

Antioxidant Depletion from a High Density Polyethylene Geomembrane under Simulated Landfill Conditions

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Abstract: Accelerated aging tests to evaluate the depletion of antioxidants from a high density polyethylene geomembrane are described. The effects of temperature, high pressure, and continuous leachate circulation on the aging of geomembranes in composite liner systems are examined. The antioxidant depletion rates (0.05, 0.19, and 0.41 month⁻¹ at 55, 70, and 85°C, respectively) obtained for the simulated landfill liner at 250 kPa vertical pressure are consistently lower than that obtained from traditional leachate immersion tests on the same geomembrane (0.12, 0.39, and 1.1 month⁻¹ at 55, 70, and 85°C). This difference leads to a substantial increase in antioxidant depletion times at a typical landfill liner temperature (35°C) with 40 years predicted based on the data from the landfill liner simulators tests, compared to 15 years predicted for the same geomembrane based on leachate immersion tests. In these tests, the crystallinity and tensile yield strain of the geomembrane increased in the early stages of aging and then remained relatively constant over the testing period. There was no significant change in other geomembrane properties within the testing period.

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Introduction

A modern municipal solid waste (MSW) landfill basal liner system typically consists of, from top to bottom: a granular leachate drainage/collection layer, a needle-punched nonwoven geotextile (GT) protection layer, and a geosynthetic composite liner, typically comprising a 1.5- or 2.0-mm-thick geomembrane and either a geosynthetic clay liner (GCL) or compacted clay liner or both. Because of their excellent resistance to advective flow and diffusive migration of inorganic contaminants, high density polyethylene (HDPE) geomembranes are extensively used as part of a composite liner in modern landfills (Rowe et al. 2004; Rowe et al. 2007; Bouazza et al. 2008; Brachman and Gudina 2008a,b; Saidi et al. 2008; Rowe et al. 2009). Although, the long-term performance of geomembrane liners under field conditions is unknown, the potentially contaminating lifespan of the landfills is likely to be centuries (Rowe et al. 2004). The geomembrane should per-

form adequately as an effective hydraulic and diffusive barrier throughout the potentially contaminating lifespan of the landfill. Some field investigations (Schmidt et al. 1984; Brady et al. 1994; Rollin et al. 1994; Maisonneuve et al. 1997; Rowe et al. 2003) provide evidence that the HDPE geomembrane may experience aging or degradation with time.

HDPE geomembranes may undergo degradation due to oxidation, extraction, ultraviolet degradation, and thermal degradation. Among these, oxidation of the polymer is considered to be the most significant degradation mechanism (Hsuan and Koerner 1995). With the progression of oxidation, the physical and mechanical properties of the geomembrane decrease leading eventually to the failure of the geomembrane. To limit the oxidation of polyethylene, suitable stabilizers (antioxidants) are added to the resin used to manufacture the geomembrane. The most common types of antioxidants added to HDPE geomembranes along with their effective temperature ranges have been described by Fay and King (1994) and Hsuan and Koerner (1998). Viebke et al. (1994) and Hsuan and Koerner (1998) described the oxidative degradation as a three-stage process. Stage I involves the depletion of antioxidants which is caused by the chemical reactions of antioxidants with oxygen, free radicals or hydroperoxide and/or physical loss by diffusion, evaporation, extraction, or washing out (Gedde et al. 1994; Hsuan and Koerner 1998; Haider and Karlsson 2002; Sangam and Rowe 2002; Dopico Garcia et al. 2004). During Stage I, the engineering properties of the geomembrane do not change significantly. Stage II is an induction time to the onset of the degradation and begins after the antioxidants are depleted. The end of Stage II corresponds to the time when oxidation causes the first measurable changes in the geomembrane. In Stage III, oxidation causes significant changes to the physical and mechanical properties which will eventually lead to geomembrane failure. Failure in this context refers to a decrease in an engineering property (e.g., stress-crack resistance, tensile break stress, and

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tensile break strain) to a specified value. The value defining the end of Stage III is somewhat subjective and engineers may select different definitions depending on circumstances. The two most commonly used values correspond to 50% of the initial property or the specified property value (the latter is fairer for products whose initial value of a property, such as stress-crack resistance, significantly exceeds the minimum specified value). The service life of the HDPE geomembrane is taken as the sum of the duration of the above three stages.

Because of the long time required to obtain results from actual field conditions, laboratory accelerated aging tests are conducted to evaluate the components of geomembrane service life. Most commonly, immersion tests have been used to evaluate the antioxidant depletion (Stage I) for HDPE geomembranes (e.g., see Hsuan and Koerner 1998; Sangam and Rowe 2002; Muller and Jacob 2003; Gulec et al. 2004; Rimal et al. 2004; Jeon et al. 2008; Rowe and Rimal 2008b; Rowe et al. 2008; Rimal and Rowe 2009a,b). Immersion tests are conducted by incubating the geomembrane in the medium of interest, for example, air, water, leachate, acid mine drainage, or jet fuel. Antioxidant depletion times predicted from immersion tests are expected to underestimate the actual depletion times relative to most field applications since both sides of the geomembrane are exposed to leachate. The actual antioxidant depletion time will likely be longer in a landfill because, in areas where there are no holes in the geomembrane, only one side of the geomembrane will be exposed to the landfill leachate. However, there are only three research studies in the literature (Hsuan and Koerner 1998; Rowe and Rimal 2008a,b) that have attempted to investigate the aging of the geomembrane under simulated liner conditions as discussed below.

Hsuan and Koerner (1998) conducted accelerated aging tests using a 1.5 mm HDPE geomembrane at four elevated temperatures (55, 65, 75, and 85°C) under 260 kPa vertical pressure. There was a 100-mm-thick water saturated sand layer above the geomembrane and the geomembrane rested on dry sand. Antioxidant life time (Stage I) was predicted to be 200 to 215 years at 20°C in this study. No change in other geomembrane properties [density, melt index (MI), or tensile properties] was evident within the 24-month aging period. It should be noted that this case is more applicable to a water reservoir application in an arid area (where there is water above but dry sand below the geomembrane) than to a landfill where there will be a near-saturated clay liner below the geomembrane and landfill leachate above it.

Rowe and Rimal (2008b) examined the depletion of antioxidants from a 1.5-mm HDPE geomembrane at 26, 55, 70, and 85°C for a simulated composite liner. The internal diameter and height of the testing apparatus were approximately 150 and 170 mm, respectively. The composite liner consisted of (from the top down): a gravel (19 mm nominal) layer, a GT protection layer (exposed to synthetic MSW landfill leachate), a 1.5-mm HDPE geomembrane, and a hydrated GCL over a moist sand layer. They predicted the antioxidant depletion time to be about 135 years at 20°C for the specific geomembrane examined. The tensile properties and MI did not show any significant change within the testing period of 35 months.

For comparison with the behavior using a traditional GT protection layer as used by Rowe and Rimal (2008b), Rowe and Rimal (2008a) examined the depletion of antioxidants for two different protection layers: (1) a 15-mm-thick sand layer above the GT and (2) a saturated GCL above the GT. All other variables (temperature, size of apparatus, leachate type, gravel type, etc.) were the same as before. The antioxidant depletion times were calculated to be 180, and 230 years, respectively, for the sand and

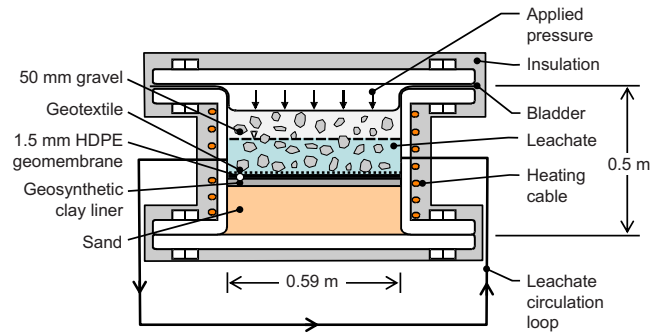


Fig. 1. Cross section through GLLS

GCL protection layers at 20°C as compared to 135 years for the conventional GT protection layer. These results suggest that the additional sand or GCL protection layer may be beneficial to the long-term performance of HDPE geomembranes. The GCL performed the best because it attenuated the leachate constituents (trace metals and surfactant) from coming into direct contact with the geomembrane. Both modified protection layers decreased the potential for the outward diffusive flux of antioxidant from the geomembrane.

The investigations noted above all have limitations with respect to simulating field conditions in a MSW landfill. For example, Hsuan and Koerner (1998) examined a geomembrane alone (i.e., not a composite liner) in contact with water on one side (not leachate). Rowe and Rimal (2008a,b) simulated the full liner system but did not apply stress to the geomembrane. Although the leachate used by Rowe and Rimal (2008a,b) was replaced every two weeks, there was no circulation of leachate within the 2-week replacement period.

Recently, new laboratory apparatus and experimental procedures have been developed to simulate the chemical, temperature, and physical exposure conditions that are expected for a MSW landfill basal liner system in the field (Brachman et al. 2008). The objective of this paper is, for the first time, to investigate the depletion of antioxidants under simulated landfill conditions, involving flowing synthetic leachate above the protection layer and applied stress similar to what might be expected in the field.

Experimental Investigation

GLLS

Accelerated aging tests were conducted using a specially designed geosynthetic liner longevity simulator (GLLS). Fig. 1 shows a vertical cross section through the GLLS. The GLLS is a cylindrical steel pressure vessel having an internal diameter of 590 mm and a height of 500 mm. The tests reported herein were conducted with a 250-kPa vertical pressure (equivalent to approximately 20 m of waste) applied by inflating a rubber bladder from the top with compressed air. To limit the boundary friction on the side wall of the GLLS, a friction treatment comprised of two thin (0.1 mm) polyethylene sheets lubricated with high-temperature bearing grease. With this treatment, the interface friction angle on the sides of the GLLS is less than 5° (Tognon et al. 1999) and results in more than 95% of the applied vertical pressure acting on the geomembrane (Brachman and Gudina 2002).

Tests were conducted at three elevated temperatures by wrapping heating cables around the outer circumference of the cylin-

Table 1. Initial Properties of the Geomembrane Examined

Properties	Method	Unit	Value mean \pm standard deviation
Nominal thickness	(ASTM 2008h)	mm	1.5
Standard oxidative induction time (Std-OIT)	(ASTM 2008j)	min	115 \pm 1.5
High-pressure oxidative induction time (HP-OIT)	(ASTM 2008k)	min	241 \pm 13
Crystallinity	(ASTM 2008i)	%	47.6 \pm 1.4
MI (21.6 kg/190°C)	(ASTM 2008a)	g/10 min	14.3 \pm 0.8
Density	(ASTM 2008b)	g/mL	0.947
Single point stress-crack resistance	(ASTM 2008d)	h	1432 \pm 186
Tensile properties (machine direction)	(ASTM 2008c)		
Strength at yield		kN/m	26.7 \pm 0.86
Strength at break		kN/m	46.0 \pm 5.3
Strain at yield		%	23.9 \pm 1.7
Strain at break		%	825 \pm 81
Tensile properties (cross-machine direction)	(ASTM 2008c)		
Strength at yield		kN/m	29.0 \pm 0.48
Strength at break		kN/m	43.7 \pm 6.1
Strain at yield		%	18.5 \pm 0.40
Strain at break		%	830 \pm 95

drical portion of the GLLS. Based on prototype experiments, the type and length of the heating cable as well as the insulation systems were selected to maintain set point temperatures at the geomembrane of 55, 70, and 85°C to within $\pm 1^\circ\text{C}$ (Brachman et al. 2008).

Simulated Composite Liner

The composite liner tested was comprised of (from top down): a 150-mm-thick coarse gravel layer, a GT protection layer, a virgin 1.5-mm-thick HDPE geomembrane, and a GCL overlaying a 150-mm-thick compacted sand foundation layer (Fig. 1). The gravel was a nominal 50-mm crushed limestone typically used in landfill collection layers in Ontario, Canada and was placed uncompacted at a bulk density of 1.5 g/cm³. The GT was nonwoven needle-punched with a thickness of 4.1 mm [(ASTM 2008h)], a mass per unit area of 580 g/m² [(ASTM 2008g)], and grab tensile strength and elongation of 1690 N and 45–105%, respectively [(ASTM 2008e)]. The HDPE geomembrane was manufactured by Solmax International, Varennes, Quebec. Table 1 presents the initial properties of the geomembrane. The GCL had a slit-film woven carrier and a nonwoven cover GTs and was hydrated under 20-kPa pressure for 15 days before placing it in the GLLS. The mass per unit area of the GCL [(ASTM 2008f)], carrier GT [(ASTM 2008g)], and cover GT [(ASTM 2008g)] were 3.66 kg/m², 105, and 200 g/m², respectively. The average thickness of the hydrated GCL was about 9–12 mm. A bentonite seal was placed at the outer edge of the circular geomembrane in the GLLS to prevent leachate from leaking below the geomembrane. Poorly graded medium sand having specific gravity of 2.67 was used as the foundation layer. The sand was compacted at 7.5% water content (field capacity for this sand) in six sublayers using a flat-bottom rammer to a dry density of 1.65 g/cm³.

Synthetic Leachate

The synthetic leachate used in this study was produced by mixing trace metals, surfactant, and reducing agent in distilled water as detailed in Table 2. This leachate was selected based on a study

by Rowe et al. (2008) which showed that it contained the components of MSW leachate (i.e., trace metals and surfactant) that affect aging of HDPE geomembranes.

To simulate the possible scenario in a landfill where leachate is continuously collected through a leachate collection system, the leachate in this study was completely replaced with a newly prepared leachate every two weeks. The 2-week leachate renewal frequency adopted in this paper was based on a study that examined different leachate renewal frequencies on antioxidant depletion (Rowe et al. 2008). The leachate in the GLLS was continuously mixed between the 2-week refreshment periods using an external recirculation pump (Fig. 1). Several mixing trials were conducted by changing port configuration and circulation flow rate to ensure a system that provided uniform mixing and

Table 2. Composition of Synthetic Leachate

Component	Concentration (mg/L) (except where noted)
Trace metal solution ^{a,b} (mL/L)	1
Surfactant, Igepal CA720 (mL/L)	5
E_h (adjusted by Na ₂ S·9H ₂ O) (mV)	~–120
Composition of trace metal solution	
FeSO ₄ ·7H ₂ O	2,000
H ₃ BO ₃	50
ZnSO ₄ ·7H ₂ O	50
CuSO ₄ ·5H ₂ O	40
MnSO ₄ ·H ₂ O	500
(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	50
Al ₂ (SO ₄) ₃ ·16H ₂ O	30
CoSO ₄ ·7H ₂ O	150
NiSO ₄ ·6H ₂ O	500
H ₂ SO ₄ (mL/L)	1

^aComposition of trace metal solution.

^bModified from Hrapovic (2001), 1 mL of trace metal solution was added in 1 L of synthetic leachate.

avoided areas of stagnant flow of leachate within the GLLS (Brachman et al. 2008). The results of the trial mixing showed that a flow rate of 225 mL/min in the circulation loop produced the best mixing result and this rate was adopted in this study.

Test Methods

The level of antioxidant present in the geomembrane is normally evaluated in terms of the oxidative induction time (OIT) of the geomembrane (Hsuan and Koerner 1995, 1998; Surmann et al. 1995; Maisonneuve et al. 1997; Sangam and Rowe 2002; Muller and Jacob 2003; Gulec et al. 2004; Rimal et al. 2004; Rowe and Rimal 2008a,b; Rowe et al. 2008, 2010). The standard OIT (Std-OIT) tests [(ASTM 2008j)] were conducted at 200°C at 35 kPa using a TA Instruments Q-100 series differential scanning calorimeter (DSC) equipped with an autosampler. The high-pressure OIT (HP-OIT) tests [(ASTM 2008k)] were conducted at 150°C and 3,500 kPa using a TA Instruments 2910 DSC.

The degree of crystallinity of the geomembranes was measured in accordance with ASTM E794 (ASTM 2008i) using the same DSC that was used to measure Std-OIT. The percent crystallinity was calculated by dividing the measured heat of fusion of the geomembrane by that of the heat of fusion of 100% crystalline HDPE sample [i.e., 293 J/g (Brandrup et al. 1999)].

The MI test is a qualitative test for evaluating the molecular weight of different polymers and can be used to monitor the changes in molecular weight due to oxidative degradation (Hsuan and Koerner 1998). Oxidation in the polymer can cause either cross-linking or chain scission reactions in the polymer (Hsuan and Koerner 1998; Peacock 2000). Generally, a cross-linking reaction results in a decrease in MI values whereas a chain scission reaction causes an increase in MI values. A Dynisco Melt Indexer (model D4002) was used to measure the MI of the geomembrane in accordance with ASTM D1238 (ASTM 2008a).

Tensile tests were performed in accordance with ASTM D6693 (ASTM 2008c) (Type IV) using dumbbell-shaped specimens in a Zwick Roell tensile testing machine (model Z20) at a strain rate of 50 mm/min. Ten replicate samples were tested at any sampling event: five along machine direction and five along cross-machine direction, and the average in each direction was reported.

Results and Discussion

Std-OIT versus HP-OIT Tests for the Evaluation of Antioxidant Depletion

There is a possibility that the temperature used in the Std-OIT test (200°C) could volatilize some antioxidants (e.g., hindered amines and thiosynergists) used in the formulation of some geomembranes. To assess whether this was a problem for the geomembrane used in this study, the results of HP-OIT tests were compared with the Std-OIT test (Fig. 2). The linear relationship between HP-OIT and Std-OIT implies that there was no thiosynergists or hindered amines in the geomembrane examined (Hsuan and Koerner 1998), and that either the Std-OIT or the HP-OIT test could be used to evaluate the depletion of antioxidants for this geomembrane.

The types of antioxidants used in the formulation of the geomembrane were not provided by the manufacturer. To provide direct evidence in support of the inference noted above, a virgin geomembrane sample was sent to Ciba Testing Services, Tarrytown, N.Y. for antioxidant analysis. The results indicated the pres-

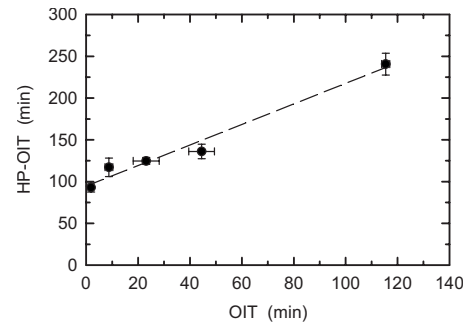


Fig. 2. HP-OIT and Std-OIT at 85°C

ence of the following antioxidants in the geomembrane: hindered phenols (Irganox 1010 and Irganox 1076) and phosphites [Irgafos 168 (PO₃) and Irgafos 168 (PO₄)] (Islam 2009). The maximum effective temperature of these antioxidants is 300°C. No hindered amine light stabilizer (HALS) or thiosynergists (whose maximum effective temperature is in the range of 150–200°C) were identified in the geomembrane. Consequently, the results described in the following sections are based on the Std-OIT tests.

Spatial Variation of OIT in the GLLS Test

The physical appearances of the HDPE geomembrane before and after performing a test are shown in Figs. 3 and 4, respectively. Due to the applied vertical stress and the testing temperature, numerous permanent deformations were evident in all geomembrane samples after the completion of a test (Fig. 4). Consequently, samples for the OIT tests were taken from several locations beneath and in between gravel contacts to evaluate the variability of OIT between these locations. Fig. 4 shows the OIT sampling locations for the 2-month GLLS test at 70°C. At each sampling location at least three replicate samples were tested and the average OIT values were plotted with respect to the distance from the GLLS' inner wall (Fig. 5). The average OIT values for between gravel contacts locations (65 ± 4.6 min for the 2-month GLLS tests at 70°C) were lower than for beneath gravel contact locations (69 ± 7.4 min for the 2-month GLLS tests at 70°C). This difference may be because there was less flow of leachate beneath the gravel contacts. However given the standard deviation of the results, one cannot conclude that the difference in the

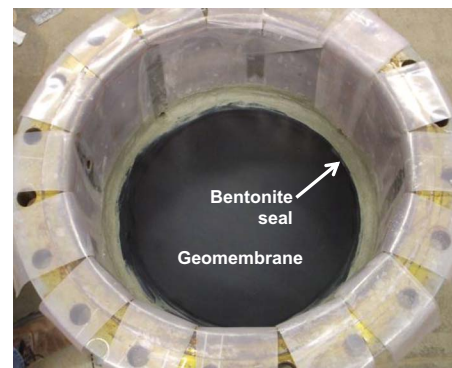


Fig. 3. Photograph showing the inside of a GLLS after placing the geomembrane. Bentonite paste was placed around the perimeter of the geomembrane to prevent leachate leakage.

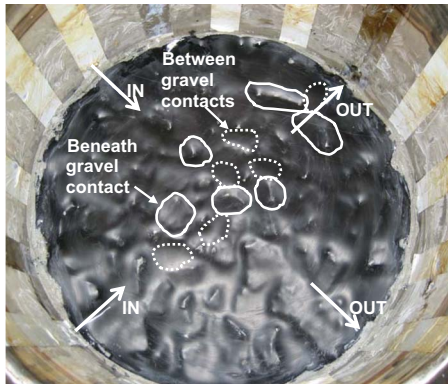


Fig. 4. Photograph of the 2-month GLLS test at 70°C showing OIT sampling locations circled as solid (for beneath gravel contact) and dotted lines (for between gravel contacts). Leachate inlet and outlet ports are shown by arrows.

average OIT values obtained for the beneath gravel contact and between gravel contacts locations is statistically significant.

Fig. 5 shows that there was no significant difference in OIT values from the center to the outer edge of the GLLS. Similar results were observed for all other GLLS tests (Islam 2009). Given that there was no apparent significant difference between the OIT values from beneath gravel contact and between gravel contacts, the OIT values reported in the rest of this paper are based on the average OIT values considering both.

Antioxidant Depletion at Elevated Temperatures

The OIT values decreased with time [Fig. 6(a)] with the rate of OIT depletion increasing with the increase of temperature as has been observed in other studies (Hsuan and Koerner 1995, 1998; Hsuan and Guan 1998; Sangam and Rowe 2002; Gulec et al. 2004; Rowe and Rimal 2008a,b; Rowe et al. 2008, 2010). The OIT values decreased to the residual value of about 1.5 min after about 7–8 months at 85°C. At 70°C OIT was approaching an equilibrium value at 21 months. At 55°C, the OIT values had not reached the residual value by the end of the reporting period (21 months), however sufficient data had been collected to allow an assessment of the rate of OIT depletion at each temperature as demonstrated below.

The depletion of OIT can be described by a first-order decay relationship (Hsuan and Koerner 1998), viz.:

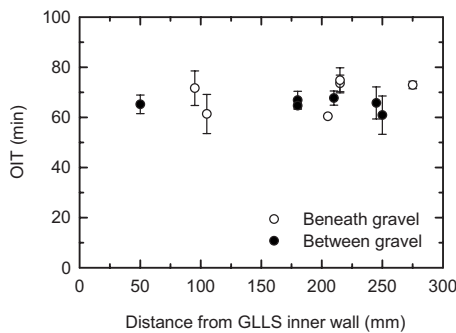


Fig. 5. Spatial variation of OIT after 2 months at 70°C. Error bars indicate standard deviation of test results at each location.

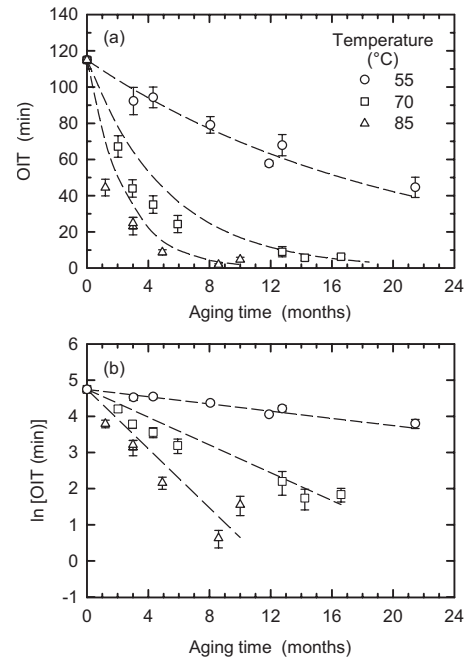


Fig. 6. Variation in (a) OIT; (b) $\ln[\text{OIT}]$ with time at 85, 70, and 55°C

$$\text{OIT}_t = \text{OIT}_o e^{-st} \quad (1)$$

Taking the natural logarithm on both sides, this becomes

$$\ln(\text{OIT}_t) = -st + \ln(\text{OIT}_o) \quad (2)$$

where $\text{OIT}_t = \text{OIT}$ at time t (min); $\text{OIT}_o = \text{initial OIT}$ (min); $s = \text{antioxidant depletion rate}$ (months^{-1}); and $t = \text{exposure time}$ (months). The variation in $\ln(\text{OIT})$ with time at 55, 70, and 85°C is shown in Fig. 6(b). The slope of the linear regression lines gives the antioxidant depletion rate at each temperature (Table 3). It should be noted that the depletion of antioxidants from an HDPE geomembrane depends on various factors, for example, type of antioxidants present, total and relative amounts of antioxidants, type of polymer resin etc. The first-order approximation [linear when the logarithm of OIT is plotted as shown in Fig. 6(b) and Fig. 7] is consistent with the approach used by other researchers in analyzing OIT results (Hsuan and Koerner 1995, 1998; Sangam and Rowe 2002; Gulec et al. 2004; Rowe and Rimal 2008a,b). Rimal and Rowe (2009a,b) used the diffusion theory to model the depletion of OIT, and they obtained a better fit to the early time data than was obtained by a first-order approximation. They confirmed that the poor fit of the first-order relationship to the OIT data during the initial stage of aging is not because of simple experimental scatter but rather because of real physical behavior associated with the depletion of antioxidants due to diffusion. However, they also demonstrated that the outward diffu-

Table 3. Comparison of Antioxidant Depletion Rates between GLLS and Leachate Immersed Geomembranes (Rounded to Two Significant Digits)

Temperature (°C)	Antioxidant depletion rate (month^{-1})	
	GLLS	Leachate immersed ^a
85	0.41	1.1
70	0.19	0.39
55	0.05	0.12

^aData from Rowe et al. (2010).

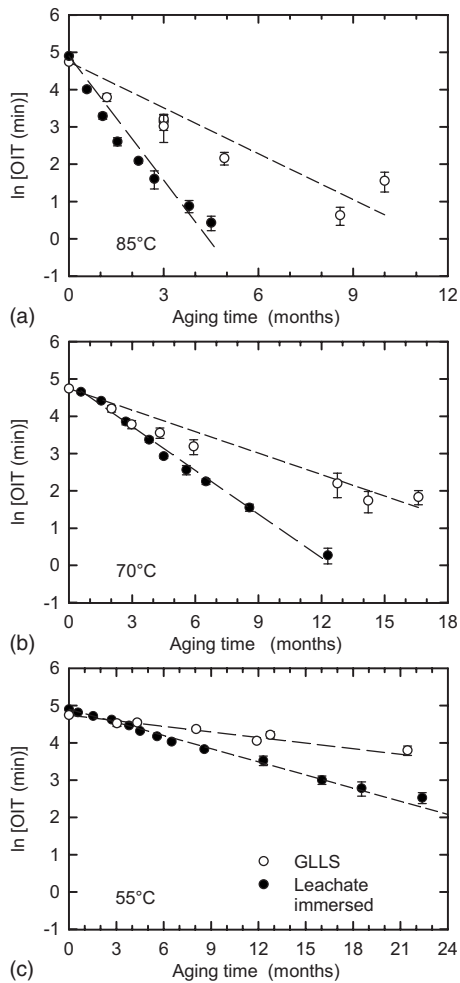


Fig. 7. Variation in $\ln[\text{OIT}]$ with time at (a) 85°C ; (b) 70°C ; and (c) 55°C for GLLS aged specimens and leachate immersed specimens of the same geomembrane. Leachate immersed data are from Rowe et al. (2010).

sion of antioxidants can be approximated by a linear relationship between $\ln(\text{OIT})$ and time, and therefore provided a theoretical basis for the widely adopted empirical approach which is used in the present paper. Because of the difference between the diffusion theory and the first-order approximation typically used, a first-order fit to early time data gives a conservative prediction of antioxidant depletion time.

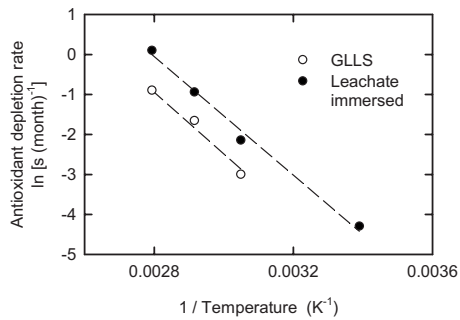
Comparison of OIT Depletion between GLLS, Leachate Immersion, and Other Composite Liner Tests in the Literature

The geomembrane used in the GLLS tests (current paper) was also used in the leachate immersion test described by Rowe et al. (2010). Fig. 7 compares the variation in OIT with time for the GLLS and leachate immersed geomembranes at 85°C . It should be noted that the initial OIT of the geomembrane was different owing to the 2.5 years difference in time between the start of the two different series of tests, during which the time of the OIT is depleted from 134 to 115 min at room temperature. Table 3 shows the antioxidant depletion rates for both the GLLS and leachate immersed geomembranes. Antioxidant depletion rates were consistently lower for the GLLS geomembrane compared to the leachate immersed geomembrane at all temperatures. For example, the antioxidant depletion rates for the GLLS and leachate immersed geomembranes were 0.41 and 1.1 month^{-1} , respectively, at 85°C . The lower antioxidant depletion in the GLLS geomembrane is considered to be due to the fact that (1) the geomembrane in the GLLS tests is only exposed to leachate on one side, whereas it is exposed to leachate on both sides in the immersion tests and (2) a build up of concentration of antioxidants in the upper GT protection layer and in the bottom GCL layer which reduces the concentration gradient and consequently the outward diffusive flux of antioxidants. The repeatability of the GLLS tests was checked by conducting a replicate test at 85°C (3-month test) and the OIT data are plotted in Fig. 7. There was statistically no significant difference at the 95% confidence level in the mean OIT values between the two 3-month GLLS tests suggesting that these tests are quite repeatable within the same experimental framework.

The antioxidant depletion rates observed in the present tests (e.g., 0.05 and 0.41 month^{-1} at 55 and 85°C , respectively; Table 3) were 2.3 and 2.9 times greater than those reported by Hsuan and Koerner (1998) (e.g., 0.022 and 0.14 month^{-1} at 55 and 85°C , respectively; Table 4) for comparable temperatures. Although different geomembranes were tested (the Std-OIT and HP-OIT were 81 and 210 min, respectively, for the geomembrane tested by Hsuan and Koerner (1998), and 115 and 241 min, respectively for the geomembrane in the present study), the difference in depletion rate is primarily attributed to the fact that the Hsuan and Koerner (1998) tests had water on one side of the geomembrane and dry sand on the other as compared to leachate on one side and saturated GCL on the other in the present tests. For comparison, in the immersion studies described by Sangam and Rowe (2002), the antioxidant depleted 3.2 and 2.3 times faster for a leachate immersed geomembrane than for a water

Table 4. Antioxidant Depletion Rates in the Literature for Different Geomembranes Used in Simulated Landfill Liners at Different Temperatures

Exposure condition and reference	Temperature ($^\circ\text{C}$)	Antioxidant depletion rate (month^{-1})
1.5-mm geomembrane with water saturated sand above and dry sand below with 260 kPa normal stress; initial standard-OIT=80.5 min and HP-OIT=210 min (Hsuan and Koerner 1998)	85	0.140
	75	0.080
	65	0.059
	55	0.022
1.5-mm geomembrane used in simulated composite liner with top face of the geomembrane exposed to synthetic MSW leachate and the bottom face exposed to water hydrated GCL; initial standard-OIT=135 min and HP-OIT=660 min (Rowe and Rimal 2008a)	85	0.275
	70	0.212
	55	0.054
	26	0.005



$$\ln(s) = \ln(A) - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \quad (4)$$

Fig. 8. Arrhenius plot of antioxidant depletion rate for the GLLS and synthetic leachate immersed geomembranes. Synthetic leachate immersed data are from Rowe et al. (2010).

immersed geomembrane at 55 and 85°C, respectively. Rowe et al. (2008) observed 3.5 times faster antioxidant depletion rate for a leachate immersed geomembrane than for a water immersed geomembrane at 85°C.

The liner configuration used in this study was most similar to the small scale simulated composite liner test conducted by Rowe and Rimal (2008b). The depletion rates in the present paper are different from those reported by Rowe and Rimal (2008b) (Tables 3 and 4). This is probably due to a combination of factors including (1) the continuous circulation of leachate in the current study and (2) the use of geomembranes with different initial properties and antioxidant packages in the two studies. With respect to the second point, the initial Std-OIT and HP-OIT of the geomembrane used in the current paper were 115 and 241 min, respectively, compared with 135 and 660 min, respectively, in the geomembrane used by Rowe and Rimal (2008b).

Arrhenius Modeling of Antioxidant Depletion Rate and Prediction of Antioxidant Depletion Time

The Arrhenius equation is widely used to provide an estimate of the antioxidant depletion rate at a given temperature, different to those used in a testing program and is generally expressed as follows (Hsuan and Koerner 1998):

$$s = Ae^{-[E_a/(RT)]} \quad (3)$$

Taking the natural logarithm on both sides gives

where s =antioxidant depletion rate (month^{-1}); E_a =activation energy ($\text{J}\cdot\text{mol}^{-1}$); R =universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$); T =absolute temperature (K); and A =constant often called a collision factor. In using the Arrhenius equation for the purpose of extrapolation, it is assumed that: (1) the antioxidant depletion rate s is highly dependent on temperature; (2) the value of the collision factor A does not change with temperature; and (3) the activation energy E_a remains constant over the temperature range of interest (Koerner et al. 1992).

Fig. 8 shows the Arrhenius plots of antioxidant depletion rates based on the data in Table 3. Table 5 shows the activation energy, deduced from the slope of the line (i.e., E_a/R), along with the best fit Arrhenius equation for the GLLS tests (this paper), and the immersion tests on same geomembrane (Rowe et al. 2010) along with the values obtained from composite liner tests reported by Rowe and Rimal (2008b) and Hsuan and Koerner (1998) on different geomembranes. It can be seen that the activation energy for the geomembrane used in the GLLS test is higher ($64 \text{ kJ}\cdot\text{mol}^{-1}$) compared to the activation energy for the same geomembrane immersed in leachate ($60.7 \text{ kJ}\cdot\text{mol}^{-1}$) which quantifies the significant effect of geomembrane exposure on geomembrane aging. The higher activation energy will contribute to the longer antioxidant depletion time as discussed below.

Based on the data from the GLLS and immersion tests (Table 5), the antioxidant depletion times (time to complete Stage I) were calculated at a representative landfill temperatures between 20 and 60°C using Eq. (1). The predicted antioxidant depletion times (Table 6) varied from 6 years (at 60°C) to 130 years (at 20°C) for the GLLS geomembrane. The depletion times are significantly greater for the GLLS than for leachate immersed geomembranes (e.g., 40 and 15 years, respectively, at 35°C).

The antioxidant depletion times for the GLLS geomembrane provide practical insight regarding Stage I of geomembrane service life of this geomembrane in a MSW landfill application. The total service life of HDPE geomembrane is expected to be considerably longer than that presented in Table 6 because of the additional time in Stages II (induction time) and III (time required for the degradation of engineering properties of interest).

Table 5. Arrhenius Equation and Activation Energy from the Current Study and the Literature

Exposure condition and reference	Arrhenius equation	Activation energy E_a ($\text{kJ}\cdot\text{mol}^{-1}$)
1.5-mm geomembrane used in simulated composite liner test by applying 250 kPa normal stress, top face of the geomembrane exposed to synthetic leachate and the bottom face of the geomembrane exposed to water hydrated GCL; Std-OIT=115 min and HP-OIT=241 min (current study)	$\ln(s)=20.63-7703/T \quad R^2=0.977$	64.0
1.5-mm geomembrane used in synthetic leachate immersion tests; Std-OIT=135 min and HP-OIT=244 min (Rowe et al. 2010)	$\ln(s)=20.37-7304/T \quad R^2=0.992$	60.7
1.5-mm geomembrane used in simulated composite liner test with no applied stress, top face of the geomembrane exposed to synthetic leachate and the bottom face exposed to water hydrated GCL; initial Std-OIT=135 min and HP-OIT=660 min (Rowe and Rimal 2008a)	$\ln(s)=20.06-7540/T \quad R^2=0.977$	62.7
1.5-mm geomembrane with water saturated sand above and dry sand below with 260 kPa normal stress; initial Std-OIT=80.5 min and HP-OIT=210 min (Hsuan and Koerner 1998)	$\ln(s)=17.05-6798/T$	56.0

Table 6. Predicted Antioxidant Depletion Times at Six Different Temperatures for the Simulated Composite Liner and Leachate Immersed Geomembranes

Temperature (°C)	Antioxidant depletion time (years)		Ratio between GLLS and leachate immersed antioxidant depletion time
	GLLS ^a	Leachate immersed ^b	
20	130	45	2.9
30	55	20	2.8
35	40	15	2.7
40	25	9	2.8
50	12	4	3.0
60	6	2	3.0

Note: Numbers greater than 20 years have been rounded to the nearest 5 years and those below 20 years to one significant figure.

^aThe calculation of the antioxidant depletion time was based on a decrease of antioxidant from initial OIT value of 115 min to a final residual OIT value of 0.5 min [used by Hsuan and Koerner (1998) for pure unstabilized HDPE geomembrane].

^bBased on Rowe et al. (2010).

Results on Crystallinity, MI, and Tensile Properties

Fig. 9 shows the variation in crystallinity, MI, and machine and cross-machine directions tensile properties with time at 85°C. The crystallinity of the geomembrane increased by about 20% after 1 month of aging and remained relatively constant over the testing period (8.5 months) at 85°C. A similar increase in crystallinity was observed for the leachate immersed geomembranes described by Rowe et al. (2008, 2010) as well as in the literature (Dörner and Lang 1998; Sangam 2001; Rowe and Rimal 2008b). The tensile yield strain increased by approximately 35%, however, no significant change in yield stress was observed [Figs. 9(b and c)]. In contrast to these results, both the yield stress and yield strain increased by approximately 10% for the same geomembrane when immersed in a leachate at 85°C (Rowe et al. 2010). It is not clear if this difference is due to the reduced exposure to leachate in the GLLS tests or to the effects of the gravel indentation producing permanent deformations in the geomembrane (e.g., see Fig. 4). The MI and the machine and cross-machine direction tensile break stresses and break strains did not show any significant change over the 8.5 months of aging time at any of the testing temperatures. The changes in crystallinity and tensile yield strain observed at 70 and 55°C followed the same trend described above but were lower than that observed at 85°C (Islam 2009).

Conclusions

Accelerated aging tests were conducted to evaluate the depletion of antioxidant from an HDPE geomembrane using a specially designed laboratory apparatus (GLLS) capable of examining the effects of temperature, high pressure, and continuous synthetic leachate circulation on the aging of geomembranes in composite liner systems. Tests were conducted under a 250 kPa vertical pressure at 55, 70, and 85°C. The simulated landfill liner consisted of (from the top down) a 150-mm-thick gravel layer, a GT protection layer, a 1.5-mm HDPE geomembrane with initial properties as given in Table 1, a GCL, and a 150-mm-thick sand foundation layer. From these tests the following is concluded:

1. The antioxidant depletion rate (0.05, 0.19, and 0.41 month⁻¹ at 55, 70, and 85°C, respectively) was consistently lower for

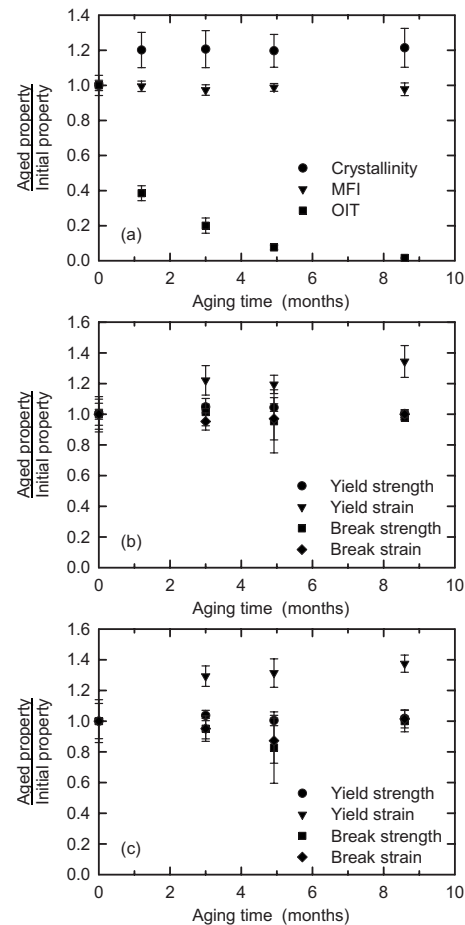


Fig. 9. Measurements of aged property normalized by initial property for: (a) OIT, melt flow index and crystallinity; (b) machine direction tensile properties; and (c) cross-machine direction tensile properties with time at 85°C

the simulated landfill liner tests than for more traditional leachate immersion tests for the same geomembrane (0.12, 0.39, and 1.1 month⁻¹ at 55, 70, and 85°C, respectively). Thus improved predictions of geomembrane service life will be obtained based on the data from studies conducted for simulated liner conditions.

2. Based on Arrhenius modeling, the estimated time for antioxidant depletion (i.e., time to complete Stage I of the geomembrane service life) in the landfill simulators ranged between 130 and 6 years for constant temperatures between 20 and 60°C.
3. For the same geomembrane, the antioxidant depletion times are substantially longer in the landfill simulators than immersed in the leachate with the projected depletion time, at 35°C, being 40 years based on the simulator tests compared to 15 years based on leachate immersion tests.
4. The crystallinity and tensile yield strain increased in the early stages of aging and then remained relatively constant over the testing period. There was no significant change in other geomembrane properties (MI and other tensile properties) within the testing period suggesting that the geomembrane had not reached the end of Stage II of the geomembrane service life in any of the tests over the testing period. The total service life of the geomembrane is expected to be substantially longer than the antioxidant life time (Stage I) esti-

mated in this paper because of the time required to complete Stages II and III of the service life.

This study has provided the closest simulation of geomembrane exposure conditions in a MSW landfill yet published, and as a consequence the estimated antioxidant depletion times are expected to provide the most realistic estimate of the likely depletion time of antioxidants in the field. Additional testing is required to allow similar estimates of Stages II and III of the service life. It is noted that the service life of a geomembrane will depend on the resin and antioxidant package used and may vary from one geomembrane to another.

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