

Depletion of Antioxidants from an HDPE Geomembrane in a Composite Liner

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Abstract: The results of two series of accelerated aging tests are reported. Both series of tests were conducted at temperatures of 85, 70, 55, and 26°C over a period of about 3 years. In the simulated liner series, the top of the geomembrane was covered with a geotextile (protection) layer that was exposed to simulated municipal solid waste (MSW) landfill leachate while the bottom of the geomembrane was in contact with a hydrated geosynthetic clay liner. In the immersion series, the geomembrane was immersed in the simulated MSW leachate, and hence, both sides were exposed to leachate. The results from oxidative induction time tests indicate that the antioxidant depletion is about 2.2–4.8 times faster for the leachate immersed geomembrane than for geomembrane in a composite liner. The higher rates are attributed to the higher extraction of antioxidants from two sides of the geomembrane immersed in leachate. The measured antioxidant depletion rates are extrapolated to a range of temperatures (0–60°C) using Arrhenius modeling. At a liner temperature of 35°C, the calculated time for the depletion of antioxidants is about 40 years for a geomembrane in a composite liner compared to 10 years if it is simply immersed in leachate. These tests suggest that to obtain realistic estimates of geomembrane service life one needs data from tests that simulate the expected field conditions and that prediction based on immersion tests may underestimate the service life.

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Introduction

Due to their ability to minimize advective flow and provide an excellent diffusive barrier to inorganic contaminants, high-density polyethylene (HDPE) geomembranes are extensively used as a part of composite base liner systems in modern landfills (Rowe 2005; Cartaud et al. 2005a,b; Barroso et al. 2006; Touze-Foltz et al. 2006). These liner systems often comprise (from top to bottom) a gravel leachate collection layer, a geotextile protection layer, a 1.5 or 2 mm thick HDPE geomembrane, and either a geosynthetic clay liner (GCL) or a compacted clay liner. HDPE geomembranes have been shown to have good chemical resistance to wide range of contaminants found in landfill leachate constituents (Tisinger et al. 1991; Eith and Koerner 1997; Koerner 1998; Rowe et al. 2004). The long-term behavior of geomembranes in landfill base liners is initially controlled by the rate of extraction of antioxidants. This process involves the dissolution or chemical reaction of antioxidants at the surface of the geomembrane and their diffusion from the core structure to the surface due to concentration gradient (Hsuan and Koerner 1998;

Sangam and Rowe 2002). The loss of antioxidants leaves the geomembrane vulnerable to the second principal degradation mechanism of oxidative degradation as described by Grassie and Scott (1985).

HDPE geomembrane degradation is envisaged as having three distinct stages (Viebke et al. 1994; Hsuan and Koerner 1998), antioxidant depletion (Stage I), induction time to the onset of polymer degradation (Stage II), and polymer degradation involving the decrease in a geomembrane property to an arbitrary level often taken to be 50% of the original value (Stage III). The sum of the three stages is regarded as the service life of geomembrane. The most reliable way of assessing the length of the three stages, and hence, the service life of the geomembrane would be to exhume samples from the field at different time intervals over the service life. However, this is not feasible due to the long time it would take to obtain useful results under field conditions. Consequently, laboratory-based accelerated aging tests are utilized to estimate the length of these stages with the emphasis to date being on Stage I (Hsuan and Koerner 1998; Sangam and Rowe 2002; Müller and Jacob 2003; Rimal et al. 2004; Gulec et al. 2004; Müller 2007). These previous studies have examined extraction of antioxidants from geomembrane immersed in air, water, leachate, and various hydrocarbons. Hsuan and Koerner (1998) also examined a case with water-saturated sand above and dry sand below the geomembrane. It has been shown that there can be a substantial difference in the projected time to depletion of antioxidants (Stage I) depending on the exposure conditions (Sangam and Rowe 2002; Rimal et al. 2004). However, to date there has been no examination of the depletion rate for a geomembrane in a simulated composite liner environment nor any comparison of this with that obtained from more conventional immersion tests. Thus, the objective of this paper is to provide results to address this issue.

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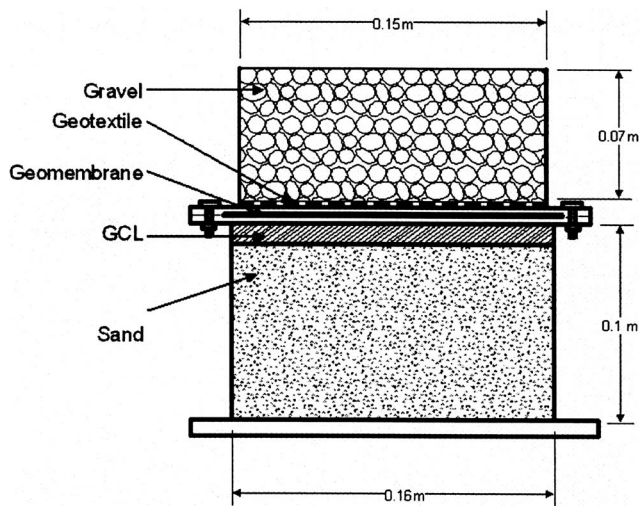


Fig. 1. Schematic of composite liner cell

Experimental Investigation

Materials

The simulated liner examined in these tests is shown schematically in Fig. 1. The components are described below from top down. The gravel (leachate “collection” layer) was 19 mm crushed, washed, limestone. The 2 mm thick [ASTM D5199 (ASTM 2006k)] geotextile protection layer had a mass per unit area of 270 g/m^2 [ASTM D5261 (ASTM 2006l)], a hydraulic conductivity of $3 \times 10^{-3} \text{ m/s}$ [ASTM D4491 (ASTM 2006f)], an apparent opening size of 0.180 mm [ASTM D4751 (ASTM 2006h)], a grab tensile strength of 975 N, and a grab elongation 50% [ASTM D4632 (ASTM 2006g)]. The smooth 1.5 mm thick HDPE geomembrane (GSE Linings Inc., Houston, Tex.) had the properties given in Table 1.

The GCL used in the composite liner cell was Bentofix Thermal Lock NWL (Terrafox Geosynthetics Inc., Toronto, Canada). This needlepunched GCL had a layer of granular sodium bentonite with mass per unit area of 3.66 kg/m^2 [minimum average roll value (MARV)], [ASTM D5993 (ASTM 2006q)] encapsulated between a scrim reinforced nonwoven carrier geotextile (mass per unit area of 200 g/m^2 MARV) and a virgin staple fiber nonwoven cover geotextile [mass per unit area of 200 g/m^2 MARV; ASTM D5261 (ASTM 2006l)]. The needlepunched fibers were thermally fused to the carrier geotextile to improve the reinforcing bond. It had a hydraulic conductivity of $5 \times 10^{-11} \text{ m/s}$ [ASTM D5084 (ASTM 2006j)], an internal shear strength of 24 kPa [ASTM D5321 (ASTM 2006m)], and a minimum bentonite swell index of 24 mL/2 g [ASTM D5890 (ASTM 2006p)]. The underlying foundation layer was poorly graded clean (washed) grade 24 Ottawa silica sand without contaminants such as dust, clay, or iron compounds. It had specific gravity of 2.65 and sieve testing for grain size distribution [ASTM D6913 (ASTM 2006r)] indicated mean grain size, D_{50} , of 0.5 mm with coefficient of uniformity C_u of 3 and coefficient of curvature C_c of 1.02. The Standard Proctor optimum moisture content was 13.7% at dry density of 1.6 g/cm^3 [ASTM D698 (ASTM 2006a)].

The synthetic leachate used in this study was based on

Table 1. Properties of the 1.5-mm-Thick HDPE Geomembrane Examined

Property	Method (ASTM)	Average	COV (%)
Density (g/cm^3)	D1505 ^a	0.944	2.43
Carbon black content (%)	D1603 ^b	2.43	—
OIT (min)	D3895 ^c	135	3.3
HP-OIT (min)	D5885 ^d	660	4.4
Crystallinity (%)	E794 ^e	49	6.1
MFI (g/10 min.)	D1238 ^f	0.553	0.4
Tensile properties (machine direction)	D6693 ^g		
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 ^g		
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 (h)	D5397 ^h (Appendix)	>400	

Note: COV=coefficient of variation.

^aASTM (2006c).

^bASTM (2006d).

^cASTM (2006e).

^dASTM (2006o).

^eASTM (2006t).

^fASTM (2006b).

^gASTM (2006s).

^hASTM (2006n).

leachate from the Keele Valley municipal solid waste landfill and comprised volatile fatty acids, inorganic salts, trace metals, and surfactant (Table 2).

Once assembled, the stainless-steel composite liner cells (Fig. 1) were placed in 117 cm \times 86 cm \times 40 cm (high), fully insulated, incubation baths made of 3 mm thick stainless steel. A pump was used to provide circulation and an immersion heater with Omega CN1A series temperature control system was used to maintain the bath temperature at $\pm 1^\circ \text{C}$ of the specified value.

Aging Procedure

Moist Ottawa sand (14% moisture content) was compacted in the bottom part of the cell in three equal layers in a similar manner as that described in the Standard Proctor test [ASTM D698 (ASTM 2006a)]. Fifty blows were applied to each layer using the Standard Proctor compaction rammer ensuring that the rammer is lifted all the way to the top. The average properties of the compacted sand were: porosity 0.41, void ratio of 0.71, dry density of 1.55 g/cm^3 , and a degree of saturation of 52%. About 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. The precut GCL sample was placed on top of the sand. The precut HDPE geomembrane sample was then placed on top. The upper part of the cell was installed on top of the geomembrane sample,

Table 2. Composition of Keele Valley Landfill Synthetic Leachate [Adapted from Hrapovic (2001); Sangam and Rowe (2002)]

Component	Concentration (mg/L)
(a) Volatile fatty acids	
Acetic acid	4,000
Propionic acid	3,000
Butyric acid	500
(b) Inorganics	
Na ⁺	1,615
K ⁺	354
NH ₄ ⁺	618
Ca ²⁺	1,224
Mg ²⁺	473
Cl ⁻	4,414
HCO ₃ ⁻	4,876
NO ₃ ²⁻	40
SO ₄ ²⁻	137
HPO ₄ ²⁻	18
CO ₃ ²⁻	156
CO(NH ₂) ₂	772
(c) Trace metal solution components—1 ml/L in synthetic leachate	
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
Sulfuric Acid (+96% purity)—1 mL	
(d) Surfactant	
Igepal CA-720	5,000
(e) E _h and pH adjustment	
E _h (adjusted by NaS ₉ H ₂ O)	~-120 mV
pH (adjusted by NaOH)	~6

and was connected to the bottom part of the cell. The geotextile protection layer was placed over the geomembrane and clean gravel was placed above the geotextile.

To assess the hydration of the GCL, cells were prepared and left at laboratory temperature for hydration. These cells were opened at various times and the moisture content of GCL and sand layers was measured to obtain the moisture content profile (Fig. 2). 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%.

Synthetic leachate was added to the gravel portion of the composite liner cells allowing the geomembrane to be exposed to the synthetic leachate from the top. The leachate was replaced with new leachate at about every two weeks. The geomembrane to be immersed in leachate was cut into 10 cm × 6 cm coupons, placed upright in glass containers, and separated by 5 mm diameter glass rods. The container was filled with synthetic leachate. The glass rod was used to ensure that coupons did not touch, and hence, that

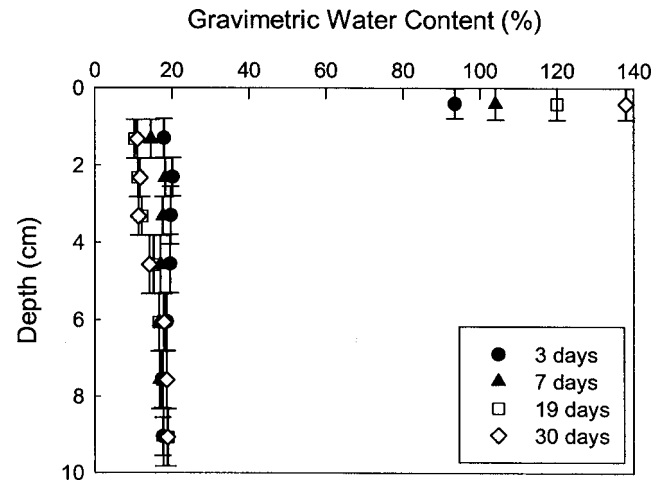


Fig. 2. Moisture content profile beneath the geomembrane

both faces of the geomembrane were completely exposed to synthetic leachate. The synthetic leachate immersed geomembrane specimens were also placed in the incubation baths. The synthetic leachate was replaced in the glass containers at the same time as in the composite liner cells.

The incubation baths were maintained at temperatures of 85, 70, 55, and 26°C. These temperatures were selected to meet the following criteria:

1. The incubation temperatures should be high enough to accelerate the aging process and practically allow the aging evaluation in a reasonably short time period. Similar temperature ranges were used by Hsuan and Koerner (1998) and Sangam and Rowe (2002).
2. The incubation temperatures should not be so high that modification on the nature of material occurs (Verdu 1988). The melt point of the geomembrane, measured by a differential scanning calorimeter, was 131 ± 1°C. The glass transition temperature of polyethylene occurs at very low temperature, within -130 to 100°C (Peacock 2000). The highest incubation temperature examined in this study (85°C) is 46°C below the melting point. The glass transition temperature is well below the range of temperature examined or that anticipated in typical field applications.
3. The selected temperatures should not destroy the antioxidants present in the geomembrane. Antioxidants have specific ranges of temperature in which they are effective (Fay and King 1994; Lutz and Grossman 2001). Antioxidants such as hindered phenols (primary antioxidant with an effective temperature range 0–300°C), thiosynergists (secondary antioxidant with an effective temperature range 0–200°C), and hindered amines (secondary antioxidant which are most effective below 135°C and preferably below 120°C; Fay and King 1994). Hence, the selected temperatures were well within the effective range of primary and secondary antioxidants. Prior studies on polyethylene pipe have shown that at temperatures over 95°C, volatilization of antioxidants may be a concern (Karlsson et al. 1992; Smith et al. 1992).

The simulated composite liner cells were removed from the incubation tanks at after different times and the geomembrane samples were retrieved, rinsed with distilled water, wiped, and prepared for testing. The GCL thickness was measured, and both GCL and sand specimens were immediately placed in the oven to

obtain the gravimetric water content. Various analytical and mechanical tests were performed on the geomembrane sample as described in the following section.

Analytical Testing Methods for HDPE Geomembrane

The standard oxidative induction time (Std-OIT) test [ASTM D3895 (ASTM 2006e)] is a well-known indicator of the amount of antioxidant present in the geomembrane. Yim and Godin (1993) demonstrated the relationship between long-term aging and the OIT. They showed that there is no relationship between the initial OIT value and the long-term stability of polyethylene. The high initial OIT value does not mean that the polyethylene is highly stable. They also showed that several combinations of stabilizers with different initial OIT values gradually declined with time during oven aging. OIT has been used by many researchers (Hsuan and Koerner 1995, 1998; Sangam and Rowe 2002; Müller and Jakob 2003; Rimal et al. 2004; Gulec et al. 2004) for monitoring the depletion of antioxidant in the HDPE geomembrane. For this study, the standard OIT tests were carried out using two differential scanning calorimeters (DSC): TA Instruments 2910 and Q100. For the evaluation of OIT the testing temperature of 200°C was used at a pressure of 35 kPa and flow of ultrahigh pure nitrogen and oxygen of 50 mL/min. Three to five replicate specimens were tested from each geomembrane sample.

High-pressure oxidative induction time tests (HP-OIT) [ASTM D5885 (ASTM 2006o)] were also used to monitor the antioxidant depletion from some samples. This test has been utilized in the past by Hsuan and Koerner (1998) and Sangam and Rowe (2002) to assess aging of HDPE geomembranes. A TA Instrument 2910 DSC with a special pressure cell having a maximum capacity 7000 kPa was used to conduct the HP-OIT test. The specimen was kept isothermally at 150°C and 3,500 kPa in an oxygen environment until the exothermic peak was detected. For both the Std-OIT and HP-OIT tests, OIT is taken as the time to the onset of the exothermal peak.

Each approach has advantages and disadvantages. The standard OIT test is more sensitive for measurement of low OIT values and is simpler to conduct. However, in the standard OIT test at 200°C, hindered amines lose their effectiveness (Hsuan and Koerner 1998). In contrast, Thomas and Ancelet (1993) demonstrated that hindered amines were active at 150°C in the HP-OIT test. Thus, the use of the lower testing temperature (150°C) in the HP-OIT test decreases the potential for volatilization of these antioxidants during testing and the high pressure increases the concentration of the reacting oxidizing gas (Tikusis et al. 1993), giving more accurate OIT results when hindered amines are present in the geomembrane. Thomas and Ancelet (1993) established a relationship between Std-OIT and HP-OIT values for 12 different combinations of phenols, hindered amines, and phosphites. It was found that the additive packages with hindered amines yielded low initial Std-OIT values but high initial HP-OIT values. Thus, the HP-OIT test was found to be useful in distinguishing the additive type.

The crystallinity of polyethylene can be obtained from various simple and advanced methods such as density, differential scanning calorimetry, wide-angle x-ray diffraction, nuclear magnetic resonance spectroscopy, and ultrasonic techniques. In this investigation crystallinity tests were performed on the geomembrane samples according to ASTM E794 (ASTM 2006t) using a DSC. The geomembrane specimen of known mass was placed in the DSC and heated at the rate of 20°C/min. to 200°C in nitrogen.

The percentage crystallinity was obtained as a ratio of measured heat of fusion with the heat of fusion of 100% crystalline HDPE, 290 J/g (Flory and Vrij 1963).

Mechanical Testing Methods for HDPE Geomembrane

Tensile tests were performed in Instron 3396 universal testing machine in accordance with ASTM D6693 (ASTM 2006s). Tensile properties have been widely used in evaluating the oxidative stability of polymeric materials and geosynthetics (Sung and Nikolov 1992; Salman et al. 1997; Dörner and Lang 1998; Hsuan and Koerner 1998; Sangam 2001). In particular, the elongation at break is known to a good indicator of oxidative degradation (Hamid et al. 1992).

The melt flow index test (MFI) is useful in for assessing the changes in molecular weight of the polymer due to aging. The MFI is inversely proportional to the molecular weight (Shah 2002), e.g., a low molecular weight polymer has high MFI value and vice versa. The oxidative degradation of polyethylene results in either a cross-linking or a chain scission reactions (Peacock 2000). A cross-linking increases the molecular weight (higher molecular weight molecules are formed) whereas the chain scission decreases the molecular weight (Hsuan and Koerner 1998; Peacock 2000). Hence, as MFI and molecular weight are inversely proportional to each other, the decrease in MFI value (increase in molecular weight) suggests cross-linking and the increase in MFI value suggests chain scission. The MFI test was performed in Dynisco LMI 4000 series melt flow indexer according to ASTM D1238 (ASTM 2006b) for Condition E at 190°C with the geomembrane melt being extruded through the orifice at a load 2.16 kg.

The gravimetric moisture content of the GCL and sand [ASTM D4959 (ASTM 2006i)] and thickness of the GCL was measured after the composite liner cells were taken out of the incubation cell.

Results

Std-OIT versus HP-OIT

Both Std-OIT and HP-OIT tests were performed for the composite liner geomembrane sample incubated at 70°C and the test results are shown in Fig. 3. The OIT depletion rates were estimated from the exponential decay fit to the data. Because of the very different initial OIT values obtained with the two tests, the antioxidant depletion rates are quite different (0.212 per month and 0.132 per month for the Std-OIT and HP-OIT tests, respectively), however, both methods give the same time for OIT depletion.

Fig. 4 shows the relationship between Std-OIT and HP-OIT test results. The linear correlation between the data from the two tests suggests that either test could be used to evaluate the depletion of antioxidant for the specific antioxidant package used in the geomembrane examined. More importantly the linear relationship provides evidence that the higher temperature in the Std-OIT test did not destroy the antioxidants used in this geomembrane. These findings are similar to those of Hsuan and Koerner (1998) and Sangam and Rowe (2002) for the geomembrane they tested. Hsuan and Koerner (1998) indicate that a linear relationship between the data from the two tests implies that there are no hindered amine antioxidants present in the geomembrane. Thus, the major antioxidant in the geomembrane probably consists of hin-

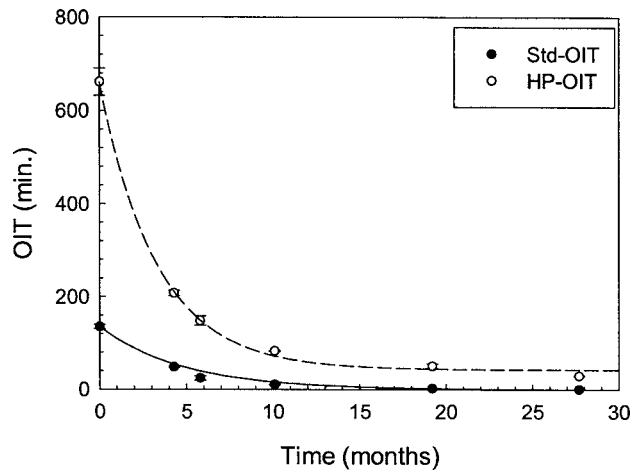


Fig. 3. Variation of Std-OIT and HP-OIT versus time for geomembrane in composite liner cells at 70°C

dered phenols (primary antioxidant) and phosphites (secondary antioxidant added for polymer processing), which are effective at the temperature of 200°C used in Std-OIT test (Hsuan and Guan 1997; Hsuan and Koerner 1998; Sangam and Rowe 2002). The initial HP-OIT of the geomembrane was 660 min. Several previous investigators have found that the combination of phenols and phosphites do not produce initial HP-OIT values of above about 370 min (Thomas and Ancelet 1993; Hsuan and Guan 1997). Thus, it is possible that another class or combination of stabilizers is present in the geomembrane and that this gives rise to the high HP-OIT value. Hsuan and Guan (1997) have reported Std-OIT of 126 min and HP-OIT of 1125 min for an antioxidant combination of phenols, phosphites, and thiosynergists. Although their HP-OIT (1125 min) is higher than that for the geomembrane used in this study (660 min), a different combination of phenols, phosphites, and thiosynergists may be present. It is also possible that different members of an antioxidant group, such as hindered phenols, exhibit different responses with respect to laboratory measurements of OIT in the Std and HP tests and that this reflects a different formulation than tested by others when reporting typical Std-OIT and HP-OIT results, even though they are of the same type. Since the manufacturer would not supply the details regard-

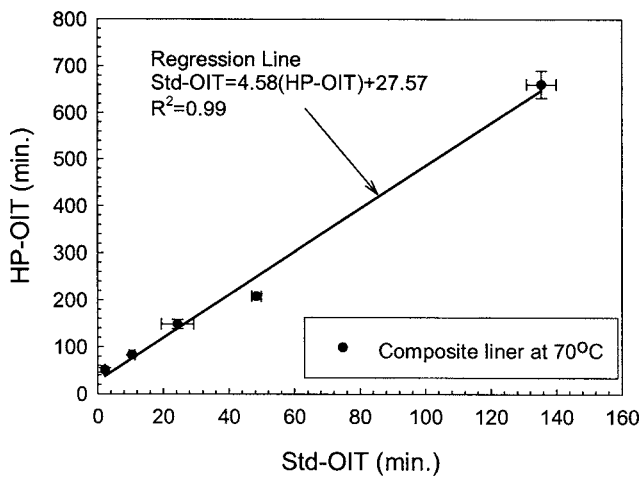


Fig. 4. Relationship between Std-OIT and HP-OIT for the geomembrane in composite liner cells at 70°C

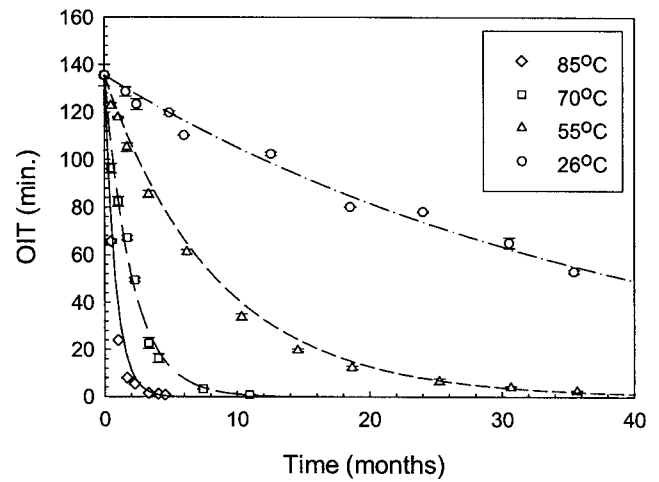


Fig. 5. Variation in OIT versus time in the leachate immersed geomembrane at all incubation temperatures. The data points are the average values and the vertical bars represent standard deviation.

ing the antioxidant type, ratio, or concentration used in this geomembrane, the reason for the difference with other published values must remain hypothesis and it is entirely possible that there are additional components affecting the OIT performance.

The OIT was measured for both the composite liner geomembrane samples and leachate immersed coupons incubated at all temperatures and one illustrative set of data is given in Fig. 5. The OIT values decreased exponentially with time and the OIT reduction was faster at higher incubation temperatures as previously observed by Hsuan and Koerner (1998) and Sangam and Rowe (2002). It was found that the depletion of antioxidants was dependent on the exposure conditions. For example, Fig. 6 shows that the leachate immersed geomembrane experienced a faster reduction in OIT than the geomembrane in the composite liner. At 70°C it took about 11 months for the decrease from the initial OIT value of 135 min to the value less than 1 min for the leachate immersed geomembrane, whereas for the composite liner it took about 28 months for this same reduction to occur. A similar trend

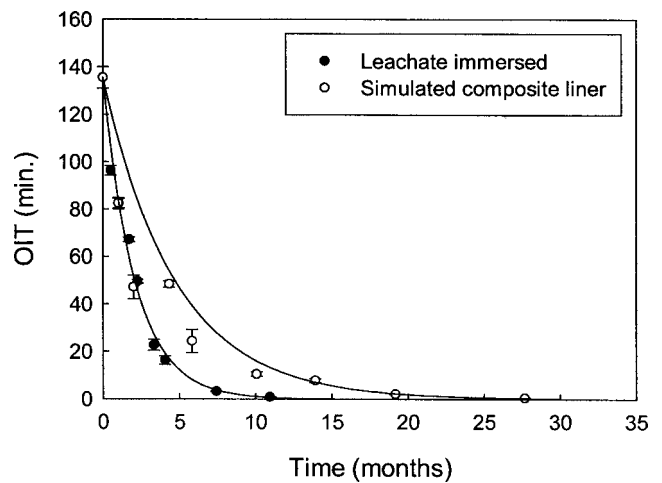


Fig. 6. Variation in OIT versus time at 70°C in composite liner geomembrane sample and leachate immersed geomembrane sample

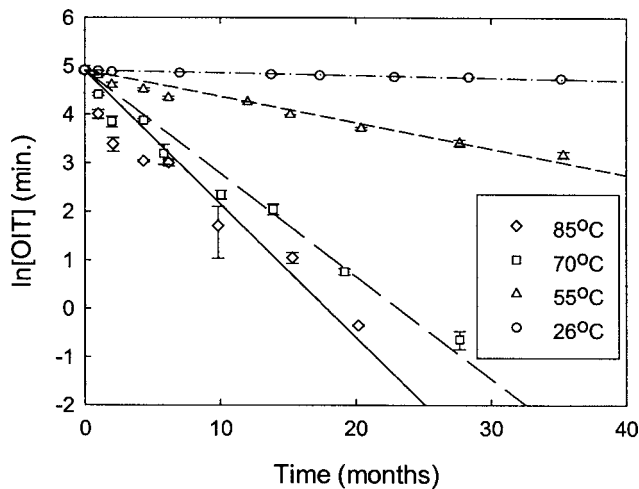


Fig. 7. Logarithm of OIT versus incubation time for the composite liner geomembrane samples

was observed at the other temperatures with the depletion being consistently faster for the leachate immersed geomembrane than for the composite liner geomembrane.

Since antioxidants depletion follows a first-order decay model, the OIT value at time t , can be expressed as (Hsuan and Koerner 1998)

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

or taking logarithm of both sides

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

where OIT_o =initial OIT (min); s =antioxidant depletion rate (month^{-1}); and t =time (months).

Figs. 7 and 8 show the plot of $\ln(\text{OIT})$ with incubation time, which yields the linear response curves given by Eq. (2). The slope of the lines represents antioxidant depletion rates at each temperature and these are summarized in Table 3. The antioxidant depletion rates obtained at each temperature were significantly higher (2.2–4.8 times) for the leachate immersed geomembrane samples than for the composite liner. For example, the depletion rate at 85°C was 1.24 month^{-1} for the leachate immersed sample

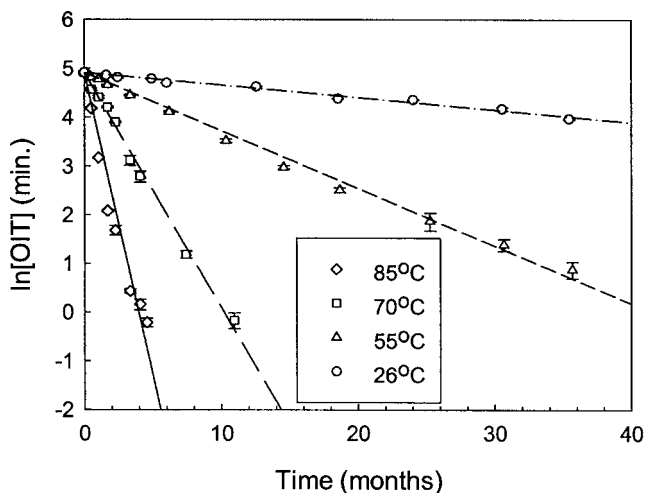


Fig. 8. Logarithm of OIT versus incubation time for the leachate immersed geomembrane samples

Table 3. List of First-Order Antioxidant Depletion Rates for 1.5-mm-Thick HDPE Geomembrane at Different Incubation Temperatures

Exposure	Temperature ($^\circ\text{C}$)	Antioxidant depletion [Rate, $\text{s} (\text{month}^{-1})$]	R^2
Leachate immersed	85	1.2423	0.95
	70	0.4809	0.99
	55	0.1183	0.99
	26	0.0253	0.98
Simulated composite liner	85	0.2750	0.89
	70	0.2123	0.96
	55	0.0539	0.94
	26	0.0053	0.95

compared to 0.275 month^{-1} for the composite liner geomembrane sample. This difference is attributed to the fact that for simple leachate immersion (a) the antioxidants diffusing out of the geomembrane could be readily removed into the leachate, hence, maintaining a relatively high concentration gradient and outward diffusive flux, and (b) the geomembrane was directly exposed to the constituents in the leachate. In contrast, for the simulated liner there could be a build up of concentration of antioxidant in the GCL and geotextile on either side of the geomembrane, thereby reducing the concentration gradient and outward diffusive flux. Furthermore, only one side of the geomembrane was exposed to leachate.

Exposure to leachate can increase antioxidant depletion. In particular, the presence of surfactant in leachate plays a major role in the depletion of antioxidants from a geomembrane (Islam and Rowe 2007). This is attributed to the fact that the surfactant increases the wettability of the geomembrane by decreasing the surface tension and allowing the antioxidant on the surface of the geomembrane to more readily dissolve in the leachate. This increases the concentration gradient between the core and the surface of the material, and hence, the outward diffusive flux of antioxidants. The trace metals have also been reported to increase the consumption of antioxidants under anoxic conditions (Osawa and Saito 1978; Wisse et al. 1990).

Sangam and Rowe (2002) have shown that the antioxidant depletion rate in synthetic leachate is 1.6–3.2 times faster than in water. Dörner and Lang (1998) monitored the decline in OIT from polyethylene pipes (wall thickness 2 mm) immersed in water. Although they did not explicitly state the antioxidant depletion rate, one can deduce a rate of 0.173 per month from their data at 85°C . This is very close to 0.175 per month obtained by Sangam and Rowe (2002) for 2 mm thick geomembrane in water.

Islam and Rowe (2007) examined OIT depletion for 1.5 mm thick geomembrane immersed in four different leachates (all containing trace metals and surfactant) and observed depletion rates very similar to those obtained for synthetic leachate immersion in this study.

The antioxidant depletion rates published in the literature for various HDPE geomembranes are given in Table 4. The rate of antioxidant depletion obtained for leachate immersed 1.5 mm thick HDPE geomembrane sample at 85°C (1.24 month^{-1}) in this study is higher than that obtained by Sangam and Rowe (2002) for 2 mm thick HDPE geomembrane immersed in the same leachate (i.e., 0.407 month^{-1}). The difference is most probably due to a difference in antioxidant formulation. In support of this hypothesis it is noted that the geomembrane tested by Sangam and Rowe (2002) had an HP-OIT of 380 min, while the present

Table 4. List of Antioxidant Depletion Rates in the Literature for Different Exposure Conditions

Exposure condition	Incubation temperature (°C)	Antioxidant depletion rates (month ⁻¹)
1.5-mm thick geomembrane with saturated sand on the top with static compressive stress of 260 kPa and dry sand on the bottom. Initial Std-OIT=80.5 min; HP-OIT =210 min. (Hsuan and Koerner 1998)	85	0.1404
	75	0.0798
	65	0.0589
	55	0.0217
2-mm thick geomembrane immersed in synthetic MSW leachate. Initial Std-OIT =133 min; HP-OIT=380 min. Crystallinity =44%. (Sangam and Rowe 2002)	85	0.4074
	55	0.1504
	40	0.0886
	22	0.0188
2-mm thick geomembrane immersed water. Initial Std-OIT=133 min; HP-OIT=380 min. Crystallinity=44% (Sangam and Rowe 2002)	85	0.1746
	70	0.1050
	55	0.0470
	40	0.0362
	22	0.0043
1.5-mm geomembrane immersed in AMD. Initial Std-OIT=208 min; HP-OIT=484 min. (Gulec et al. 2004)	80	1.2056
	60	0.0906
	40	0.0480
	20	0.0051

geomembrane had an HP-OIT of 660 min, and as discussed above, appears to have a different antioxidant package. Gulec et al. (2004) aged a 1.5 mm geomembrane in synthetic acid mine drainage (AMD) leachate, and the antioxidant depletion rate at 80°C was 1.206 month⁻¹. A recent study of 2.5 mm thick specimens cut out of HDPE leachate collection pipe immersed in a synthetic leachate at 85°C gave a depletion rate of 1.18 per month (Krushelnitzky 2006). This rate is similar to the value of 1.24 per month obtained for the leachate immersed 1.5 mm HDPE geomembrane examined in this study.

It is noted that Müller and Jakob (2003) observed an initial sharp decline in OIT shortly after geomembrane immersion in water at 80°C. This was followed by a slow subsequent decline. This two-stage exponential decline in OIT was attributed to an initial hydrolytic deterioration of phosphite followed by slower depletion of the remaining phenolic antioxidants.

The renewal rate of immersion fluid can also affect the loss in OIT (Islam and Rowe 2007). A slow renewal rate of the fluid appears to allow a buildup of antioxidant concentration in the immersion fluid. Thus, the outward diffusion of antioxidants from the geomembrane will be retarded. This may be a factor affecting depletion rates. The leachate in the present tests was renewed at a frequency (2 weeks), which based on studies by Islam and Rowe (2007) was sufficiently frequent to prevent a buildup of antioxidants that would significantly affect the results.

Arrhenius Modeling of Antioxidant Depletion Rates

The Arrhenius [Eq. (3)] is a relationship between antioxidant depletion rates and temperature,

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

Taking the logarithm of both sides the above equation can also be expressed as

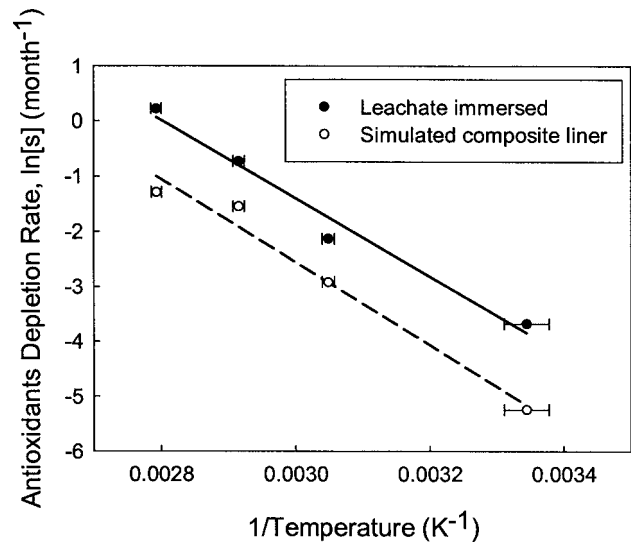


Fig. 9. Arrhenius plot of antioxidant depletion rate

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

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 Arrhenius equation is commonly used to extrapolate the experimental data obtained at high temperatures to the site-specific lower temperatures (Koerner et al. 1992; Viebke et al., 1994; Hsuan and Koerner 1995; Hsuan and Koerner 1998; Sangam and Rowe 2002; Gulec et al. 2004). The assumptions associated with the use of the Arrhenius equation are (1) the antioxidant depletion rate is a function of temperature; (2) the value of constant A does not affect the temperature sensitivity of the reaction; and (3) the activation energy remains constant over the time and temperature range of interest for evaluation, extrapolation, and prediction.

The data listed in Table 3 can be used to obtain a relationship between the logarithm of antioxidant depletion rate and inverse of the temperature, as shown in Fig. 9. The activation energy can be deduced from the slope E_a/R of the regression curve and both the Arrhenius equation and the corresponding inferred activation energy are given in Table 5 for the composite liner geomembrane (62.7 kJ/mol) and leachate immersed geomembrane sample (58.9 kJ/mol). Although there was not a big difference in activation energies, the higher activation energy was obtained for the composite liner.

Rowe (2005) has discussed the temperatures observed for landfill liners. For a normal MSW landfill operation the liner temperatures can be expected to reach 30–40°C and 35°C can be taken as a representative temperature based on currently available data. If the landfill has augmented moisture to accelerate degradation of organics the liner temperature may increase faster than in normal operations and could exceed 40°C (Koerner and Koerner 2006). In the presence of a significant leachate mound, liner temperatures of 40–60°C may occur. Using the equations listed in Table 5, the antioxidant depletion rates at site-specific lower temperatures were estimated and are given for temperatures ranging from 10 to 60°C in Table 6.

Table 5. Arrhenius Equation and Inferred Activation Energy

Exposure condition	Arrhenius equation	E_a (kJ/mol)
Leachate immersed geomembrane (current study)	$\ln(s)=19.85-7084/T$ $R^2=0.98$	5.89
Composite liner geomembrane (current study)	$\ln(s)=20.06-7540/T$ $R^2=0.98$	62.7
1.5 mm thick geomembrane with saturated sand on the top with static compressive stress of 260 kPa and dry sand on the bottom (Hsuan and Koerner 1998)	$\ln(s)=17.045-6798/T$ $R^2=—$	56
2 mm thick geomembrane immersed in synthetic MSW leachate (Sangam and Rowe 2002)	$\ln(s)=13.768-5213/T$ $R^2=0.985$	43.3
2 mm thick geomembrane immersed water (Sangam and Rowe 2002)	$\ln(s)=16.054-6305/T$ $R^2=0.989$	52.4
1.5 mm geomembrane immersed in AMD (Gulec et al. 2004)	$\ln(s)=19.16-7099/T$ $R^2=0.93$	58.9

Note: The Arrhenius equation for composite liner geomembrane is different from that reported in Rowe (2005). The equation reported here is updated and obtained from longer term testing data. Differences arise due to slight variation in the updated antioxidant depletion rates.

Prediction of Antioxidant Depletion Time

Based on the depletion rates in Table 6, the time for depletion of antioxidants can be calculated. The antioxidant depletion time was calculated as the time taken for depletion of OIT from the initial value of 135 minutes to final residual value of 0.5 minutes reported for pure HDPE resin (Hsuan and Koerner 1998). For example, based on the Std-OIT data the antioxidant depletion time for the composite liner at 70°C can be calculated from Eq. (2) as follows: $\ln(0.5)=-0.2123t+\ln(135)$, giving $t=26.4$ months (2.2 years). Likewise from the HP-OIT data, and using the initial measured value of 660 min and the residual value for pure unstabilized HDPE resin of 20 min (Hsuan and Koerner 1998), the time required for OIT depletion is given by $\ln(20)=-0.1318t+\ln(660)$, and hence, $t=26.5$ months (2.2 years). Thus, both the Std-OIT and HP-OIT data give very similar predictions.

The results, shown in Fig. 10, indicate that the antioxidant depletion times in composite liner geomembrane were substantially longer than for leachate immersed geomembrane. The depletion time at 35°C for the composite liner geomembrane was about 40 years compared to about 10 years for the leachate immersed geomembrane. The predicted antioxidant depletion time ranged from 335 years at 10°C to 6 years at 60°C for the composite liner geomembrane. For the leachate immersed geomembrane, the depletion time ranged from 85 years at 10°C to 2 years at 60°C. These results clearly demonstrate the importance of liner temperature on the antioxidant depletion time of the geomem-

Table 6. Predicted Antioxidant Depletion Rates at the Service Temperatures Ranging from 10 to 60°C

Temperature (°C)	Antioxidant depletion rate [s (month ⁻¹)]	
	Leachate immersed	Composite liner
10	0.0056	0.0014
20	0.0132	0.0034
30	0.0293	0.0080
35	0.0429	0.0121
40	0.0619	0.0178
50	0.1248	0.0376
60	0.2412	0.0757

brane. They also show that immersion tests are too severe and the service life will be substantially greater for a composite liner than implied by immersion tests in leachate.

Crystallinity

The degree of crystallinity was measured for both composite liner geomembrane and leachate immersed coupons incubated at 85°C. Fig. 11 shows the change in crystallinity with respect to time for the composite liner geomembrane. It was observed that aging at 85°C resulted in an increase in crystallinity from an unaged value of 49–56% within 2 months. This initial increase in crystallinity remained stable (between 54 and 56%) at later times and no significant further change was observed. Similar results were observed for the leachate immersed geomembrane. These results are in agreement with the results obtained by Dörner and Lang (1998) for the hot water aging of polyethylene and Sangam

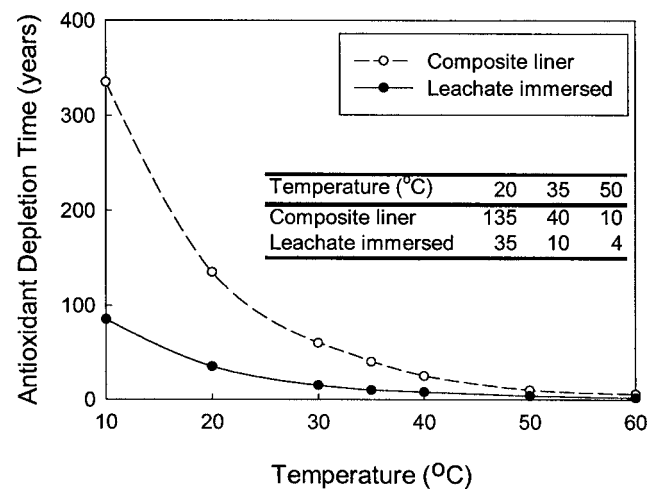


Fig. 10. Estimated antioxidant depletion times for the composite liner and leachate immersed geomembrane. Note: The antioxidant depletion times for the composite liner geomembrane may slightly differ from that reported in Rowe (2005). The values reported here are obtained from longer term testing. The results may differ due to updated values of antioxidant depletion rates and rounding.

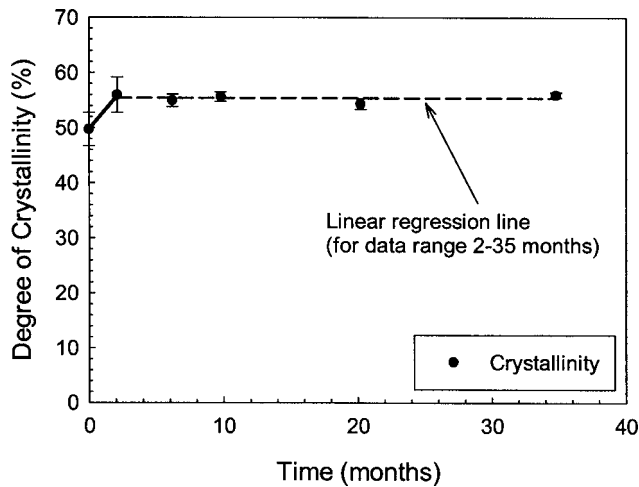


Fig. 11. Change in crystallinity versus incubation time for the composite liner geomembrane at 85°C

(2001) on HDPE geomembrane. The increase in crystallinity may be attributed to recrystallization and/or postcrystallization that takes place due to incubation at high temperature (Dörner and Lang 1998).

Melt Flow Index

MFI was measured for both leachate immersed and composite liner geomembranes. At 85°C the MFI experienced a slight decrease over the 35 months of testing, however, the change was not significant and no change in the molecular structure of the polymer was evident over this testing period for either the leachate immersed or composite liner geomembranes. Given the three stage aging process discussed earlier, the mechanical properties would not be expected to change significantly until after completion of the induction period (Stage II) (Hsuan and Koerner 1998). Thus, the MFI results suggest that the leachate immersed geomembrane was still in the second stage of degradation at 35 months.

Tensile Properties

Tensile tests were conducted only on the composite liner geomembrane samples. No significant change in tensile properties at yield and break was observed over the 35 months of testing at 85°C for the geomembrane in the composite liner. The yield properties were evaluated for composite liner samples incubated at 85°C and the impact on the yield strength was examined.

With the increase in crystallinity a small increase in tensile strength at yield was observed after 2 months. The tensile strength of the virgin geomembrane was 26.9 kN/m (SD=0.67). After two months it slightly increased to 28.8 (SD=0.43). At 35 months the tensile strength at yield was 27.4 kN/m (SD =0.49). Although there was a slight increase in the yield strength there was also some scatter in the data and the differences were not large. This suggests that there was no significant mechanical degradation of geomembrane over the testing period. This is consistent with the MFI results. Even after the antioxidants are depleted significant reduction in tensile properties would not be expected until after Stage 2 of aging (induction time) is com-

pleted. The tensile data are consistent with the other data in suggesting that this had not happened on the 35 months of testing reported herein.

Water Content of the GCL and Sand Subgrade

The gravimetric water content in GCL and sand were measured after the cells were taken out of incubation. It was found that the water content in GCL increased with time. The water content increased more readily at higher temperatures than lower temperatures. For example, after one month of incubation the average water content in GCL taken from replicates of three simulated composite liner GCL specimens were 156% (at 85°C), 147% (70°C), 142% (55°C), and 131% (26°C). After a six month incubation the water content increased to 262% (85°C), 261% (70°C), 204% (55°C), and 140% (26°C). The water content in sand was lower close to the GCL-sand interface and it was found to increase with depth. The water content in the sand ranged from 8 to 10% near the GCL to 17 to 20% at the base of the cell.

Summary and Conclusions

The results of accelerated aging tests conducted at elevated temperatures on leachate immersed geomembranes and composite liner geomembranes have been described. In the composite liner the top face of the geomembrane was exposed with leachate while the bottom face was exposed to the hydrated GCL. The results from OIT tests indicated that the antioxidant depletion rates were about 2.2–4.8 times faster for the leachate immersed than the simulated composite liner geomembrane specimens. The higher rates are attributed to the higher extraction of antioxidants from two sides of the geomembrane immersed in leachate. The different exposure to leachate on the top and bottom face of the composite liner geomembrane, and possible buildup of antioxidants on the bottom interface of geomembrane retarded the antioxidant depletion processes.

The measured antioxidant depletion rates were extrapolated to a range of temperatures (10–60°C) using Arrhenius modeling and depletion time for the consumption of antioxidant were estimated. The results indicated that at a liner temperature of 35°C the antioxidant depletion time would be 40 years for the composite liner geomembrane compared to 10 years for the leachate immersed geomembrane. The prediction from simple immersion test was found to be quite conservative. These tests show that to obtain more realistic estimate of geomembrane service life one needs to perform a test that simulated the expected liner condition in a composite liner. This paper has presented the first such results for the time of antioxidant depletion for a geomembrane in a composite liner with a GCL. Additional research is needed to assess the subsequent stages of the aging of a geomembrane under simulated field conditions.

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