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Ageing and Long-term Performance of Geomembrane Liners

R.K. Rowe, GeoEngineering Centre at Queen's-RMC, Queen's University, Kingston, Canada
S. Rimal, GeoEngineering Centre at Queen's-RMC, Queen's University, Kingston, Canada

ABSTRACT
The latest findings on the long-term performance of high density polyethylene (HDPE) geomembranes (GMs) are summarized. Insights from accelerated ageing tests of GMs in air, water and synthetic municipal solid waste leachate are discussed. A comparison is made with the test results on GMs in a composite landfill liner. The service life of the GM in landfill liners is addressed and is found to be long except at high temperatures. The results of long-term testing on outdoor natural weathering test on GMs are presented and it is indicated that the service life exposed to the atmosphere, while reduced compared to unexposed, is long as long as it is not physically damaged. Finally, laboratory results to assess the durability of the fluorinated GMs exposed to hydrocarbons are described and it is shown that for this GM, immersion in hydrocarbons can substantially increase the depletion of antioxidants evident in the standard OIT test.

1. INTRODUCTION

High density polyethylene (HDPE) geomembranes (GM) are used as a part of liner systems in modern landfills and hydrocarbon contaminated sites. The GM provides a barrier to advective and diffusive migration of contaminants (Rowe 2005). Some field and laboratory data suggest that the properties of polyethylene based GMs change with time (see Rowe et al. 2004 for a summary and Rowe 2005 and Müller 2007 for more recent results). Thus it is important to assess the long-term performance of the GM for typical exposure conditions.

Conceptually HDPE GM service life is envisaged as having three stages (Hsuan and Koerner 1998). Stage I: Antioxidant depletion, Stage II: Induction time to the onset of polymer degradation, and Stage III: Polymer degradation involving the decrease in a GM property to an arbitrary level often taken to be 50% of the original value or "half-life". The sum of the three stages is regarded as the service life of GM. Given the long time it would take to obtain results under field conditions, laboratory accelerated ageing studies are performed using time-temperature acceleration methods. The emphasis of most of these studies to date has been on Stage I (e.g. Hsuan and Koerner 1998; Sangam and Rowe 2002; Müller and Jacob 2003; Rimal et al. 2004; and Müller 2007). These past studies have examined depletion of antioxidants exposed to media such as air, water, landfill leachate, and hydrocarbons. The majority of these studies have utilized immersion tests. These studies have shown that the antioxidant depletion time depends on the exposure conditions (Sangam and Rowe 2002; Rimal et al. 2004).

This paper provides an overview of the latest findings on the long-term performance of the HDPE GMs. It discusses the latest results from accelerated ageing tests of GM in air, water and synthetic municipal solid waste (MSW) leachate (hereafter just refereed to as leachate). The objective of this study was to examine the stages of service life of GM in three immersion media. These samples have now been ageing for 8 to 10 years. An update is provided on Stage I since the data reported in Sangam and Rowe (2002). Some of the samples are in Stage II, some in Stage III and some have completed all three stages of the service life. To provide an improved estimate of Stage I for municipal landfill liner applications than that obtained by accelerated immersion tests, a GM was tested in three simulated composite liner configurations. Furthermore, the results of long-term testing on outdoor natural weathering of GM are presented. Finally, the results of laboratory studies used to assess the effect of immersion in hydrocarbons (jet fuel) on the antioxidant depletion time for the fluorinated and conventional HDPE GMs are described.

2. AGEING OF GM IN CONVENTIONAL IMMERSION TESTS

Laboratory-accelerated tests conducted on GM-1 (Table 1) involved immersion of the GM in air, distilled water and leachate. Coupons of the GM were placed in the incubation media at 85, 70, 55, 40^{o}C and room temperature. For air exposure the coupons were about 30 cm x 15 cm, for water immersion about 40 cm x 15 cm and for leachate immersion the maximum size of the sample were about 15 cm x 12 cm.The synthetic leachate used in this study was based on leachate from the Keele Valley municipal solid waste landfill and comprised volatile fatty acids, inorganic salts, trace metals, and surfactant (Sangam and Rowe 2002). The leachate was replaced with new leachate at about every two weeks to ensure relatively constant strength and reduced conditions. At various time intervals the incubated GM samples were retrieved and tested for oxidative induction time (OIT), crystallinity, melt flow index (MFI), tensile properties and single point notched constant tensile load (SP-NCTL) test. The initial results for Stage I were reported by Sangam and Rowe (2002).

Table 1. Properties of HDPE GMs examined.

Property	Method (ASTM)	Immersion study/Natural weathering study		Composite liner study		Jet fuel durability study: untreated		Jet fuel durability study: treated	
		GM-1		GM-2		GM-3		GM-4	
		Avg.	COV	Avg.	COV	Avg.	COV	Avg.	COV
Thickness (mm)	As received	2.0	1.4	1.5	--	1.5	--	1.5	--
Density (g/cm^3)	D1505	0.940	0.3	0.944	2.43	--	--	--	--
Carbon Black Content (%)	D1603	2.54	--	2.43	--	--	--	--	--
OIT (min)	D3895	133	3.7	135	3.3	135	1.5	137	0.7
HP-OIT (min)	D5885	380	1.3	660	4.4	227	2.5	175	7.4
Crystallinity (%)	E794	44	1.2	49	6.1	52	2.4	51	2.2
MFI (g/10 min.)	D1238	0.42	1.5	0.55	0.4	0.47	3.7	0.46	3.1
Tensile Properties (Machine)	D6693								
Tensile-strength at yield (kN/m)		34	0.9	26.9	2.5	23.9	3.7	23	2.4
Tensile-strength at break (kN/m)		80.5	3.2	64.7	1	50.9	10.6	54	2.8
Tensile-strain at yield (%)		22	1.6	18.1	3.7	19.8	1.9	20	2.8
Tensile-strain at break (%)		1034	62	962	0.8	869	12.0	979	2.8
SP-NCTL (hrs)	D5397, Appendix	>300	--	>400	--	--	--	--	--

The results from Standard OIT and HP-OIT tests indicated a linear relationship between the two tests (Sangam and Rowe 2002). This demonstrates that the standard OIT test did not destroy the antioxidants present in the GM and hence can be used to assess the depletion of antioxidants in the GM examined. The OIT was measured for air, water and leachate immersed coupons incubated at all temperatures and an illustrative set of data at 55^{o}C is given in. Figure 1. Antioxidants depletion follows a first-order decay relationship (Hsuan and Koerner 1998) and the OIT value at time t is given by:

$$\mathrm{OIT_t} = \mathrm{OIT_o}.e^{-s.t} \qquad [1]$$

where $\mathrm{OIT_o}$ = initial OIT (in minutes); s = antioxidant depletion rate (in month^{-1}); and t = time (in months).

The OIT values decreased exponentially with time (equation 1) and the OIT reduction was faster at higher incubation temperatures. It was found that the depletion of antioxidants was dependent on the exposure conditions. The depletion of antioxidants was fastest in leachate and slowest in air. The antioxidant depletion rates (calculated from slope of the logarithmic form of equation 1) obtained for the leachate immersed GM at each temperature were significantly (2.5-4.0 times) higher than for the water immersed GM and 2.8-6.7 times higher than for GM in air. This is attributed to the fact that the surfactant in leachate increases the wettability of the GM by decreasing the surface tension and allowing the antioxidant on the surface of the GM 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 Arrhenius relationship between the antioxidant depletion rates and temperatures can be expressed in logarithmic form as:

$$\ln(s) = \ln(A) - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \qquad [2]$$

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 relationship between logarithm of antioxidant depletion rate and inverse of the temperature is shown in Figure 2 together with the activation energy (Ea).

Using the Arrhenius equations the antioxidant depletion rates at site specific lower temperatures were estimated. 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 OITo=133 min to final residual value of $\mathrm{OIT_t}$=0.5 min (Hsuan and Koerner 1998). The values for each exposure condition at typical liner temperatures are also provided in Table 2. Also given are approximations for unsaturated soil ([Air+Water]/2) and an approximation for a composite liner ([leachate+unsaturated soil]/2). Antioxidant depletion times for leachate immersed GM were lower than other exposure conditions at all service temperatures. 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. Taking 35°C to be a representative temperature based on currently available data, it is estimated that it would take at least 30 years (for leachate-unsaturated soil) to deplete the antioxidants from the GM. Provided that the GM is exposed with leachate on top and unsaturated soil at the bottom. These estimates differ from those provided by Sangam and Rowe (2002) because of the additional 5 years of data available at the time of writing this paper.

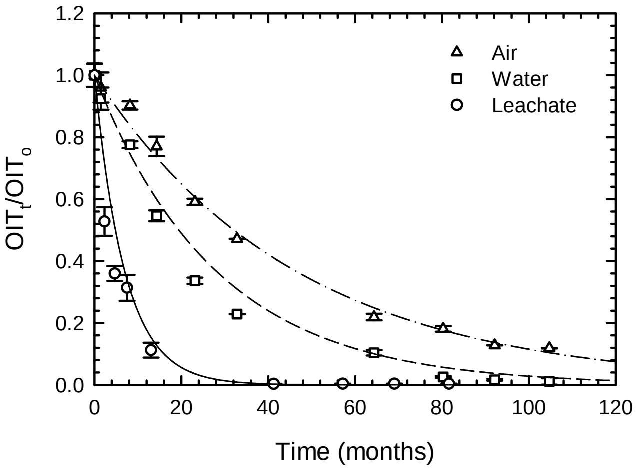

Figure 1. OIT versus time at 55°C in different exposure conditions. Each data point represents the average of 3 to 5 replicate OIT measurements and the vertical bars represent one standard deviation.

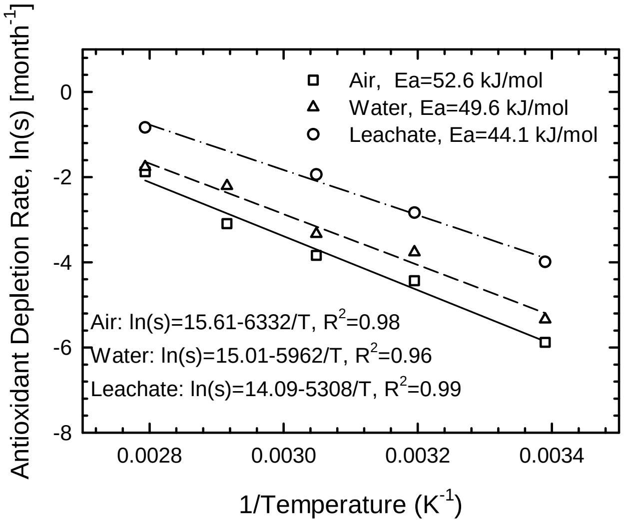

Figure 2. Arrhenius plot of antioxidant depletion rate for different exposure conditions.

Table 2. Time to complete Stage I at typical liner temperatures.

Temperature (°C)	Air (years)	Water (years)	Leachate (years)	Air-water Unsaturated Soil (years)	Leachate-Unsaturated Soil (years)
20	190	95	25	140	85
35	65	35	10	50	30
50	25	15	5	20	10

Note: Values are rounded to nearest 5 years.

3. AGEING IN SIMULATED LINER TEST VERSUS LEACHATE IMMERSION TEST

It may be argued that simple immersion in leachate is too severe a condition to represent a real landfill liner and the estimates for real conditions (leachate-unsaturated soil) presented in Table 2 are a rough approximation. To provided a better estimate of the likely performance in an actual liner, Rowe and Rimal (2008a) performed tests involving simulated liners and compared the results with those from conventional leachate immersion tests on the same GM. From top down, the composite liner cells comprised a 19 mm gravel ("leachate collection") layer, a 270 g/m^2 needle punched nonwoven geotextile protection layer, a GM (GM-2 in Table 1), a hydrated geosynthetic clay liner (GCL) and compacted moist Ottawa silica sand. The circular GM sample had diameter of 15 cm. The gravel layer was saturated with leachate that was refreshed every two weeks. The composite liner cells were placed in incubation baths at 85, 70, 55, and 26^{o}C (room temperature). The leachate immersion test on the same GM was conducted simultaneously. The leachate immersed samples had dimensions of 10 cm x 6 cm. The simulated composite liner cells were removed from the incubation tanks at after different times and the GM was tested for OIT, crystallinity and tensile properties.

The linear correlation between Std-OIT and HP-OIT was found during ageing of the sample (Rowe and Rimal 2008a). The leachate immersed GM experienced a consistently faster reduction in OIT than the GM in the composite liner at all test temperatures. The antioxidant depletion rates obtained at each temperature were significantly (2.2-4.8 times) higher for the leachate immersed GM samples than for the composite liner. This difference is attributed to the fact that for simple leachate immersion (a) the antioxidants diffusing out of the GM could be readily removed into the leachate hence maintaining a relatively high concentration gradient and outward diffusive flux, and (b) the GM 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 GM, thereby reducing the concentration gradient and outward diffusive flux. Furthermore only one side of the GM was exposed to leachate.

Although there was not a big difference in activation energies (58.9 kJ/mol for leachate immersed and 62.7 kJ/mol for the composite liner), the antioxidant depletion times in composite liner GM were substantially longer than for leachate immersed GM. The projected depletion time at 35^{o}C for the composite liner GM was about 40 years compared to about 10 years for the leachate immersed GM. The predicted antioxidant depletion time ranged from 335 years at 10^{o}C to 6 years at 60^{o}C for the composite liner GM. For the leachate immersed GM the depletion time ranged from 85 years at 10^{o}C to 2 years at 60^{o}C. These results clearly demonstrate the importance of liner temperature on the antioxidant depletion time of the GM. 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. These tests show that to obtain a more realistic estimate of GM service life one needs to perform test which simulated the expected liner condition in a composite liner.

For the composite liner GM at 85^{o}C there was an increase in crystallinity from an unaged value of 49% to 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. The increase in crystallinity may be attributed to re-crystallization and/or and post-crystallization that takes place due to incubation at high temperature (Dörner and Lang 1998). At 85^{o}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 GM. Given the three stage ageing process discussed earlier, the mechanical properties would not be expected to change significantly until after completion of the induction period (Hsuan and Koerner 1998). Thus the MFI results suggest that the GM was still in the second stage of degradation at 35 months. Tensile tests were conducted only on the composite liner GM samples. No significant change in tensile properties at yield and break was observed over the 35 months of testing at 85^{o}C for the composite liner GM. With the increase in crystallinity a small increase in tensile strength at yield was observed at 2 months. These results suggested that there was no significant physical and mechanical degradation of GM over the testing period.

4. AGEING IN THREE COMPOSITE LINER CONFIGURATIONS

For a landfill with a single liner, the barrier system is typically comprised of, from top to bottom, a gravel leachate drainage layer, a protection layer, a HDPE GM and either a geosynthetic clay liner (GCL) or a compacted clay liner (CCL) over the native subgrade. The protection layer is intended to protect the GM from physical damage. It is anticipated that it will also 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. Three protection layers above the GM were considered are as follows. The first involved a GT protection layer above the GM (denoted as CL-T). The second type consisted of GT and GCL above the GM (denoted as CL-TG). The third comprised a 1.5cm thick sand layer contained between two GT layers (denoted as CL-TST).

In 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 municipal solid waste (MSW) leachate (Lange et al. 2005). Furthermore, surfactants are known to get adsorbed in clay (Beigel et al. 1998). Thus, it was hypothesised that the GCL above the GM may provided 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. 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. In many practical applications the layer of sand will likely be thicker that 1.5 cm and the effect can be expected to be greater in these cases. The details regarding materials and procedure are given by Rowe and Rimal (2008a,b).

At each test temperature the antioxidant depletion rates for configuration CL-TG with the GCL above the GM was slower than for configuration CL-TST with the sand above the GM which, in turn, was slower than for the conventional GT protection layer configuration CL-T. It was found that the antioxidant depletion rates at each test temperature associated with CL-TG was 59 to 66% of that for CL-T. Also the CL-TST was 72 to 75% of that for CL-T. 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.

Arrhenius modeling of the antioxidant depletion rates is summarized in Table 3. There was only a very small percentage difference in the activation energies (+/-1%) for the three cases and this suggests that the tests are monitoring the same reactions. Higher activation energies were observed for all simulated liner GMs than that for leachate immersion 58.9 kJ/mol test. The excellent correlation (R^2 values around 0.98) for each Arrhenius equations (Table 3) suggests that the antioxidant depletion rates can be fairly well estimated at field temperatures.

Table 3. Arrhenius equations and activation energies for the three composite liner GM.

Exposure	Arrhenius Equation	E_a (kJ/mol)	R^2
CL-T	ln(s) = 20.06 – 7540/T	62.7	0.98
CL-TST	ln(s) = 19.56 – 7475/T	62.1	0.98
CL-TG	ln(s) = 19.88 – 7639/T	63.5	0.98

The time for depletion of antioxidants (Stage I) at 35^{o}C was 65 years for the CL-TG case, 50 years for CL-TST and 40 years for CL-T. In contrast, the antioxidant depletion time for immersed GM at 35^{o}C was 10 years. Two key observations can be made based from these results. First, the results obtained from immersion test which have been commonly used for assessing Stage I (antioxidant depletion time) of service life a 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^{o}C it was 230 years for CL-TG, 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 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 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 ageing and improve the long term performance of GM liners.

5. STAGE II AND III AND SERVICE LIFE IN LEACHATE IMMERSION TESTS

In this section the Stage II and Stage III of GM-1 described in Section 2 of this paper will be discussed. The change in tensile strength and strain at break at 85^{o}C are shown in Figure 3 together with OIT and MFI results. Stage I was completed with the reduction of OIT residual levels. In order to estimate Stage II and III a regression line was obtained for the break strength and strain data once it began to decrease. The intersection of the regression line with the 100% property retained line was taken as the end of Stage II. The intersection of the regression line with 50% property retained line was taken as the end of Stage III. At 85^{o}C the GM has completed the three stages (Table 4). The service life at 85^{o}C is estimated to be 67 months for tensile strength at break.

At a testing temperature of 55^{o}C, the GM is still in Stage II. The latest tensile strength test at 55^{o}C was taken after 54 months in Stage II. On basis of this information, a lower bound estimate of Stage II can be predicted assuming the Arrhenius time-temperature relationship between the Stage II time and temperature. The Arrhenius plot and activation energy of Stage II are shown in Figure 4. From this relationship, a conservative estimate of Stage II can be made at other service temperatures. The predictions from time time-temperature relationship for Stage II are provided in Table 5 for tensile properties at break.

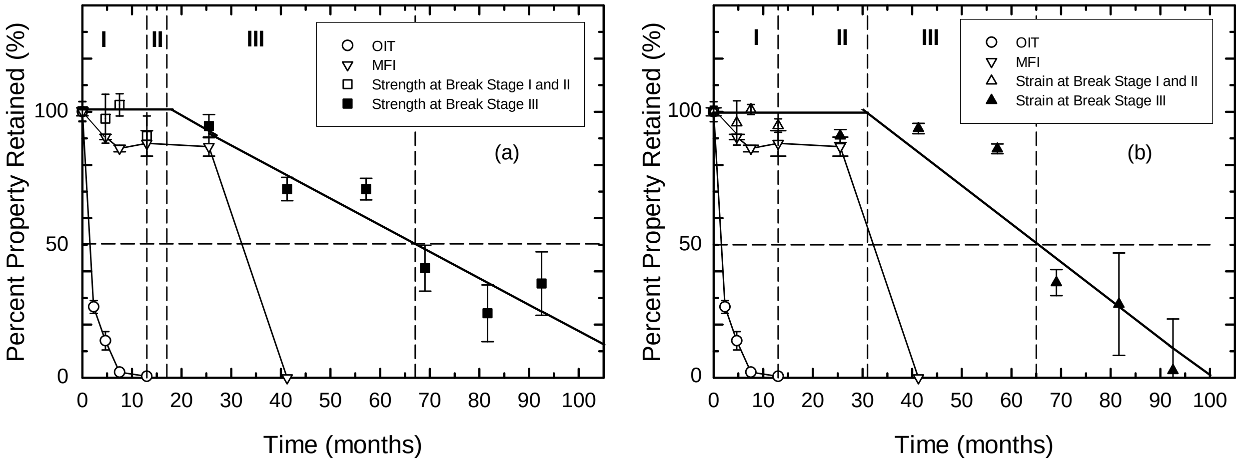

Figure 3. Plot of property retained at 85^{o}C in leachate (a) OIT, MFI and tensile break strength, (b) OIT, MFI and tensile break strain).

Table 4. The three stages in degradation of GM at 85^{o}C and 55^{o}C.

Temp. (^{o}C)	Stage I* (months)	Stage II (months)	Stage III (months)	Service life (months)	Property evaluated for stage II and III
85	13	4	50	67	Break strength
85	13	18	34	65	Break strain
55	39	>54	--	>93	Break strength
55	39	>54	--	>93	Break strain

Note: *Stage I calculated from measured depletion rates. Stage I from predicted depletion rates is 12 months at 85^{o}C and 45 months at 55^{o}C.

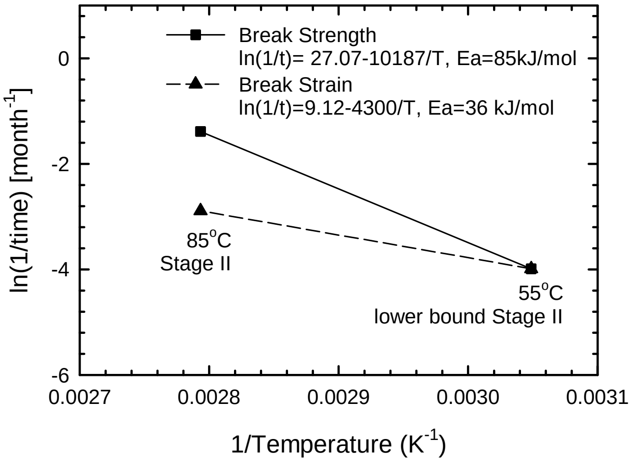

Figure 4. Arrhenius plot of Stage II. (Note: the GM has not completed Stage II at 55^{o}C. The lower bound value of 54 months used is the current time in Stage II).

From laboratory data for Stage III at 85^{o}C and activation energy of degradation mechanism (80kJ/mol) for air-water exposed PE pipe (Viebke et al. 1994; Bonaparte et al. 2002), Stage III can be estimated at different temperatures from:

$$\frac{s_{T1}}{s_{T2}} = \exp\left(-\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right) \qquad [3]$$

where, T_1= 85°C = 358K, T_2=extrapolation temperature, s_{T1} and s_{T2} are reaction rates, E_a=activation energy of 80kJ.mol^{-1} and R= universal gas constant (8.31 J.mol^{-1}.K^{-1}). Thus if t_1 and t_2 are the times for Stage III at temperature 85°C (based on the lab tests) and T_2 (temperature of interest).

$$t_2 = \frac{s_{T1}}{s_{T2}} \times t_1 \qquad [4]$$

The calculated length of Stage III at typical liner temperatures are given in Table 5. The estimated service life of the GM at 35°C as estimated from leachate immersion tests is 370 years (tensile strength at break) and 245 years (tensile strain at break). As noted in Section 3, the service life in a liner configuration may be expected to be longer than when immersed in leachate. It should be emphasized that the predictions in Table 5 are based on tests a two temperatures on one GM. They suggest that previous estimates of Stage II and III may have been conservative, however these new values should be used with considerable caution until more data is available since only the test at 85°C has reached the end of Stages II and III and hence an estimate of the Stage II time at 55°C has been used to get Stage II predictions and the activation energy of Vibeke et al. (1994), which has not been confirmed for this GM, was used to get Stage III.

Table 5. Service life predictions at typical liner temperatures.

Temp. °C	Stage I leachate immersion OIT data (years)	Stage II leachate immersion (years)	Stage III leachate immersion and Ea of degradation, 80kJ/mol (years)	Service life (years)	Stage II leachate immersion) (years)	Stage III leachate immersion and Ea of degradation, 80kJ/mol (years)	Service life (years)
	Evaluated from OIT	Evaluated from tensile break strength			Evaluated from tensile break strain		
20	25	185	1620	1830	20	1100	1145
35	10	35	325	370	10	220	245
50	5	7	75	90	6	50	65

6. OUTDOOR NATURAL WEATHERING

To evaluate the degradation of GM due to exposure to sunlight and natural weather conditions, GM-1 (Table 1) was exposed to natural heat, solar radiation, rain, humidity, atmospheric contaminants, thermal cycles and oxygen in air by placing samples on a wooden test frame inclined with a slope of 2H:1V in Ontario, Canada. The test frame was located in London, Ontario, Canada, at 43° 02'-N 81° 09'-W. from winter 1997 to summer 2002 where the average daily temperature was a maximum of 32.0 °C in summer and a minimum of –20.5 °C in the winter. The samples located in Kingston, Ontario, at 44° 16'-N 76° 30'-W from summer 2002 where the average daily temperature was maximum of 34.5 °C in summer and -33.0 °C in winter. The GM coupons had dimensions of about 30.5 cm x 38 cm. The OIT decreased from 133 min. to about 50 min. (i.e by 62%) over the 9 years of weathering. Tensile tests indicated that there was no significant change in mechanical properties over this period.

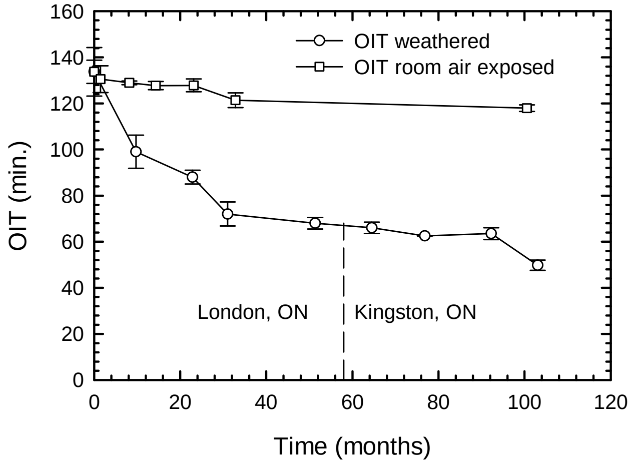

Figure 5: Depletion of antioxidant from weathered sample and laboratory air exposed sample.

Figure 5 shows significantly higher OIT depletion for the weathered GM than for a control GM sample exposed to air in the laboratory. Assuming an exponential depletion in antioxidants, the depletion rate for weathered sample was 0.0102 month^{-1}. At this rate it would take 46 years for the antioxidants to be completely depleted. The depletion rates for the control GM sample in laboratory was 0.0014 month^{-1} resulting an estimated depletion time of 333 years.

7. DURABILITY OF JET FUEL EXPOSED GM

A composite barrier comprising of a fluorinated high-density polyethylene (f-HDPE) GM and GCL was used to control the advective and diffusive migration of a hydrocarbon spill on Brevoort Island, Nunavut Territory, Canada (known as BAF-3). The f-HDPE GM were retrieved from the field site over the period of 2001 to 2004. The laboratory results of OIT, crystallinity, MFI and tensile tests indicated that the properties of the buried 1.5 mm thick f-HDPE GMs have not changed significantly since installation in 2001 (Rowe et al. 2007).

Samples of 1.5 mm thick HDPE GM (both untreated GM-3 and fluorinated GM-4 in Table 1) were exposed to jet fuel in the laboratory. The change in OIT, crystallinity, and tensile properties were monitored. Figure 6 illustrates change in standard OIT versus time in untreated GM (UGM) and fluorinated (FGM). An initial prediction of antioxidant depletion time was carried out based on 61 weeks of OIT data at room temperature (~23°C), based on initial OIT values of 135 min (UGM) and 137 min (FGM) and a residual OIT 0.5 min (unstabilized HDPE) (Rimal et al. 2007). For the untreated GM this was 112 weeks (2.2 years) while for the fluorinated GM it was 305 weeks (5.9 years). Thus the results indicated that the fluorination had beneficial effect and increases the antioxidant depletion time of the GM exposed to jet fuel.

Further monitoring of standard OIT after 61 weeks indicated that the UGM still had OIT of about 10 min at 213 weeks. The OIT value of FGM was also about 10 min at 213 weeks. Thus it was found that UGM had not completely depleted antioxidant to the residual value of 0.5 min. well past the predicted depletion time of 112 weeks. From these results it is concluded that the time for depletion of antioxidants will be well over 213 weeks (4.1 years).The antioxidant depletion times would be expected to be much longer at field temperatures in the Arctic, and so it can be inferred that the ‘‘service life’’ of the UGM will be greater than 4.1 years and that for the FGM well over 5.9 years.

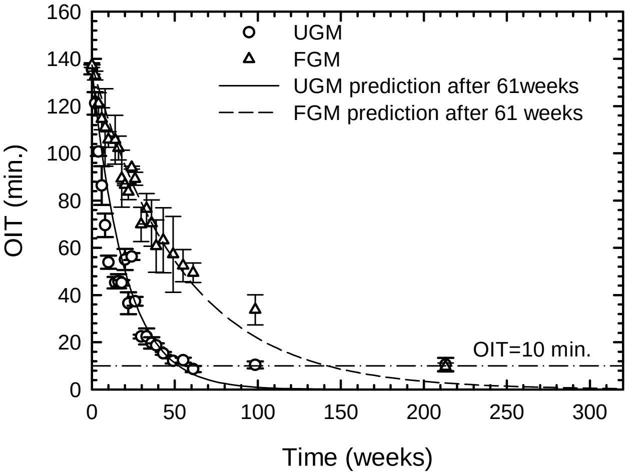

Figure 6: Variation of standard OIT with immersion time for UGM and FGM specimens exposed to jet fuel at room temperature. Error bars represent 1 standard deviation from 3-5 specimens.

8. SUMMARY AND CONCLUSIONS

The findings from a series of studies on the ageing and long-term performance of GMs have been presented. Based on the GMs tested (and it is noted that GMs are not all the same and that the results could be different for GM with different antioxidant packages) and currently available data, the following conclusions have been reached.

Immersion tests in air, water and leachate:

- Antioxidant depletion rates were faster for samples exposed to leachate than for water and slowest in air. The depletion rate in leachate-immersed samples was 2.5-4.0 times faster than that in water and 2.8-6.7 times faster than in air.

- The calculated antioxidant depletion time at a typical liner temperature of 35°C was 65 years in air, 35 years in water, 10 years in leachate and based on the immersion data, it was estimated to be 30 years for a GM with leachate on one side and unsaturated soil on the other side.
- The results from immersion test were conservative but highlighted the need for tests that more realistically simulate field exposure conditions than simple immersion tests.

Immersion versus composite liner in leachate:

- In the basic composite liner simulation, the geotextile above the GM was exposed with leachate while the bottom of the GM rested on a hydrated GCL. The results from OIT tests for this GM indicated that the antioxidant depletion rates were about 2.2-4.8 times slower for the simulated composite liner GM specimens than for leachate immersed specimens. The lower rates for the simulated liner are attributed to the slower extraction of antioxidants from two sides of the GM due to the different exposure to leachate on the top and bottom face of the composite liner GM, and possible build-up of antioxidants on the bottom interface of GM which can retard the antioxidant depletion processes.
- The results indicated that at a liner temperature of 35°C the antioxidant depletion time would be 40 years for the composite liner GM compared to 10 years for the leachate immersed GM. Thus the prediction from simple immersion test was confirmed to be quite conservative.

Ageing in three composite liner configurations:

- The results of accelerated ageing tests on GMs in composite liners were examined for three different protection layers (geotextile, geotextile and GCL and geotextile-1.5 mm sand-geotextile).
- The antioxidant depletion rates were dependent on the type of protection layer used. With the geotextile-GCL protection layer the antioxidant depleted at 59-66% of the rate for a geotextile layer alone. Also with the geotextile-sand-geotextile the depletion was 72-75% of that with a geotextile layer alone. Depletion of antioxidants in the composite liner GMs were significantly (13-46%) less than for GMs immersed in leachate.
- At 35°C, the estimate Stage 1 of the service life (antioxidant depletion) was highest for a GM with protection layers of a geotextile and GCL (65 years) followed by geotextile-sand-geotextile (50 years) and lowest for geotextile alone (40 years). These are much longer that 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-geotextile).

Service life of GM in landfill liners from immersion tests:

- The three stages of service life in leachate at 85°C was obtained for tensile properties at break. The total service life was 5.6 years (tensile break strength) and 5.4 years (tensile break strain).
- At lower testing temperature of 55°C the GM had completed Stage I in 39 months and was in Stage II for over 54 months. Thus the service life at 55°C would is greater than 93 months (7.8 years).
- The lower bound estimate of Stage II was made assuming the Arrhenius relationship for the Stage II between 85°C and 55°C. Predictions on Stage II were carried out at typical liner temperatures. A conservative estimate of the length of Stage II at 35°C was 35 years based on tensile break strength and 10 years based on tensile break strain.
- Stage III was evaluated using the stage III data at 85°C and the activation energy of degradation of 80 kJ/mol from the literature. At 35°C, Stage III was estimated to be 325 years based on tensile break strength and 220 years based on tensile break strain.
- The total predicted service life at 35°C was 245 years based on tensile break strain and 370 years based on tensile break strength.

Outdoor natural weathering:

- Results from outdoor natural weathering test at latitude 43-44°N suggested that it would take about 45 years for antioxidants to be depleted from the weathered sample. For the laboratory control sample in air it would take about 330 years.

Durability of jet fuel exposed GM:

- For the GM tested, it was found that the immersion in jet fuel substantially accelerates the standard OIT depletion rate relative to that observed in water or synthetic leachate.
- Fluorination of the HDPE GM provided a significant beneficial effect and the antioxidants depleted at much higher rate (2.7 times faster) for the untreated GM than for the fluorinated GM.
- The total standard OIT depletion time was estimated to be greater than 4.1 years for untreated GM and 5.9 years for the fluorinated GM at 23 °C and is expected to be much longer at field temperatures in the Arctic.

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REFERENCES

ASTM D 1238 Standard Test Method for Flow Rates of Thermoplastics by Extrusion Plastometer, *Annual Book of ASTM Standards,* American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA, Volume 08.01.

ASTM D1505 Standard Test Method for Density of Plastics by the Density Gradient Method, *Annual Book of ASTM Standards,* American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA, Volume 08.01.

ASTM D1603 Standard Test Method for Carbon Black Content in Olefin Plastics, *Annual Book of ASTM Standards,* American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA, Volume 08.01.

ASTM D3895 Standard Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry *Annual Book of ASTM Standards,* American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA, Volume 08.02.

ASTM D 5397 Standard Test Method for Evaluation of Stress Crack Resistance of Polyolefin Geomembranes using Notched Constant Tensile Load Test, *Annual Book of ASTM Standards,* American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA, Volume 04.13.

ASTM D5885 HP-OIT Standard Test Method for Oxidative Induction Time of Polyolefin Geosynthetics by High-Pressure Differential Scanning Calorimetry, *Annual Book of ASTM Standards,* American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA, Volume 04.13.

ASTM D6693 Standard Test Method for Determining Tensile Properties of Nonreinforced Polyethylene and Nonreinforced Flexible Polypropylene Geomembranes, Annual Book of Standards, Volume 04.13. *Annual Book of ASTM Standards,* American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA, Volume 04.13.

ASTM E794 Standard Test Method for Melting and Crystallization Temperatures by Thermal Analysis, *Annual Book of ASTM Standards,* American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA, Volume 14.02.

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, *Pesticide Science*, 54(1): 52-60.

Bonaparte, R., Daniel, D.E., and Koerner, R.M. (2002). *Assessment and Recommendations for Improving the Performance of Waste Containment Systems*, EPA/600/R-02/099, United Stated Environmental Protection Agency.

Dörner, G. and Lang, R.W. (1998). Influence of various stabilizer systems on the ageing behavior of PE-ME-I. hot water ageing compression molding plaques, *Polymer Degradation and Stability*, 62: 421-430.

Hsuan, Y.G., and Koerner, R.M. (1998). Antioxidant depletion lifetime in high density polyethylene geomembranes." *Journal of Geotechnical and Geoenvironmental Engineering, ASCE,* 124(6): 552-541.

Lange, K., Rowe, R.K., and Jamieson, H.J. (2005). Attenuation of heavy metals by geosynthetic clay liners, *Geo-Frontiers 2005 Conference*, Robert M. Koerner, George R. Koerner, Y. Grace Hsuan, Marilyn V. Ashley - Editors, January 24–26, 2005, CD-ROM, 8pp, Austin, Texas, USA.

Müller W.W. (2007). *HDPE Geomembranes in Geotechnics*. Springer Verlag, Heidelberg, Germany.

Müller, W. and Jakob, I. (2003). Oxidative resistance of high-density polyethylene geomembranes, *Polymer Degradation and Stability*, 79: 161-172.

Rimal, S., Rowe, R.K. and Bathurst, R.J. (2007). Durability of fluorinated high density polyethylene (f-HDPE) geomembrane exposed to hydrocarbons in the arctic, *60th Canadian Geotechnical Conference*, Ottawa, 2161-2166.

Rimal, S., Rowe, R.K. and Hansen, S. (2004). Durability of geomembrane exposed to jet fuel A-1, *57th Canadian Geotechnical Conference*, Quebec City, October, Section 5D, 13-19.

Rowe, R.K., Quigley, R.M., Brachman, R.W.I., and Booker, J.R. (2004). *Barrier Systems for Waste Disposal Facilities*, 2nd Edition, Spon Press, 587p.

Rowe, R. K. (2005). Long-term performance of contaminant barrier systems, *Geotechnique*, 55(9): 631–678.

Rowe, R.K., Mukunoki, T., Bathurst, R.J., Rimal, S., Hurst, P., and Hansen, S. (2007). Performance of a geocomposite liner for containing Jet A-1 spill in an extreme environment, *Geotextiles and Geomembranes,* 25: 68-77.

Rowe, R.K., and Rimal, S. (2008a). Depletion of antioxidants from an HDPE geomembrane in a composite liner, *Journal of Geotechnical and Geoenvironmental Engineering, ASCE*, *(in press)*.

Rowe, R.K., and Rimal, S. (2008b). Ageing of HDPE Geomembrane In Three Composite Landfill Liner Configurations, *Journal of Geotechnical and Geoenvironmental Engineering, ASCE*, *(in press)*.

Sangam, H.P., and Rowe, R.K. (2002). Effects of exposure conditions on the depletion of antioxidants from high-density polyethylene (HDPE) geomembranes, *Canadian Geotechnical Journal*, 39: 1221-1230.

Viebke J. Elble E., Ifwarson M. and Gedde U.W. (1994). Degradation of unstabilized medium-density polyethylene pipes in hot-water applications, *Polymer Engineering and Science*, 34(17): 1354-1361.