieved at various time intervals. The amount of antioxidant remaining in the GM was evaluated using standard OIT tests (ASTM D3895) (ASTM 2006p) and TA Instruments 2910 and Q100 differential scanning calorimeters (DSCs).

The standard OIT test is an excellent indicator of the amount of antioxidant in the material, but it does not indicate the type of antioxidant. If present in the GM, hindered amine antioxidants lose their effectiveness in the standard OIT test temperature of 200°C (Hsuan and Koerner 1998). Thomas and Ancelet (1993) have demonstrated that hindered amines were active at 150°C in the HP-OIT test. To distinguish between the types of antioxidants present in the GM, high pressure oxidative induction time tests (HP-OIT) (ASTM D5885) (ASTM 2006o) can be used (Hsuan and Koerner 1998; Sangam and Rowe 2002; Gulec et al. 2004). Rowe and Rimal (2008) reported the results of the standard OIT test and HP-OIT tests on the accelerated aged GM specimen used in the present tests. The linear correlation observed from the two tests suggested that either of the two tests could be used to evaluate the depletion of antioxidant from the GM. Both test results also gave very similar predictions for the time taken for depletion of antioxidants. Additionally, it provided evidence that the use of standard OIT test did not destroy the antioxidant package present in this GM. Therefore, the standard OIT test was used in the present study to monitor the antioxidant remaining in GM with time and, hence, calculate the antioxidant depletion rates.

Results and Discussions

Antioxidant Depletion

At any given incubation time, the OIT value is an index measure of total antioxidant amount in the GM. The depletion of antioxidant with time can be expressed as a first-order process (Hsuan and Koerner 1998; Sangam and Rowe 2002)

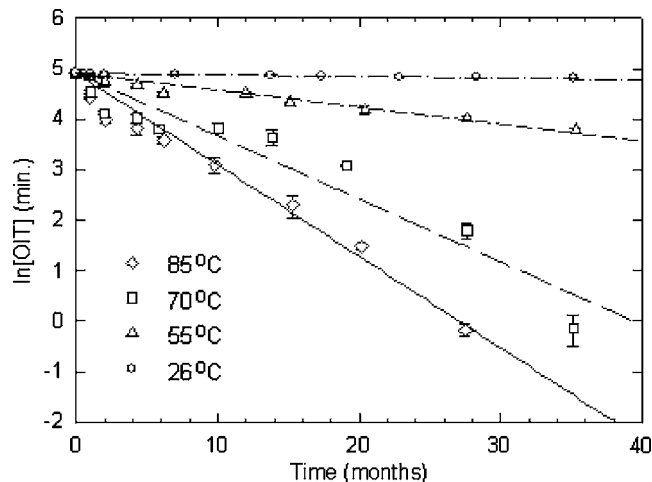


Fig. 2. Variation of logarithm of OIT with aging time at various temperatures for geomembrane in CL-TG

$$\text{OIT}(t) = \text{OIT}_0 \cdot e^{(-s \cdot t)} \quad (1)$$

or taking logarithm of both sides

$$\ln[\text{OIT}(t)] = -s \cdot t + \ln(\text{OIT}_0) \quad (2)$$

where $\text{OIT}(t)$ = OIT at a given time t ; s = antioxidant depletion rate; and OIT_0 = initial OIT.

The changes in the logarithm of OIT with aging time (one month was taken to be 30 days) at various temperatures is illustrated for the CL-TG and CL-TST GMs in Figs. 2 and 3. Each data point represents the average of three to five replicate OIT measurements and the vertical bars represent the standard deviation of the data obtained from these replicate tests. The OIT values decreased exponentially with time at all temperatures. The coefficient of determination R^2 (Table 4) of the regression line ranged from 0.91 to 0.97 for CL-TG and 0.89–0.96 for CL-TST. The exponential reduction of OIT was faster at higher temperatures. The slopes of the regression lines that represent antioxidant depletion rate are given in Table 4.

The objective of this research was to examine the effects of protection layer on reducing the rate of aging and improving the

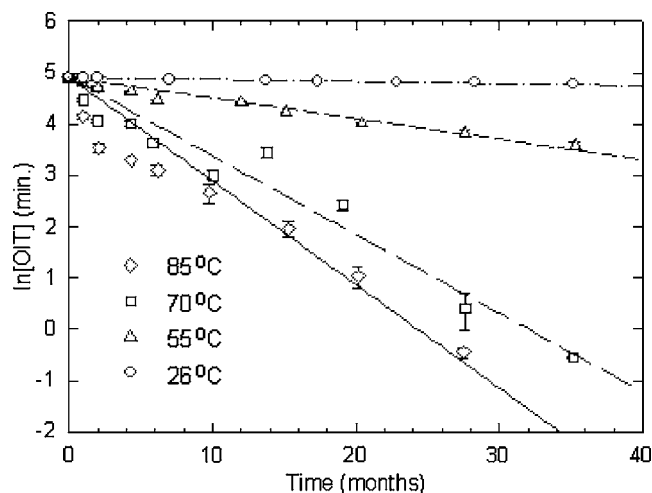


Fig. 3. Variation of logarithm of OIT with aging time at various temperatures for geomembrane in CL-TST

Table 4. List of First-Order Antioxidant Depletion Rates (Month 1) at Different Incubation Temperatures

Temperature (°C)	Composite liners			Comparison		
	CL-T ^a	CL-TST	CL-TG	TG/T	TST/T	TG/TST
85	0.2750 (0.89)	0.2019 (0.89)	0.1814 (0.97)	0.66	0.73	0.90
70	0.2123 (0.96)	0.1533 (0.95)	0.1247 (0.91)	0.59	0.72	0.81
55	0.0539 (0.94)	0.0402 (0.96)	0.0337 (0.94)	0.63	0.75	0.84
26	0.0053 (0.95)	0.0040 (0.93)	0.0032 (0.94)	0.60	0.75	0.80

Note: The number in parentheses represents coefficient of determination R^2 .

^aData from Rowe and Rimal (2008).

long-term performance of GM. Figs. 4 and 5 present comparative plots of the logarithm of OIT with incubation time for the three different protection layers at 85 and 55°C. It evident from Figs. 4 and 5 that the rate depletion of antioxidants at a particular temperature does depend on the type of protection layer used. For example, at 85°C, the antioxidant depletion rates for configuration CL-TG with the GCL above the GM was slowest at 0.181 month⁻¹, compared with 0.202 month⁻¹ for configuration CL-TST with the sand above the GM, and fastest for the conventional GT protection layer configuration CL-T (0.275 month⁻¹). A similar trend was observed at lower temperatures (Fig. 5). It was found that the antioxidant depletion rates at each test temperature associated with CL-TG was 0.59 to 0.66 times slower than for CL-T. The CL-TST was also 0.72 to 0.75 times slower than CL-T (Table 4). These results indicated that the use of the alternative protection layers slows down the rate of depletion of antioxidant from the GM.

The decrease in the antioxidant depletion rate may be attributed to: (a) Availability of additional protection to the GM from exposure to leachate; (b) possible attenuation of metals and surfactants in the leachate by the protection layers (especially GCL), thereby reducing their effects on the depletion of antioxidants; and (c) buildup of concentration of antioxidant on the either side of the GM, thereby reducing the concentration gradient and outward diffusive flux of antioxidants.

Rowe and Rimal (2008) have reported that the antioxidant depletion rates were significantly (2.2–4.8 times) higher for the same GM simply immersed in leachate than for the conventional simulated composite liner (CL-T). Antioxidant depletion rates for same 1.5 mm GM immersed in leachate were compared to the

three composite liner GMs (Table 5). At each test temperatures, the ratio of the observed depletion rate for composite liner GM to the immersed GM for CL-T ranged from 0.21 to 0.46, for CL-TST ranged from 0.16 to 0.34, and for CL-TG ranged from 0.13 to 0.28. This implies that for all three composite liners, the GM experienced significantly lower depletion rates than when simply immersed in leachate. The faster depletion observed in the leachate immersion may be due to the factors such as: (a) Antioxidants diffusing out from the leachate immersed GM could be more readily removed into the leachate, hence, maintaining a relatively high concentration gradient and high outward diffusive flux of antioxidants from the GM, whereas for the simulated liner GM there could be a buildup of concentration of antioxidant in the layers on either side of the GM, thereby reducing the concentration gradient and outward diffusive flux of antioxidants; and (b) direct exposure to leachate constituents in leachate immersed GM from both sides compared to one side protected exposure in composite liner GM.

Variation of Antioxidant Depletion with Temperature

It is evident from Table 4 and Figs. 2 and 3 that the antioxidant depletion rates are higher at high temperatures than at low temperatures. The data listed in Table 4 can be used to establish Arrhenius relationship between antioxidant depletion rate and temperature for each composite liner GM. A plot of logarithm of antioxidant depletion rates versus the inverse of the incubation temperature (in K) is shown in Fig. 6. This relationship is described by the logarithmic form of Arrhenius equation

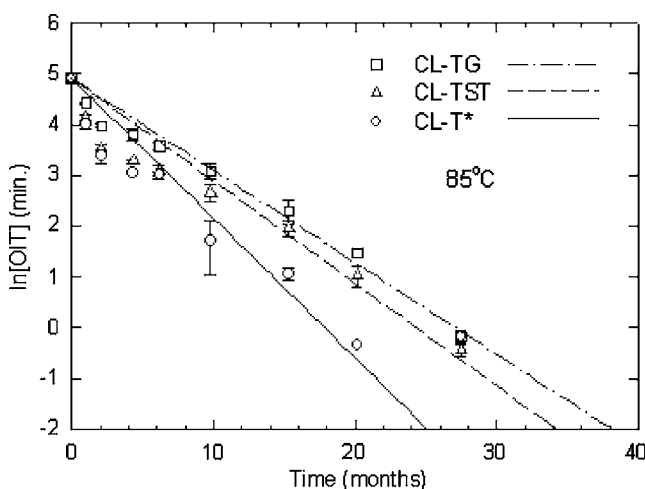


Fig. 4. Comparative plots of OIT depletion at different incubation temperatures at 85°C. *Data from Rowe and Rimal (2008).

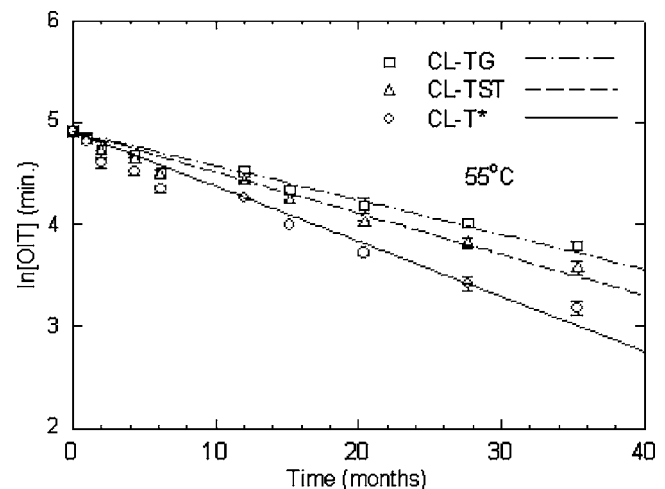


Fig. 5. Comparative plots of OIT depletion at different incubation temperatures 55°C. *Data from Rowe and Rimal (2008).

Table 5. Comparison of Antioxidant Depletion Rates for Leachate Immersed and Composite Liner Geomembrane

Temperature (°C)	Antioxidant depletion rates (month ⁻¹)		Comparison		
	leachate immersed ^a		T/Immersed	TST/Immersed	TG/Immersed
85	1.2423 (0.95)		0.22	0.16	0.15
70	0.4809 (0.99)		0.44	0.32	0.26
55	0.1183 (0.99)		0.46	0.34	0.28
26	0.0253 (0.98)		0.21	0.16	0.13

Note: The number in parentheses represents coefficient of determination R^2 .

^aData from Rowe and Rimal (2008).

$$\ln(s) = \ln(A) - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \quad (3)$$

where s =antioxidant depletion rate (month⁻¹); A =constant; E_a =activation energy (kJ/mol); R =universal gas constant (8.31 J mol⁻¹ K⁻¹); and T =absolute temperature (K).

The assumptions associated with the Arrhenius equation are: (a) The antioxidant depletion rate “ s ” is only a function of temperature; (b) the value of “ A ” (referred to as frequency factor) does not affect the temperature sensitivity of the reaction; (c) the activation energy “ E_a ,” which is defined as energy barrier that has to be overcome for the reaction to proceed, remains constant over the time and temperature range of interest for evaluation, extrapolation, and prediction.

The Arrhenius equation and inferred activation energies for each composite liner are summarized in Table 6. The activation energy, which can be deduced from the slope ($-E_a/R$) of the regression lines (Fig. 6) are 62.1 kJ/mol for the CL-TST and 63.4 kJ/mol for CL-TG. There is a small difference (1%) in the activation energies of CL-TST and CL-TG relative to CL-T (62.7 kJ/mol). This implies that the activation energies for the three composite liners are relatively similar. The similarity in the slopes suggests that the tests are monitoring the same reactions. Higher activation energies were observed for all simulated liner GMs than that of leachate immersion (58.9 kJ/mol) reported by Rowe and Rimal (2008).

The intercept of the Arrhenius equations is logarithm of frequency factor. The frequency factor is a bracketed constant term for collision frequency and orientation factor (a probability) (Ko-

erner et al. 1992). In this respect, the frequency factor is a function of the boundary conditions of the test such as exposed area of the GM to leachate and water, as well as extraction and/or volatilization of antioxidant from the surface of GM. Furthermore, it also is a function of the amount of exposure to leachate constituents, and concentration gradient of antioxidant between surface and core of the GM. The concentration gradient is influenced by frequency of leachate renewal, dissolution of antioxidants from the surface to the liquid, and buildup of concentration near the surface.

The excellent correlation (R^2 values around 0.98) for each Arrhenius equation (Table 6) suggests that the antioxidant depletion rates can be fairly well estimated at field temperatures. Recent data suggests that for normal MSW landfill operations, the liner temperatures can be expected to be between 30 and 40°C and 35°C can be taken as the median temperature (Rowe 2005). However, liner temperatures have been reported to exceed 40°C in a “wet cell” (anaerobic bioreactor landfill) with a high moisture content of the waste (Koerner and Koerner 2006). At the base of landfills where there is a significant leachate mound, liner temperatures of 40–60°C may occur (Rowe 2005). Using the Arrhenius equations listed in Table 6, the antioxidant depletion rates at site specific lower temperatures were estimated and are given for temperatures ranging from 10–60°C in Fig. 7. The depletion rates were the highest for the standard GM protection layer (CL-T).

Antioxidant Depletion

The time taken for depletion of antioxidants (Stage I of the GM service life) can be calculated as time taken for reduction of OIT from the initial value of 135 min to final residual value of 0.5 min for a pure HDPE resin without any antioxidant (Hsuan and Koerner 1998). Rearranging Eq. (2) gives

$$t_{\text{depletion}} = \frac{\ln(\text{OIT}_0) - \ln(\text{OIT}_f)}{s} \quad (4)$$

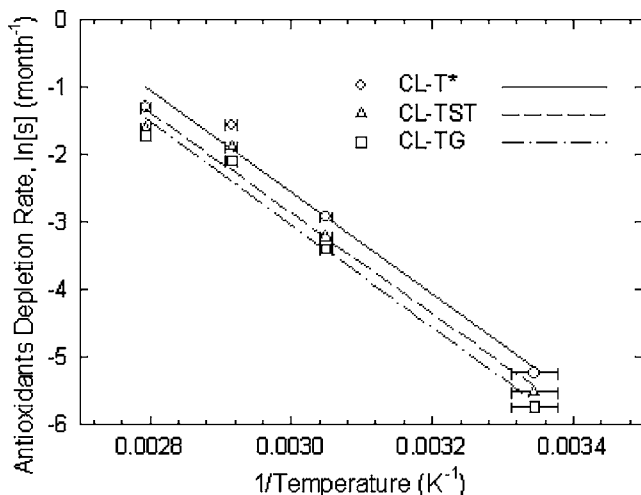
Substituting the respective values $\text{OIT}_0=135$ min, $\text{OIT}_f=0.5$ min gives:

Table 6. Arrhenius Equation and Inferred Activation Energy

Exposure	Arrhenius equation	E_a (kJ/mol)	R^2
CL-T ^a	$\ln(s)=20.06-7,540/T$	62.7	0.977
CL-TST	$\ln(s)=19.56-7,475/T$	62.1	0.978
CL-TG	$\ln(s)=19.88-7,639/T$	63.5	0.984

Note: The Arrhenius equation for the basic composite liner CL-T may slightly differ from that reported in Rowe (2005) due to the use of updated values of antioxidant depletion rates based on data obtained from longer-term testing in the present paper.

^aData from Rowe and Rimal (2008).

**Fig. 6.** Arrhenius plot of antioxidant depletion rates. *Data from Rowe and Rimal (2008).

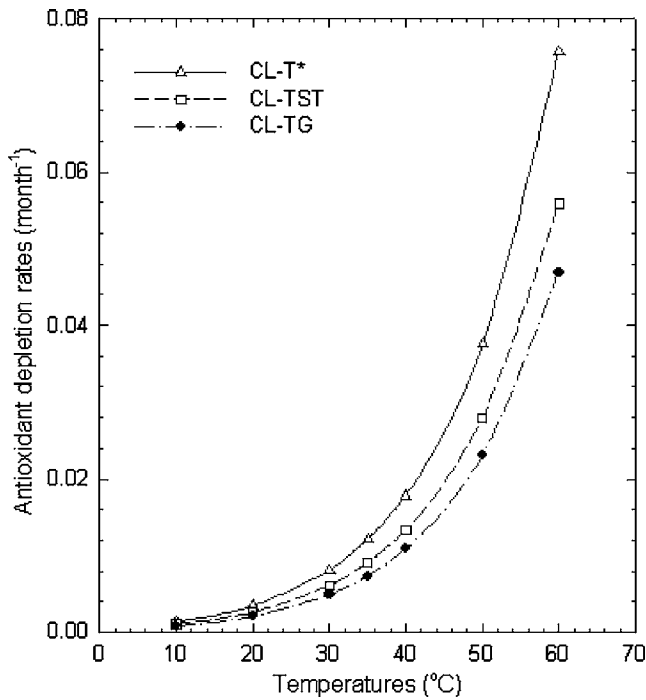


Fig. 7. Predicted antioxidant depletion rates at the service temperatures ranging from 10 to 60°C. *Data from Rowe and Rimal (2008).

$$t_{\text{depletion}} = \frac{\ln(135) - \ln(0.5)}{s} \quad (5)$$

Eq. (5) can be used to calculate the antioxidant depletion time $t_{\text{depletion}}$ for the GM. The predicted antioxidant depletion times for liner temperatures ranging from 10 to 60°C were obtained using the antioxidant depletion rates given in Fig. 7 (based on Fig. 6 and Table 6) and are illustrated as a grouped histogram in Fig. 8. The inset table in Fig. 8 gives the numerical values for predicted antioxidant depletion at 20, 35, and 50°C (rounded to nearest 5 years). The antioxidant depletion times for GMs in composite liners were substantially longer than for leachate immersed GMs. The depletion times for CL-TG are also the greatest of all the cases considered, followed by CL-TST and CL-T. For example, at 35°C, the antioxidant depletion time for CL-TG was 65 years, followed by CL-TST with 50 years, and CL-T with 40 years as compared to 10 years for an immersed GM. The predicted antioxidant depletion times ranged from 570 years at 10°C to 10 years at 60°C for CL-TG. For the CL-TST, they ranged from 440 years at 10°C to 8 years at 60°C. For CL-T, they ranged from 335 years at 10°C to 6 years at 60°C, and for leachate immersed GM (Rowe and Rimal 2008), the range was from 85 years at 10°C to 2 years at 60°C.

Two key observations can be made based on these results. First, the results obtained from the immersion test that have been commonly used for assessing stage I (antioxidant depletion time) of service life on GM are too severe and stage I is substantially longer for a composite liner test. Second, the GCL protection layer used in CL-TG increased the antioxidant depletion time (e.g., at 20°C 230 years for CL-TG, followed by 180 years for CL-TST, 135 years for CL-T, and 35 years for immersed GM). Use of sand and GT in CL-TST also improved the antioxidant depletion time as compared with the basic GT protection layer in CL-T. These results imply that the additional protection of GCL or sand would reduce the antioxidant depletion rates by reducing

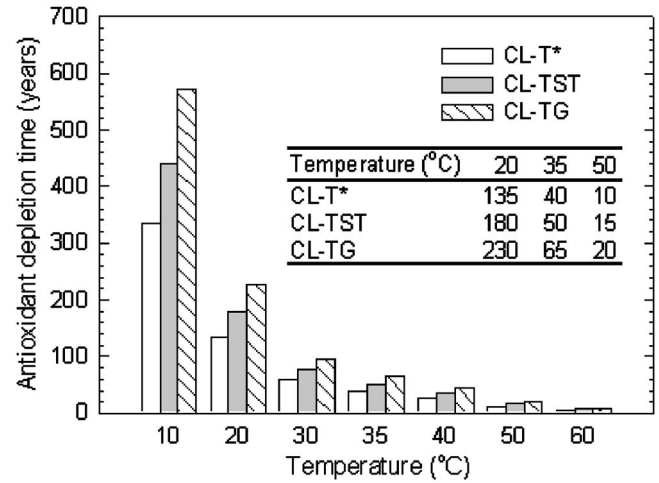


Fig. 8. Predicted antioxidant depletion times. Note: The antioxidant depletion times for the basic composite liner CL-T may slightly differ from that reported in Rowe (2005). The values reported here are obtained from longer-term testing. The results may differ due to updated values of antioxidant depletion rates and rounding. *Data from Rowe and Rimal (2008).

the effects of surfactants and transition metals in the leachate and outward diffusion of antioxidants. Thus, the use of these protection layers may reduce the rate of aging and improve the long-term performance of GM liners.

Modeling Diffusion of OIT

Background and Theoretical Basis

The antioxidant depletion from a GM can occur by two main mechanisms: Migration and consumption (Müller 2007). Migration is a physical phenomenon in which the antioxidants diffuse from the bulk HDPE material to the surface, driven by a concentration gradient. The consumption process involves chemical degradation of the antioxidant (e.g., hydrolysis of phosphites) and consumption by oxidative reactions (e.g., with oxygen, free radicals, and alkyl peroxides) as described by Grassie and Scott (1985).

When exposed to liquids, both the consumption of antioxidants at the surface of the GM and dilution in the fluid result in the establishment of a concentration gradient between the surface and core of the GM. Thus, the outward migration process of antioxidants from polyethylene involves three key steps (Calvert and Billingham 1979; Möller and Gevert 1996; Haider and Karlsson 1999): (a) An initial step in which the loss of antioxidants is controlled by desorption (i.e., partition between the outer surface of the GM and the outer medium); (b) a second intermediate step where both desorption and diffusion are of importance; and (c) a third step where the loss of additive is controlled by diffusion within the sample.

At equilibrium, the relationship between antioxidant concentration in the GM and that in the fluid is described by Henry's law

$$c_{\text{gm}} = c_f S_{\text{gf}} \quad (6)$$

where c_{gm} = equilibrium concentration in the GM (ML^{-3}); c_f = equilibrium concentration in the fluid (ML^{-3}); S_{gf} = partitioning coefficient (-) between the GM and the fluid. The partitioning coefficient is a constant for a given molecule, fluid, GM, and temperature of interest. The above relationship is valid

for the cases where the permeant does not interact with the polymer or where the concentrations are low (Rogers 1985).

The diffusion of permeant in a GM is described by Fick's first law

$$f = -D_{gm} \frac{\partial c_{gm}}{\partial z} \quad (7)$$

where f =mass flux or rate of transfer of diffusing substances through unit of a section ($ML^{-2} T^{-1}$), z =space coordinate in the direction parallel to the direction of diffusion [L]; D_{gm} =diffusion coefficient in the GM ($L^2 T^{-1}$); and c_{gm} =concentration of the diffusing substance in the geomembrane (ML^{-3}). The factors that affect the D_{gm} are temperature, permeability of polymer to additive, solubility of additive, and the crystallinity of polymer (Billingham 1990).

In the transient state, the governing differential equation is given by Fick's second law

$$\frac{\partial c_{gm}}{\partial t} = D_{gm} \frac{\partial^2 c_{gm}}{\partial z^2} \quad (8)$$

that needs to be solved for the appropriate initial and boundary conditions.

A linear relationship between OIT and antioxidant concentration has been established by previous investigators. Viebke and Gedde (1997) for an initial antioxidant concentration of between 0 to 0.3% (by weight) in polyethylene.

The OIT values measured at various times in samples from aging tests can be taken as representative of the mass of antioxidant in the GM. Thus, the OIT test data at room temperature were analyzed following the methodology described below (using the finite-layer analysis program POLLUTE (GAEA Technologies Ltd., Whitby, Ontario, Canada, v7.09) (Rowe and Booker 2004).

Estimate of Diffusion Coefficients from Immersion Tests

The outward diffusion of antioxidants from and initial concentration in the GM to the adjacent fluid was modeled for immersion tests in leachate. To simulate the interface conditions, a thin layer (0.0001 m) was modeled at the surface of the GM. Since the leachate was regularly changed, it was assumed that there was no buildup of antioxidant in the fluid adjacent to the GM. For a given diffusion coefficient, the concentration of antioxidant could be calculated at any time when the OIT had been measured. By integrating the concentration curve at that time, the total mass of antioxidant $m(t)$ could be calculated and normalized with respect to the initial mass m_0 . Since the mass of antioxidant is directly related to the OIT, the ratio $m(t)/m_0 = OIT(t)/OIT_0$ was compared to the observed ratio $OIT(t)/OIT_0$ and the diffusion coefficient was adjusted until the best match was obtained between the calculated and observed response (e.g., Fig. 9). Since the leachate has a surfactant that allows full wettability of the interface (Rowe et al. 2008), it was assumed that the properties of the thin interface layer in these tests were the same as for the main GM. This gave a diffusion coefficient $D_{gm} = D_{gm-thin-leachate}$ (diffusion coefficient of thin GM layer when exposed to leachate) = $2.1 \times 10^{-15} \text{ m}^2/\text{s}$ at room temperature.

Similarly, the water immersion test data from Sangam (2001) at room temperature were analyzed. Assuming the same diffusion coefficient in the GM ($D_{gm} = 2.1 \times 10^{-15} \text{ m}^2/\text{s}$), the diffusion coefficient for the thin GM layer when exposed to water was calculated to be $2.5 \times 10^{-16} \text{ m}^2/\text{s}$. As is evident from Fig. 9 [and as previously discussed by Sangam and Rowe (2002)], there was a significant difference between the diffusion of OIT from GM

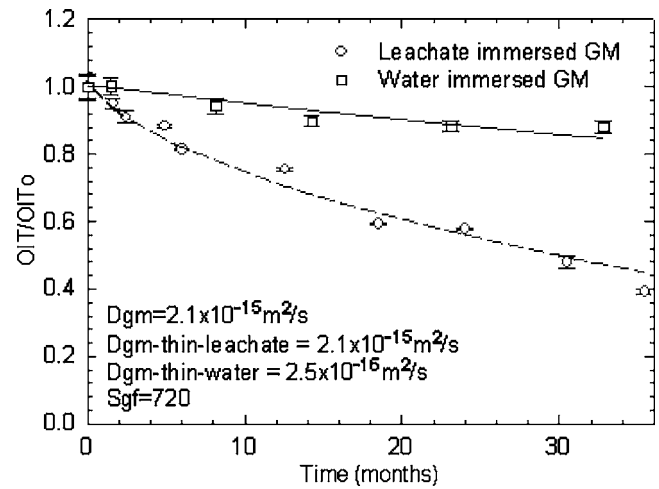


Fig. 9. Observed normalized OIT versus time in immersion tests at room temperature and the theoretical curves. Note: water immersion data from Sangam (2001).

samples immersed in water and leachate and the modeling of the interface conditions provides the means of capturing the difference.

Diffusion Coefficients and S_{gf} Values for Composite Liner Tests

The composite liner data for CL-T test at room temperature was analyzed. The model considered all the layers in CL-T (Fig. 1) with the gravel, protection layer, GCL, and sand below the composite liner all being modeled as porous media using parameters based on typical literature values (Table 7). 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) with $D_{g-thin-leachate} = D_{gm} = 2.1 \times 10^{-15} \text{ m}^2/\text{s}$, $D_{g-thin-water} = 2.5 \times 10^{-16} \text{ m}^2/\text{s}$. These were selected because in the CL-T test, the top portion of the GM is in contact with leachate in the GT, whereas, the bottom is in contact with water in the GCL. The periodic replacement of leachate, with the consequent removal of mass of antioxidant from the gravel above the protection layer, was modeled. Because of the five orders of magnitude in the diffusion coefficients in the GM and porous media, the precise value of the diffusion coefficient in the porous media is of no real consequence and the importance of the porous media lies in its availability to allow a buildup in antioxidant as they diffuse into

Table 7. Parameters Used for Diffusion Modeling in Composite Liner Cells

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

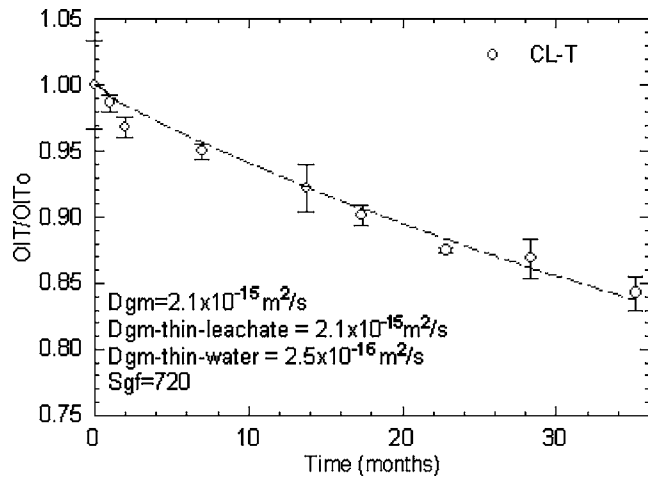


Fig. 10. Observed normalized OIT versus time at room temperature and the theoretical curves for CL-T

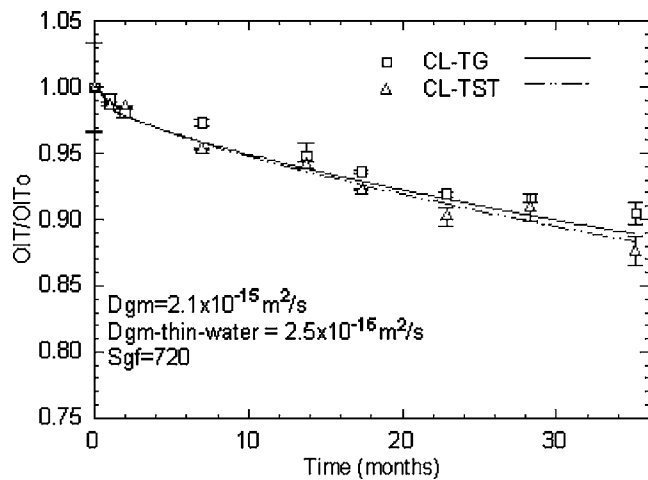


Fig. 11. Observed and predicted normalized OIT versus time at room temperature for CL-TG and CL-TST

the media and the protection it may provide the GM from contact with significant concentrations of leachate constituents such as surfactants.

The GM diffusion coefficients deduced from the immersion tests (discussed above) were used to model OIT depletion for the composite liner CL-T and an $S_{gf}=720$ was deduced. The calculated and observed depletion of antioxidants (based on OIT) for

test CL-T is shown in Fig. 10. Based on the results for the CL-T tests, predictions were made for the other two tests CL-TG and CL-TST. In CL-TG, the protection layer consisted of a GT and GCL. In CL-TST, the GM was overlain by GT, sand, and GT. Since these layers were considered to greatly inhibit the access of leachate to the GM, they were modeled with a thin layer of GM exposed to water on either side of the GM. ($D_{g\text{-thin-water}}=2.5 \times 10^{-16} \text{ m}^2/\text{s}$; $D_{gm}=2.1 \times 10^{-15} \text{ m}^2/\text{s}$; and $S_{gf}=720$) and the predicted OIT reduction for the GM in these two composite liners is shown in Fig. 11. It can be seen that the parameters deduced from other tests provide a reasonable prediction of OIT loss in these two tests, where the OIT loss was slower than for test CL-T (Fig. 10) and substantially slower than obtained in the immersion tests (Fig. 9).

The values of diffusion coefficients of antioxidants in polyolefins at various temperatures and test conditions have been inferred in past studies (Roe et al. 1974; Moisan 1980; Möller and Gevert 1994; Viebke and Gedde 1997). The diffusion coefficients for various antioxidants (phenolic, light stabilizers, thiosynergists) in LDPE were extrapolated to 25°C by Billingham (1990) from the literature values and the range at this temperature was from $1.5 \times 10^{-13} \text{ m}^2/\text{s}$ to $2.8 \times 10^{-16} \text{ m}^2/\text{s}$. The value of $D_{gm}=2.1 \times 10^{-15} \text{ m}^2/\text{s}$ obtained from the OIT depletion data for HDPE in this study is within this published range.

Fig. 12 shows a comparison of the calculated antioxidant concentration profiles for the CL-T and CL-TG tests. The concentration gradient in the GCL materials above and below the GM is very low because the diffusion coefficient in these materials is about five orders of magnitude higher than in the GM (and, hence, the precise value of diffusion coefficient in these layers is not particularly important). The normalized concentration of antioxidants in the geomembrane decreased with time between the start of the tests (0 days) and its termination (1,055 days). In the CL-TG test, the concentration in the GCL above the GM increased with time for the first 413 days and then only increased very slowly as a quasi-equilibrium was reached between the antioxidant mass flux out of the GM and its removal due to periodic changing of leachate above the GCL protection layer. Because there was no removal of antioxidant mass below the GM, the concentration in the lower GCL continued to build up for the full 1,055 days the test was run. The buildup in concentration in the GCLs above and below the GM led to the reduction in concentration gradient and outward diffusive flux of antioxidants from the GM. In the CL-T test, the concentration in the GT above the geomembrane increased with time up to 210 days and then decreased allowing further outward diffusion of antioxidants as they were removed from the system by changing of the leachate above

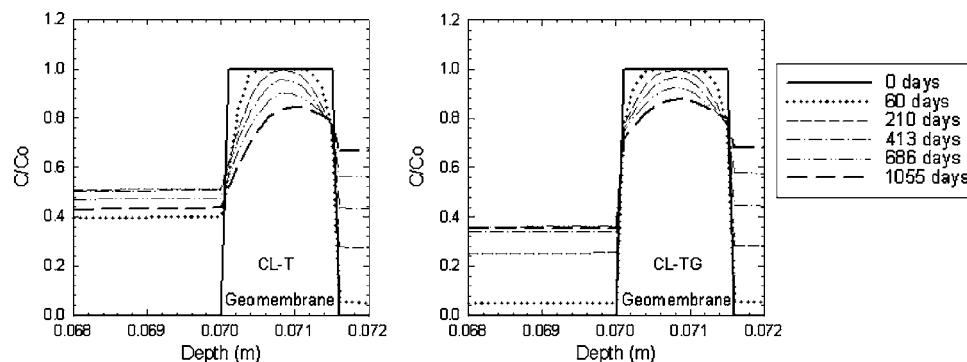


Fig. 12. Concentration profiles of antioxidants in CL-T and CL-TG

the GT. The concentration in the GCL below the GM increased with time for the full period of the test similar to that for the CL-TG test. In CL-TST, the concentration of antioxidants in the GCL below the GM increased similar to that observed for test CL-TG. Likewise, there was a generally similar buildup of concentration in the protection layer above the GM, although the difference in materials did lead to some small differences and a slight decrease in concentration was observed after 686 days.

Summary and Conclusions

The results of accelerated aging tests on geomembranes in composite liners were examined for three different protection layers (GT, GT and GCL and GT -1.5 cm sand-GT). Leachate was present in the gravel above the protection layers. The GM rested on a hydrated GCL. The results from OIT tests indicated that the antioxidant depletion rates were dependent on the type of protection layer used. With the GT-GCL protection layer, the antioxidant was depleted at 59–66% of the rate for a GT layer alone. With the GT-sand-GT, the depletion was 72–75% of that with a GT layer alone. Depletion of antioxidants in the composite liner GMs were significantly (13–46%) less than for GMs immersed in leachate. The slower depletion rates may be partially attributable to the possible attenuation of leachate constituents by the protection layers, as well as the buildup of concentration on either side, thereby, reducing the concentration gradient and outward diffusive flux of antioxidants. In practical applications, the layer of sand will likely be thicker than 1.5 cm and the effect can be expected to be greater.

The laboratory-based antioxidant depletion rates were extrapolated to a range of temperatures (10–60°C) using Arrhenius modeling and the antioxidant depletion time was estimated. For the geomembrane examined and a liner temperature of 35°C, the antioxidant depletion time was highest for a GM with protection layers of a GT and GCL (65 years) followed by GT-sand-GT (50 years), and lowest for GT alone (40 years). These are much longer than for the same GM immersed in leachate (10 years). The results suggest that the antioxidant depletion stage can be improved by using additional protection layers (e.g., GCL or sand-GT). It is recognized that the composite liner tests described herein are subject to limitations. In a real landfill, there is stress from the overburden waste; the combined effect of stress and exposure to leachate is the subject of current studies. Additional research is required to assess the subsequent stages of aging of GM. The service lives of GM are likely to be substantially greater than the time required to reach the end of Stage I as reported in this paper. Consideration would also need to be given to the other practical implications of using the different protection layers examined herein.

Acknowledgments

The research presented in this paper was funded by the Natural Science and Engineering Research Council of Canada (NSERC), Canada Foundation for Innovation (CFI), the Ontario Innovation Trust, and Centre for Research in Earth and Space Technology (and Ontario Center of Excellence). The Bentofix (Bentofix Technologies Inc., Barrie, Ontario, Canada) Thermal Lock NWL GCL tested was provided by Terrafix Geosynthetics Inc., Toronto, Canada. The writers are grateful to their industrial partners Solmax International, Terrafix Geosynthetics Inc, Ontario Ministry of Environment, Gartner Lee Ltd, AMEC Earth and

Environmental, Golder Associates Ltd., and CTT group and especially to Terrafix Geosynthetics Inc. (Toronto, Canada) for providing the geosynthetics tested. Support from Dr. Henri P. Sangam in the initial stages of this project is gratefully acknowledged. The value of discussion with Dr. Grace Hsuan and Dr. Richard Brachman is greatly appreciated.

References

- ASTM. (2006a). "Standard test method for carbon black content in olefin plastics." *Annual book of ASTM standards D1603*, Vol. 08.01.
- ASTM. (2006b). "Standard test method for density of plastics by the density gradient method." *Annual book of ASTM standards D1505*, Vol. 08.01.
- ASTM. (2006c). "Standard test method for determining apparent opening size of a geotextile." *Annual book of ASTM standards D4751*, Vol. 04.13.
- ASTM. (2006d). "Standard test method for determining apparent opening size of a geotextile." *Annual book of ASTM standards D5199*, Vol. 04.13.
- ASTM. (2006e). "Standard test method for determining the internal and interface shear resistance of geosynthetic clay liner by the direct shear method." *Annual book of ASTM standards D6243*, Vol. 04.13.
- ASTM. (2006f). "Standard test method for determining tensile properties of nonreinforced polyethylene and nonreinforced flexible polypropylene geomembranes." *Annual book of ASTM standards D6693*, Vol. 04.13.
- ASTM. (2006g). "Standard test method for evaluation of stress crack resistance of polyolefin geomembranes using notched constant tensile load test." *Annual book of ASTM standards D5397*, Vol. 04.13.
- ASTM. (2006h). "Standard test method for flow rates of thermoplastics by extrusion plastometer." *Annual book of ASTM standards D1238*, Vol. 08.01.
- ASTM. (2006i). "Standard test method for grab breaking load and elongation of geotextiles." *Annual book of ASTM standards D4632*, Vol. 04.13.
- ASTM. (2006j). "Standard test method for laboratory compaction characteristics of soil using standard effort [12,400 ft-lbf/ft³ (600 kN-m/m³)]." *Annual book of ASTM standards D698*, Vol. 04.08.
- ASTM. (2006k). "Standard test method for measurement of hydraulic conductivity of saturated porous material using a flexible wall permeameter." *Annual book of ASTM standards D5084*, Vol. 04.08.
- ASTM. (2006l). "Standard test method for measuring mass per unit area of geosynthetic liners." *Annual book of ASTM standards D5993*, Vol. 04.13.
- ASTM. (2006m). "Standard test method for measuring mass per unit area of geotextiles." *Annual book of ASTM standards D5261*, Vol. 04.13.
- ASTM. (2006n). "Standard test method for melting and crystallization temperatures by thermal analysis." *Annual book of ASTM standards E794*, Vol. 14.02.
- ASTM. (2006o). "Standard test method for oxidative-induction time of polyolefin geosynthetics by high-pressure differential scanning calorimetry." *Annual book of ASTM standards D5885*, Vol. 04.13.
- ASTM. (2006p). "Standard test method for oxidative-induction time of polyolefins by differential scanning calorimetry." *Annual book of ASTM standards D3895*, Vol. 08.02.
- ASTM. (2006q). "Standard test method for particle-size analysis distribution (gradation) of soils using sieve analysis." *Annual book of ASTM standards D6913*, Vol. 04.09.
- ASTM. (2006r). "Standard test methods for water permeability of geotextiles by permittivity." *Annual book of ASTM standards D4491*, Vol. 04.13.
- Barroso, M., Touze-Foltz, N., von Maubeuge, K., and Pierson, P. (2006). "Laboratory investigation of flow rate through composite liners consisting of a geomembrane, a GCL and a soil liner." *Geotext. Geomembr.*, 24(3), 139–155.
- Beigel, C., Barriuso, E., and Calvet, R. (1998). "Sorption of low levels of

- nonionic and anionic surfactants on soil: Effects on sorption of triticonazole fungicide." *Pestic. Sci.*, 54(1), 52–60.
- Billingham, N. C. (1990). "Physical phenomena in the oxidation and stabilization of polymers." *Oxidation inhibition in organic materials*, J. Pospisil and P. P. Klemchuk, eds., Vol. II, CRC Press, Boca Raton, Fla.
- Bouazza, A., and Vangpaisal, T. (2006). "Laboratory investigation of gas leakage rate through a GM/GCL composite liner due to a circular defect in the geomembrane." *Geotext. Geomembr.*, 24(2), 110–115.
- Brachman, R. W. I., and Gudina, S. (2008). "GM strains and wrinkle deformations in a GM/GCL composite liner." *Geotext. Geomembr.*, (In press).
- Calvert, P. D., and Billingham, N. C. (1979). "Loss of additives from polymers: A theoretical model." *J. Appl. Polym. Sci.*, 24, 357–370.
- Dickinson, S., and Brachman, R. W. I. (2006). "Deformations of a geosynthetic clay liner beneath a geomembrane wrinkle and coarse gravel." *Geotext. Geomembr.*, 24(5), 285–298.
- Grassie, N., and Scott, G. (1985). *Polymer degradation and stabilization*, Cambridge Univ. Press, New York.
- Gulec, S. B., Edil, T. B., and Benson, C. H. (2004). "Effect of acidic mine drainage on the polymer properties of an HDPE geomembrane." *Geosynthet. Int.*, 11(2), 60–72.
- Haider, N., and Karlsson, S. (1999). "Migration and release profile of chimassorb 994 from low-density polyethylene film (LDPE) in simulated landfills." *Polym. Degrad. Stab.*, 64, 321–328.
- Hrapovic, L. (2001). "Laboratory study of intrinsic degradation of organic pollutants in compacted clayey soil." Ph.D. thesis, Dept. of Civil and Environmental Engineering, Univ. Western Ontario, London, Ontario, Canada.
- Hsuan, Y. G., and Guan, Z. (1998). "Antioxidant depletion during thermal oxidation of high density polyethylene geomembrane." *Proc., Sixth Int. Conf. Geosynthetics*, Industrial Fabrics Association Int., St. Paul, Minn., 375–380.
- Hsuan, Y. G., and Koerner, R. M. (1995). "Long term durability of HDPE geomembrane: Part I—Depletion of antioxidant." *GRI Rep.* 16.
- Hsuan, Y. G., and Koerner, R. M. (1998). "Antioxidant depletion lifetime in high density polyethylene geomembranes." *J. Geotech. Geoenviron. Eng.*, 124(6), 532–541.
- Islam, M. Z., and Rowe, R. K. (2007). "Leachate composition and antioxidant depletion from HDPE geomembranes." *Proc., Geosynthetics 2007*, CD-ROM.
- Karlsson, K., Smith, G. D., and Gedde, U. W. (1992). "Molecular structure, morphology, and antioxidant consumption in medium density polyethylene pipes in hot-water applications." *Polym. Eng. Sci.*, 32(10), 649–657.
- Koerner, G. R., and Koerner, R. M. (2006). "Long term temperature monitoring of geomembranes at dry and wet landfills." *Geotext. Geomembr.*, 24(1), 72–77.
- Koerner, R. M., Lord, A. E., and Hsuan, Y. H. (1992). "Arrhenius modelling to predict geosynthetics degradation." *Geotext. Geomembr.*, 11, 151–183.
- Koerner, R. M., Wilson-Fahmy, R. F., and Narejo, D. (1996). "Puncture protection of geomembranes. Part III: Examples." *Geosynthet. Int.*, 3(5), 655–675.
- Lange, K., Rowe, R. K., and Jamieson, H. J. (2005). "Attenuation of heavy metals by geosynthetic clay liners." *Proc., Sessions of the Geo-Frontiers 2005 Congress* (CD-ROM), R. M. Koerner, G. R. Koerner, Y. G. Hsuan, and M. V. Ashley, eds.
- Moisan, J. Y. (1980). "Diffusion des additifs du polyethylene. I. Influence de la nature du diffusant." *Eur. Polym. J.*, 16, 979–987.
- Möller, K., and 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 the diffusion coefficient." *J. Appl. Polym. Sci.*, 51, 895–903.
- Möller, K., and 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." *J. Appl. Polym. Sci.*, 61, 1149–1162.
- Müller, W. W. (2007). *HDPE geomembranes in geotechnics*, Springer Verlag, Heidelberg, Germany.
- Müller, W. W., and Jakob, I. (2003). "Oxidative resistance of high-density polyethylene geomembranes." *Polym. Degrad. Stab.*, 79, 161–172.
- Osawa, Z., and Saito, T. (1978). "The effects of transition metal compounds on the thermal oxidative degradation of polypropylene in solution." *Stabilization and degradation of polymers. Advances in chemistry*, Series 169, American Chemical Society, Washington, D.C., 2897–2907.
- Qian, X., Koerner, R. M., and Gray, D. H. (2002). *Geotechnical aspects of landfill design and construction*, Prentice-Hall, Upper Saddle River, N.J.
- Rimal, S., Rowe, R. K., and Hansen, S. (2004). "Durability of geomembrane exposed to jet fuel A-1." *Proc., 57th Canadian Geotechnical Conf.*, Section 5D, 13–19.
- Roe, R. R., Bair, H. E., and Gieniewski, C. (1974). "Solubility and diffusion coefficient of antioxidants in polyethylene." *J. Appl. Polym. Sci.*, 18, 843–856.
- Rogers, C. E. (1985). "Chapter 2: Permeation of gases and vapors in polymers." *Polymer permeability*, J. Comyn, ed., Elsevier Applied Science Publishers, London, U.K., 11–73.
- Rowe, R. K. (2005). "Long-term performance of contaminant barrier systems." *Geotechnique*, 55(9), 631–678.
- Rowe, R. K., and Booker, J. R. (2004). POLLUTE, v.7—1-D pollutant migration through a nonhomogenous soil, ©1983, 1994, 1997, 1999, 2004, distributed by GAEA Technologies Ltd., <www.gaea.ca>.
- Rowe, R. K., Islam, M. Z., and Hsuan, Y. G. (2008). "Leachate chemical composition effects on OIT depletion in HDPE geomembranes." *Geosynthet. Int.*, 15(2), 136–151.
- Rowe, R. K., Quigley, R. M., Brachman, R. W. I., and Booker, J. R. (2004). *Barrier systems for waste disposal facilities*, 2nd Ed., Spon Press, London.
- Rowe, R. K., and Rimal, S. (2008). "Depletion of antioxidants from an HDPE geomembrane in a composite liner." *J. Geotech. Geoenviron. Eng.*, 134(1), 68–78.
- Sangam, H. P. (2001). "Performance of HDPE geomembrane Liners in landfill applications." Ph.D. thesis, Dept. of Civil and Environmental Engineering, Univ. of Western Ontario, Ontario, Canada.
- Sangam, H. P., and Rowe, R. K. (2002). "Effects of exposure conditions on the depletion of antioxidants from high-density polyethylene (HDPE) geomembranes." *Can. Geotech. J.*, 39, 1221–1230.
- Smith, G. D., Karlsson, K., and Gedde, U. W. (1992). "Modeling of antioxidant loss from polyolefins in hot-water applications. I: Model and application to medium density polyethylene pipes." *Polym. Eng. Sci.*, 32(10), 658–667.
- Thomas, R. W., and Ancelet, C. R. (1993). "The effect of temperature, pressure and oven ageing on the high-pressure oxidative induction time of different types of stabilizers." *Proc., Geosynthetics'93*, 915–924.
- Tognon, A. R. M., Rowe, R. K., and Brachman, R. W. I. (1999). "Evaluation of side wall friction for a buried pipe testing facility." *Geotext. Geomembr.*, 17(4), 193–212.
- Touze-Foltz, N., Duquennoi, C., and Gaget, E. (2006). "Hydraulic and mechanical behavior of GCLs in contact with leachate as part of a composite liner." *Geotext. Geomembr.*, 24(3), 188–197.
- Viebke, J., Elble, E., Ifwarson, M., and Gedde, U. W. (1994). "Degradation of unstabilized medium-density polyethylene pipes in hot-water applications." *Polym. Eng. Sci.*, 34(17), 1354–1361.
- Viebke, J., and Gedde, U. W. (1997). "Antioxidant diffusion in polyethylene hot-water pipes." *Polym. Eng. Sci.*, 37(5), 896–911.
- Wisse, J. D. M., Broos, C. J. M., and Boels, W. H. (1990). "Evaluation of the life expectancy of polypropylene geotextiles used in bottom protection structures around the Ooster Schelde storm surge barrier: A case study." *In Geomembranes and Related Products, Proc., 4th Int. Conf. on Geotextiles*, Vol. 2, The Hague, The Netherlands, 697–702.