

Leachate chemical composition effects on OIT depletion in an HDPE geomembrane

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Received 19 June 2007, revised 25 November 2007, accepted 17 December 2007

ABSTRACT: Results of series of tests examining the effect of different chemical constituents found in municipal solid waste leachate on the degradation of a high-density polyethylene (HDPE) geomembrane are reported. Geomembrane samples were incubated in four synthetic leachates consisting of different combinations of volatile fatty acids, inorganic nutrients, trace metal solution, and surfactant at temperatures of 85°C, 70°C, 55°C, 40°C and 22°C. It is shown that the leachate should be replaced every two weeks to maximise the depletion of antioxidants from the geomembrane. Arrhenius modelling gave activation energies for antioxidant depletion of between 62.5 and 64.0 kJ/mol. The small difference in activation energies implies that the four leachates examined are similar in terms of antioxidant depletion rate. There was no evident effect of the difference in these leachates on crystallinity, MFI, or tensile properties during the testing period. However, the fastest antioxidant depletion was observed for the simplest leachate, comprising trace metals and surfactant in water. Results are also reported for a second series of tests involving 18 different immersion media with different concentrations of trace metals and surfactant. Based on an examination of solutions with pH between 4 and 10, it is found that antioxidant depletion is the fastest for relatively acidic or basic solutions and the slowest for neutral solutions. Antioxidant depletion is the most sensitive to the presence of surfactant. As the surfactant concentration increases to about 1 ml/l the majority of the effect is evident. There was no further increase in effect for any increase in concentration beyond 5 ml/l.

Keywords: Geosynthetics, Geomembranes, Ageing, Antioxidant depletion, HDPE, Leachate

REFERENCE: Rowe, R. K., Islam, M. Z. & Hsuan, Y. G. (2008). Leachate chemical composition effects on OIT depletion in an HDPE geomembrane. *Geosynthetics International*, 15, No. 2, 136–151. [doi: 10.1680/gein.2008.15.2.136]

1. INTRODUCTION

High-density polyethylene (HDPE) geomembranes are extensively used as liners for municipal solid waste (MSW) landfills because of their excellent chemical resistance, high puncture and tensile strength, and high modulus of elasticity (August and Tatzky 1984; Haxo 1990). As a result, unaged geomembrane behaviour and leakage through composite liners used in landfills have been the subject of considerable recent research (e.g. Cartaud *et al.* 2005a, 2005b; Chai *et al.* 2005; Stark and Choi 2005; Bouazza and Vangpaisal 2006; Koerner and Koerner 2006; Touze-Foltz and Barroso 2006; Take *et al.* 2007; Thusyanthan *et al.* 2007). However, an intact

geomembrane will experience some ageing or degradation due to the various physico-chemical effects that occur during its service life. Given that the contaminating lifespan of many of these landfills is in excess of a century, and may be many centuries (Rowe *et al.* 2004), it is important to address the question of long-term durability. Given the timescales involved, field experiments to assess the ageing characteristics are not feasible. Thus service life is usually assessed using laboratory-accelerated ageing tests. This may involve the immersion of the geomembrane in a fluid similar to that expected in the field. The composition of MSW landfill leachate depends on the age and nature of the waste, operating

conditions and the hydrological budget of the landfill (Castaldo *et al.* 1996). The concentrations of constituents in leachate can change daily; however, the basic components are well established, and comprise organics (predominantly volatile fatty acids, VFAs), inorganics (predominantly salts, but with low concentrations of trace metals), and surfactants. Given the variability in concentrations, it is almost impossible to carry out a reproducible tests using actual field leachate. A synthetic leachate overcomes the shortcomings of using real leachate provided that the fundamental degradation mechanisms are not altered. This paper seeks to identify the critical characteristics of leachate with respect to antioxidant depletion and hence the first stage in geomembrane ageing.

Hsuan and Koerner (1998) conducted accelerated ageing tests on 1.5 mm HDPE geomembrane in two different incubation systems at four elevated temperatures (55–85°C). In the first system, the geomembrane samples were fully immersed in water, whereas in the second system geomembrane samples were sandwiched between saturated sand (above) and dry sand (below) at 260 kPa. The results of the testing protocol suggested that antioxidants depleted at a faster rate for the water-immersed samples than for the samples with moist sand on one side only. These tests did not address the effect of leachate on the geomembrane.

Sangam and Rowe (2002b) conducted accelerated ageing tests using a 2.0 mm HDPE geomembrane at five different temperatures (22–85°C). They used three different incubation media: synthetic municipal solid waste (MSW) leachate, distilled water, and air. They showed that antioxidant depletion was much faster in liquids than in air. However, there was also a substantially higher depletion rate for synthetic-leachate-immersed samples than for water-immersed samples.

Accelerated ageing tests were performed by Müller and Jacob (2003) using 2.5 mm HDPE geomembranes at 80°C. Results were reported for samples immersed in a water bath for 6 years and in a forced-air oven for 13 years. Müller and Jacob described a two-stage degradation model for antioxidant depletion. Testing results showed that antioxidants depleted at a faster rate in water than in air. The authors showed that failure of the geomembranes was due to brittleness that developed in the geomembrane after complete depletion of the antioxidant. Thus they concluded that the slow loss of stabilisers controls the service life of HDPE geomembranes.

Studies conducted by Gulec *et al.* (2004) involved a 1.5 mm HDPE geomembrane incubated in synthetic acid mine drainage (AMD), acidic water with pH = 2, and deionised water at three different temperatures (60°C, 40°C and 20°C). Their results showed a faster antioxidant depletion rate in synthetic AMD than in acidic or deionised water.

It can be concluded from these investigations on HDPE geomembranes that: (a) liquid immersion gives faster antioxidant depletion than air ageing; and (b) the constituents in the immersion fluid can affect antioxidant depletion, with the lowest rate being for water. Since there are

different components in the MSW leachate, as discussed above, it is of interest to establish which components are responsible for the difference in depletion rate between water and synthetic leachate. Thus the objective of this study is to examine the effect of different components of a synthetic leachate on oxidative induction time (OIT) depletion, and to identify what the critical constituents are that need to be considered in future ageing tests.

2. DEGRADATION MECHANISMS AND DEPLETION OF ANTIOXIDANTS

Ageing is defined as a slow and irreversible evolution of material properties under environmental stresses. According to Hsuan and Koerner (1998), physical and chemical ageing mechanisms can take place simultaneously in the geomembrane. Physical ageing is a slow process, in which the polymer attempts to establish equilibrium from its as-manufactured non-equilibrium state. As a result of physical ageing, the crystallinity of the HDPE geomembrane increases (Petermann *et al.* 1976), but the covalent bonds do not break down. On the other hand, chemical ageing is associated with the breaking of covalent bonds, which leads to a reduction in engineering properties and eventually to the failure of the geomembrane (Schnabel 1981).

As a result of ageing or degradation, several detrimental effects occur in the polymer: loss of additives and plasticisers, change in molecular weight, formation of free radicals, and brittleness (Kulshershta 1992). Based on the exposure condition and polymer properties, different types of degradation mechanism can take place in the geomembrane, for example ultraviolet degradation, chemical degradation, biological degradation, degradation by swelling, degradation by extraction, oxidative degradation, and thermal degradation (Haxo and Nelson 1984; Koerner *et al.* 1990). Generally, there is more than one degradation mechanism acting at a given time, and the synergistic effects can accelerate degradation. Of the degradation mechanisms, oxidative degradation is believed to be the most harmful for HDPE geomembranes (Hawkins 1984). Owing to the oxidation of the polymer, free radicals are formed by auto-oxidation chain reactions (Kelen 1983). The formation of free radicals causes the breakdown of polymer chains, which leads to a decrease in molecular weight, and the geomembrane eventually become brittle and susceptible to environmental stress cracking (Tisinger and Giroud 1993). The oxidative reaction accelerates in the presence of transition metals (Osawa and Ishizuka 1973). The details of oxidative degradation can be found elsewhere (Grassie and Scott 1985; Hsuan and Koerner 1998; Sangam and Rowe 2002b). As described by Viebke *et al.* (1994) and Hsuan and Koerner (1998), the oxidative degradation of HDPE geomembrane can be divided into three distinct stages: Stage I, depletion time of antioxidants; Stage II, induction time to onset of polymer degradation; and Stage III, degradation of the polymer to decrease some property or properties to an arbitrary level (e.g. to 50% of the original value).

Antioxidants prevent the degradation of HDPE geomembrane during manufacturing, and prevent the oxida-

tion reactions from taking place during the first stage of service life. As ageing progresses, the amount of antioxidants gradually decreases. The depletion can be caused either by chemical reactions with oxygen, free radicals or hydroperoxide, and/or by physical loss (e.g. diffusion, extraction and volatilisation) due to leaching (Gedde *et al.* 1994; Hsuan and Koerner 1998; Sangam and Rowe 2002b). In addition, the rate of depletion is related to the type, amount and combination of antioxidants used, the temperature, and the nature of the exposure medium (Fay and King 1994; Hsuan and Koerner 1998; Sangam and Rowe 2002b).

3. EXPERIMENTAL INVESTIGATION

3.1. Materials

The 1.5 mm HDPE geomembrane used in this study was manufactured by GSE Lining Technology Inc., Houston, TX. The average properties of the geomembrane are as follows: Std-OIT (ASTM D3895) = 174 min; HP-OIT (ASTM D5885) = 903 min; crystallinity (ASTM E794) = 37.7%; MFI (ASTM D1238) = 0.43 g/10 min; density (ASTM D792) = 0.946 g/cm³; tensile properties (ASTM D6693): yield stress = 28.5 kN/m, yield strain = 23.5%, break stress = 60.8 kN/m, break strain = 945%.

3.2. Exposure conditions

Two series of tests were conducted. In Series 1, the geomembrane samples were incubated in four different leachates (Tables 1 and 2) at five different temperatures (85°C, 70°C, 55°C, 40°C and 22°C), whereas in Series 2

the samples were incubated in 18 different leachates (Table 3) at 85°C only. Distilled water was used in making leachates for both testing programmes.

Geomembrane coupons (190 mm by 100 mm) were placed in 4 l glass containers. The coupons were separated using 5 mm glass rods to ensure that there was leachate in contact with all surfaces. The synthetic leachates for the Series 1 tests were prepared by using different combinations of volatile fatty acids, inorganic nutrients, trace metals, and surfactant. The chemistry of synthetic leachate 1 was based on data for leachate from the Keele Valley Landfill in Ontario. It is important to note that surfactants are common in MSW landfills, arising predominantly from the disposal of laundry detergents or bath soaps in the waste stream. Several researchers have observed the presence of surfactant in different MSW landfill leachates (e.g. Maisonneuve *et al.* 1997; Hrapovic 2001; Kjeldsen *et al.* 2002; Borghi *et al.* 2003). In this study, a representative surfactant, Igepal[®] CA720, which is generally used in environmental stress crack tests at temperature exceeding 50°C, was used. The leachates of the Series 2 tests were prepared by changing the concentration of surfactant, trace metals, and pH (Table 3). To examine the effect of a change in the surfactant, one test (Test TD) was conducted using commercial Tide[®] powder. The concentration of Tide[®] powder detergent was 5 g/l.

To evaluate the effects of leachate renewal duration on the depletion of antioxidants in the Series 1 tests, leachates at 85°C were completely replaced at periodicities of every one, two, and four weeks. At other testing temperatures (70°C, 55°C, 40°C and 22°C), the leachates were renewed every two weeks.

Table 1. Composition of synthetic leachates in Series 1 tests

Component	Concentration (mg/l, except where noted)			
	Leachate 1 ^a	Leachate 2	Leachate 3	Leachate 4
Volatile fatty acids				
Acetic acid (ml/l)	7	–	–	7
Propionic acid (ml/l)	5	–	–	5
Butyric acid (ml/l)	1	–	–	1
Inorganic nutrients				
NaHCO ₃	3012	–	3012	–
CaCl ₂	2882	–	2882	–
MgCl ₂ .6H ₂ O	3114	–	3114	–
MgSO ₄ .7H ₂ O	319	–	319	–
NH ₄ HCO ₃	2439	–	2439	–
CO(NH ₂) ₂	695	–	695	–
NaNO ₃	50	–	50	–
K ₂ CO ₃	324	–	324	–
KHCO ₃	312	–	312	–
K ₂ HPO ₄	30	–	30	–
Trace metal solution ^b (ml/l)	1	1	1	1
Others				
Surfactant, Igepal [®] CA720 (ml/l)	5	5	5	5
pH (adjusted by adding either NaOH or H ₂ SO ₄) (–)	6	6	6	6
Eh (adjusted by adding 3% w/v Na ₂ S.9H ₂ O) (mV)	–120	–	–120	–120

^aBased on Hrapovic (2001).

^bSee Table 2 for the compositions.

Table 2. Composition of trace metal solution (modified from Hrapovic 2001)

Component	Formula	mg/L (except where noted)
Ferrous sulphate	FeSO ₄ .7H ₂ O	2000
Boric acid	H ₃ BO ₃	50
Zinc sulphate heptahydrate	ZnSO ₄ .7H ₂ O	50
Cupric sulphate pentahydrate	CuSO ₄ .5H ₂ O	40
Manganous sulphate monohydrate	MnSO ₄ .H ₂ O	500
Ammonium molybdate tetrahydrate	(NH ₄) ₆ Mo ₇ O ₂₄ .4H ₂ O	50
Aluminium sulphate 16-hydrate	Al ₂ (SO ₄) ₃ .16H ₂ O	30
Cobaltous sulphate heptahydrate	CoSO ₄ .7H ₂ O	150
Nickel (II) sulphate	NiSO ₄ .6H ₂ O	500
Sulphuric acid (ml/l)	H ₂ SO ₄	1

Table 3. Test description with antioxidant depletion rate for Series 2 tests

Test designation	Composition	pH	Antioxidant depletion rate (month ⁻¹)
CL2 ^a	S + TM + W	6	1.169
SW	S + W + R	6	1.172
TMW	TM + W + R	6	0.333
pH4L2	S + TM + W + R	4	1.216
pH6L2	S + TM + W + R	6	1.173
pH8L2	S + TM + W + R	8	1.200
pH10L2	S + TM + W + R	10	1.305
pH4W	W + R	4	0.339
pH6W	W + R	6	0.331
pH8W	W + R	8	0.335
pH10W	W + R	10	0.345
2SL2	2 × S + TM + W + R	6	1.183
2TML2	S + 2 × TM + W + R	6	1.170
SD2L2	0.5 × S + TM + W + R	6	1.116
SD5L2	0.2 × S + TM + W + R	6	1.045
SD10L2	0.1 × S + TM + W + R	6	0.871
SD100L2	0.01 × S + TM + W + R	6	0.367
TD	Tide detergent + W + R	6	0.424

^aControl test same as test with leachate 2.

Note: S = surfactant; TM = trace metal; W = water; R = reducing agent (Na₂S.9H₂O).

3.3. Test methods

3.3.1. Oxidative induction time (OIT) test

The oxidative induction time (OIT) can be used to assess the amount of antioxidant present in the geomembrane (Tisinger 1989; Dudzik and Tisinger 1990; Hsuan and Koerner 1995, 1998; Surmann *et al.* 1995; Maisonneuve *et al.* 1997; Sangam and Rowe 2002b; Gulec *et al.* 2004; Rimal *et al.* 2004). A TA Instruments Q-100 series differential scanning calorimeter (DSC) was used in this study. Both standard OIT (Std-OIT) and high-pressure OIT (HP-OIT) tests were conducted in accordance with ASTM D3895 and ASTM D5885, respectively; however, most of the tests were performed using the Std-OIT method. The Std-OIT tests were conducted at an isothermal temperature of 200°C and 35 kPa oxygen pressure with a flow rate of 50 ml/min. The HP-OIT tests were conducted at a test temperature of 150°C under 3500 kPa of oxygen pressure. A 6–10 mg specimen was used in both testing methods.

3.3.2. Crystallinity test

The degree of crystallinity greatly interferes with some of the physical and mechanical properties of polymeric

materials, e.g. yield stress, modulus of elasticity, impact resistance, density, and permeability (Sperling 1992; Fann *et al.* 1998; Kong and Hay 2002). In this study, the percentage crystallinity of the HDPE geomembrane was measured according to ASTM E794 using the same DSC as used to obtain OIT. In this test, a known mass of geomembrane sample was heated to 200°C at a rate of 10°C/min under nitrogen atmosphere. The heat of fusion of 100% crystalline HDPE, i.e. 293 J/g (Brandrup *et al.* 1999), was used to calculate the percentage crystallinity of the samples.

3.3.3. Melt flow index (MFI) test

The MFI test was conducted in accordance with ASTM D1238 using a Dynisco Melt Indexer (model D4002). The test measures the amount of molten polymer extruded through an orifice of specified diameter at 190°C in 10 min under a constant load of 2.16 kg. The result is expressed in g/10 min. The MFI is a qualitative testing method for assessing the molecular weight of polymeric materials, and is a good indicator of oxidation in different polymers (Hsuan and Koerner 1998). Generally, a decrease

in MFI indicates an increase of molecular weight by cross-linking reactions, whereas an increase in MFI indicates a decrease in molecular weight due to chain scission reactions.

3.3.4. Tensile test

The tensile properties of the geomembrane were evaluated according to the ASTM D6693 testing method using an Instron[®] Universal Testing Machine (model 3396) equipped with a 5 kN load cell and self-aligning wedge grips. The test was performed using dumbbell-shaped specimens at a strain rate of 50 mm/min. For any specific sampling event, ten samples were tested—five along the machine direction and five along the cross direction—and the average is reported in the results section.

4. RESULTS AND DISCUSSION

The samples in Series 1 were tested for OIT, crystallinity, MFI, and tensile properties. The samples in Series 2 were tested for OIT only. Moreover, results presented below in Sections 4.2–4.4 for crystallinity, MFI and tensile properties are from samples for which leachates were replaced every two-weeks.

4.1. Antioxidant depletion evident from Std-OIT and HP-OIT tests

The type of antioxidants used during the manufacture of the geomembrane was not known. Therefore several HP-OIT tests were conducted to verify that the higher temperature in the Std-OIT test did not volatilise the antioxidants used in the formulation of the geomembrane. Figure 1 shows a linear relationship between Std-OIT and HP-OIT for samples incubated at 85°C in leachate 1. A similar linear relationship has been observed by other researchers for other geomembranes (Hsuan and Koerner 1998; Sangam and Rowe 2002b; Gulec *et al.* 2004). The linear relationship indicates that either Std-OIT or HP-OIT

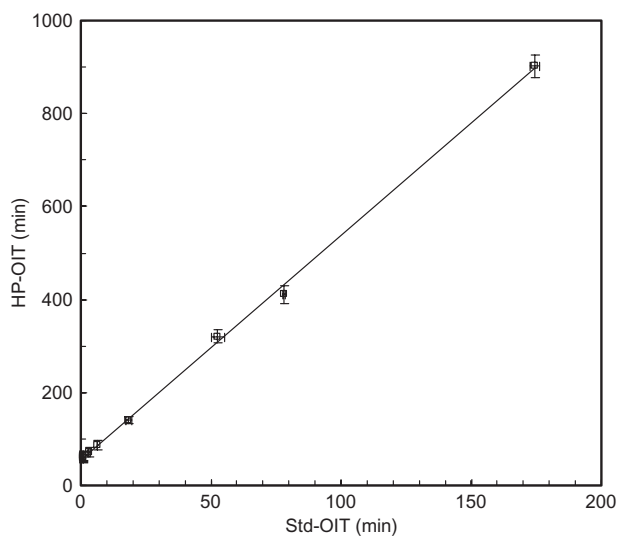


Figure 1. Variation in Std-OIT and HP-OIT in leachate 1 at 85°C (Series 1)

can be used to predict the depletion of antioxidants of this geomembrane. The linear variation also suggests that thiosynergists or hindered amines whose effective temperature is less than 200°C are not present in the geomembrane, and most likely the antioxidants used in the formulation of this geomembrane are phosphites and hindered phenols, which are effective up to a temperature of 300°C (Hsuan and Koerner 1998).

4.2. Antioxidant depletion in the Series 1 tests

The depletion of antioxidant in the immersion media (e.g. leachate and water) followed an exponential decay pattern, as expressed by

$$\text{OIT}_t = \text{OIT}_0 e^{-st} \quad (1)$$

where OIT_t is the OIT remaining at any time t in the geomembrane (minutes), OIT_0 is the initial OIT (minutes), s is the antioxidant depletion rate (month^{-1}), and t is the leaching time (month). By taking natural logarithms on both sides, Equation 1 can also be expressed as

$$\ln(\text{OIT}_t) = -st + \ln(\text{OIT}_0) \quad (2)$$

The variation in logarithm of OIT ($\ln(\text{OIT})$) with time for geomembranes immersed in leachate 1 at different temperatures is shown in Figure 2. At least five replicate samples were tested at each sampling event, and the average was taken for each data point. The standard deviation of the data points is represented by the vertical bars. The straight-line relationship between $\ln(\text{OIT})$ and ageing time represents a first-order decay pattern for the antioxidant depletion, and the slope of each line represents the antioxidant depletion rate. It can be seen that the slope of the lines increased with increasing temperature, which indicates that OIT depleted at a greater rate at higher temperature. These results are similar to those observed by other researchers for other geomembranes (Hsuan and Koerner 1995, 1998; Hsuan and Guan 1998; Sangam and Rowe 2002b; Gulec *et al.* 2004). There was complete depletion of antioxidant after around 4.5 and 20 months at 85°C and 70°C, respectively, indicating that Stage I of the

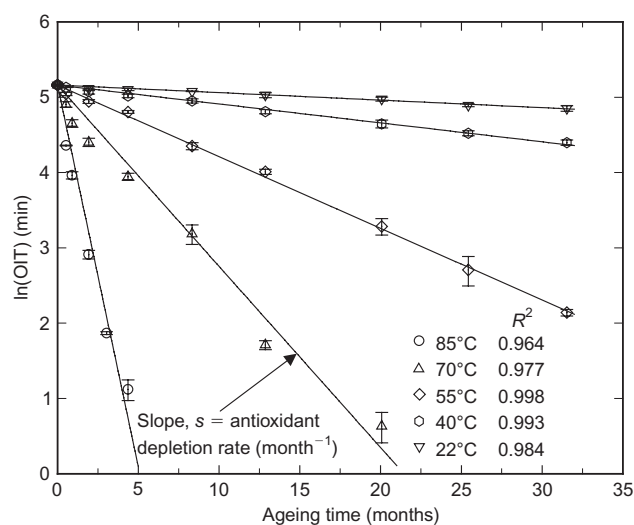


Figure 2. Variation in $\ln(\text{OIT})$ with time at different temperatures in leachate 1 (Series 1)

three stage degradation model described by Hsuan and Koerner (1998) had been completed at these temperatures. Antioxidants have not been consumed completely at other testing temperatures (e.g. 55°C, 40°C and 22°C) within the testing period of 31.5 months. Similar trends were also observed for geomembrane samples incubated in other leachates. The data points after 4.5 and 20 months at 85°C and 70°C, respectively, are not included in producing the regression line because of the complete depletion of antioxidants beyond those times at these temperatures.

4.2.1. Effects of leachate renewal durations

Figure 3 shows the variation in $\ln(\text{OIT})$ with time at 85°C when leachates were renewed at one-, two- and four-week intervals. Table 4 provides a comparison of antioxidant depletion rates for different leachate renewal intervals. The depletion rate of four-week leachate renewal interval was found to be statistically different from that for one-

and two-week replacement, and was approximately 90% of that observed with a one-week renewal period. However, there was no statistically significant difference for one- and two-week renewal intervals. According to Bertoldo and Ciardelli (2004), the depletion of phenolic antioxidants in hot water is caused by complex chemical reactions. They also observed degradation by-products of phenolic antioxidants in the leached water. It is possible that the reaction kinetics would be slower if enough degradation by-products were present in the water. Thus the slower depletion rate at four-week replacement interval compared with one- and two-week replacement may be due to: (a) the increased level of antioxidants, and/or antioxidant by products, in the leachate decreasing the outward diffusion of antioxidant from the geomembrane into the leachate, and/or (b) consumption of the small amount of dissolved oxygen (1.5 mg/l) in the leachate. In any event, to be conservative, it appears that for labora-

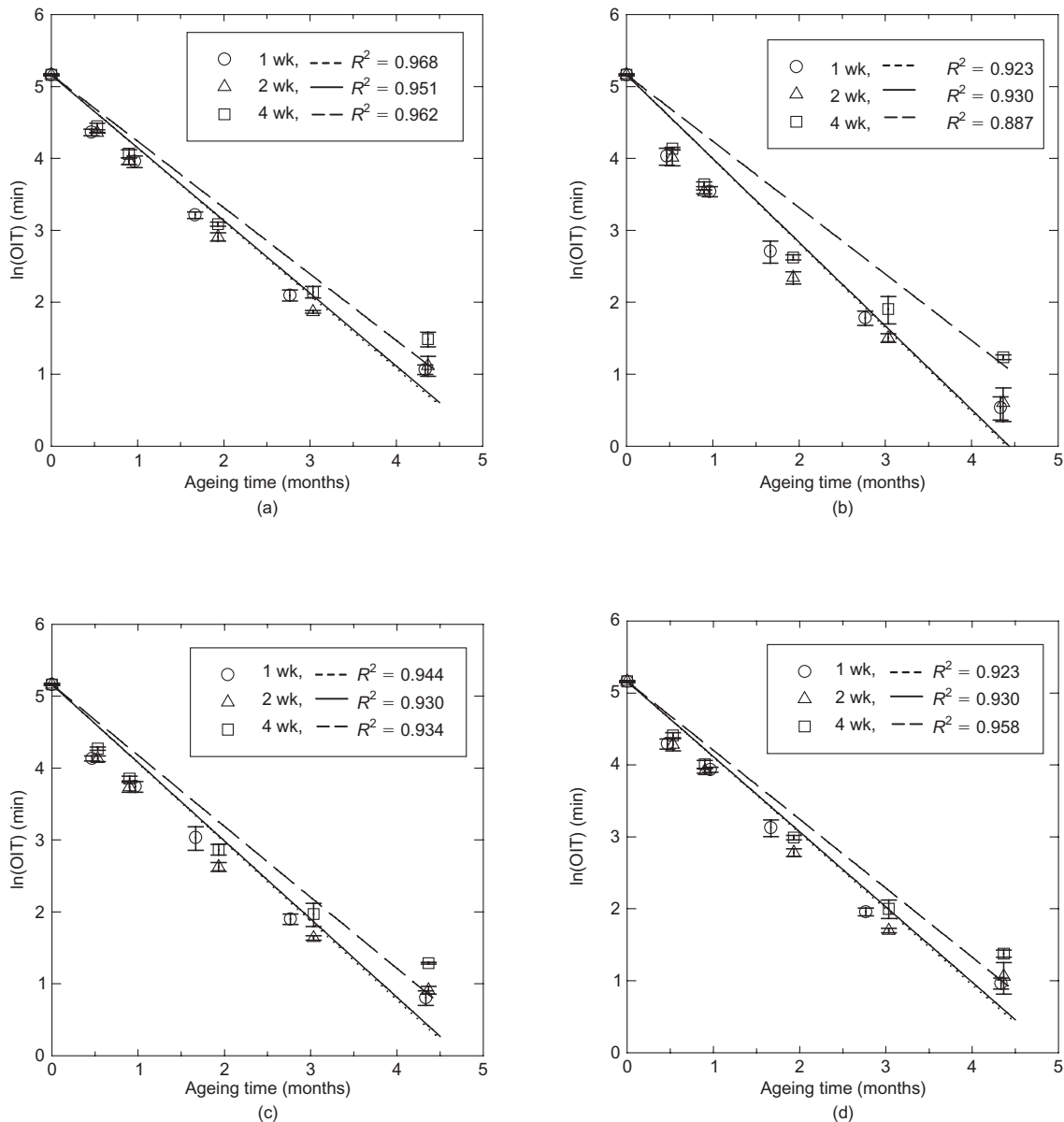


Figure 3. Variation in $\ln(\text{OIT})$ with time at 85°C in four different leachates when leachates were renewed at one, two, and four-week intervals (Series 1): (a) leachate 1; (b) leachate 2; (c) leachate 3; (d) leachate 4

Table 4. Comparison of antioxidant depletion rate in four different leachates for one, two, and four-week leachate renewal intervals at 85°C in Series 1 tests

Leachate type	Antioxidant depletion rate (month ⁻¹)			Antioxidant depletion rate normalised to one week		
	1-week interval (s_1)	2-week interval (s_2)	4-week interval (s_4)	s_1/s_1	s_2/s_1	s_4/s_1
Leachate 1	1.021	1.012	0.924	1.00	0.99	0.90
Leachate 2	1.172	1.164	1.022	1.00	0.99	0.87
Leachate 3	1.097	1.087	0.987	1.00	0.99	0.90
Leachate 4	1.055	1.045	0.959	1.00	0.99	0.91

tory-accelerated ageing tests, such as those undertaken in this paper, leachate should be replaced every two weeks.

4.2.2. Effects of leachate composition

Figure 4 shows the variation in $\ln(\text{OIT})$ as a function of leaching time in four different leachates at five different temperatures, with the leachates being replaced every two weeks. No statistically significant difference was observed (at the 95% confidence level) between the OIT depletion data for samples immersed in leachates 1 and 4. However, there were some (albeit small) differences between leachates 1 and 3, between leachates 1 and 2, between leachates 2 and 3, and between leachates 2 and 4. Samples that were immersed in leachate 2, which comprised trace metals and surfactant, exhibited the highest antioxidant depletion rate (Table 5). It should be noted that the same amounts of trace metals and surfactant were added to all four leachates. The lower depletion rate in leachates 1, 3 and 4 is probably due to the presence of fatty acids and/or inorganics. However, while one could not conclude that the results for leachates 1, 3 and 4 were the same as for leachate 2 at the 95% confidence level, the difference was small and may not be real. Assuming that the differences are real, the apparent trend in antioxidant depletion rates follows the order (highest to lowest): leachate 2 (trace metals and surfactant only) > leachate 3 (trace metals, surfactant, and inorganics) > leachate 4 (trace metals, surfactant, and VFAs) \geq leachate 1 (full leachate), as is evident from Table 5. If these differences are real, it is not clear why there would be faster antioxidant depletion for the simplest leachate (leachate 2).

4.3. Antioxidant depletion in the Series 2 tests

Given that the Series 1 tests found that the fastest depletion of antioxidants was for the simplest leachate (no. 2), it was of interest to establish the effect of the concentration of surfactant and trace metals in the leachate, and the effect (if any) of pH. Thus the Series 2 tests seek to address this question. Some Series 2 tests were conducted by changing the pH of water and leachate 2 (in a reduced condition) to 4, 6, 8 and 10. MSW landfills typically generate a highly reduced anaerobic leachate (except at very early times), and so a reducing agent was added in all of the immersion media to simulate field conditions. Table 3 shows the composition of all leachates with pH conditions and the observed antioxidant depletion rates at the end of the testing period.

Figures 5 and 6 show the depletion of antioxidant with

time at pH 4–10 for samples immersed in water and leachate 2, respectively. No statistically significant difference in antioxidant depletion rate was observed with respect to the change of pH of water alone. For leachate 2, changing the pH did have some effect, and the antioxidants depleted at a somewhat faster rate at pH 4 and pH 10 than for the typical leachate pH range from 6 to 8. Test CL2 (Series 2) is a replicate of the Series 1 test in leachate 2 at 85°C. The depletion rate of antioxidant was almost the same in these two tests: for example, 1.169/month in Test CL2 in Series 2 (Table 3) and 1.164/month in test with leachate 2 in Series 1 at 85°C (Table 5). These results suggest that these tests are quite repeatable within the same experimental framework. Furthermore, the addition of reducing agent did not result in any change in antioxidant depletion rate. For example, the depletion rates of Test pH6L2 (1.173/month) and Test CL2 (1.164/month) were comparable (Table 3).

Figure 7 shows the depletion of antioxidant with time at pH 6 for different combinations of surfactant and trace metals. The presence of trace metals had little or no effect on OIT depletion (e.g. Test TMW gives a depletion rate, 0.333/month, similar to the rate of 0.331/month obtained for Test pH6W with water; Table 3). In contrast, the presence of surfactant (e.g. in Tests SW, 2SL2 and 2TML2) had a dominant effect on antioxidant depletion. The depletion rate in leachate with 5 ml/l of surfactant (Test SW) was 3.5 times higher than in tests where there was no surfactant (Tests TMW and pH6W). These results suggest that, for this geomembrane, trace metals do not affect Stage I of the three-stage oxidative degradation process. However, this does not necessarily mean that they would not accelerate the degradation process in Stage II and/or Stage III.

The depletion rate in full leachate (leachate 1, Series 1 test) was 3.1 times faster than in pure water (e.g. Test pH6W). This difference in antioxidant depletion rates is comparable to that observed by Sangam and Rowe (2002b) for a 2.0 mm geomembrane: they observed a 1.6–3.2 times faster antioxidant depletion rate in synthetic leachate than in water.

Figures 8 and 9 show the effect of surfactant concentration on the depletion of antioxidant. A sharp increase in antioxidant depletion rate was observed when the concentration of surfactant increased from 0.05 ml/l (Test SD100L2) to 1 ml/l (Test SD5L2). The rate of increase of the antioxidant depletion rate gradually decreased between the surfactant concentration of 1 and 5 ml/l (Figure 9).

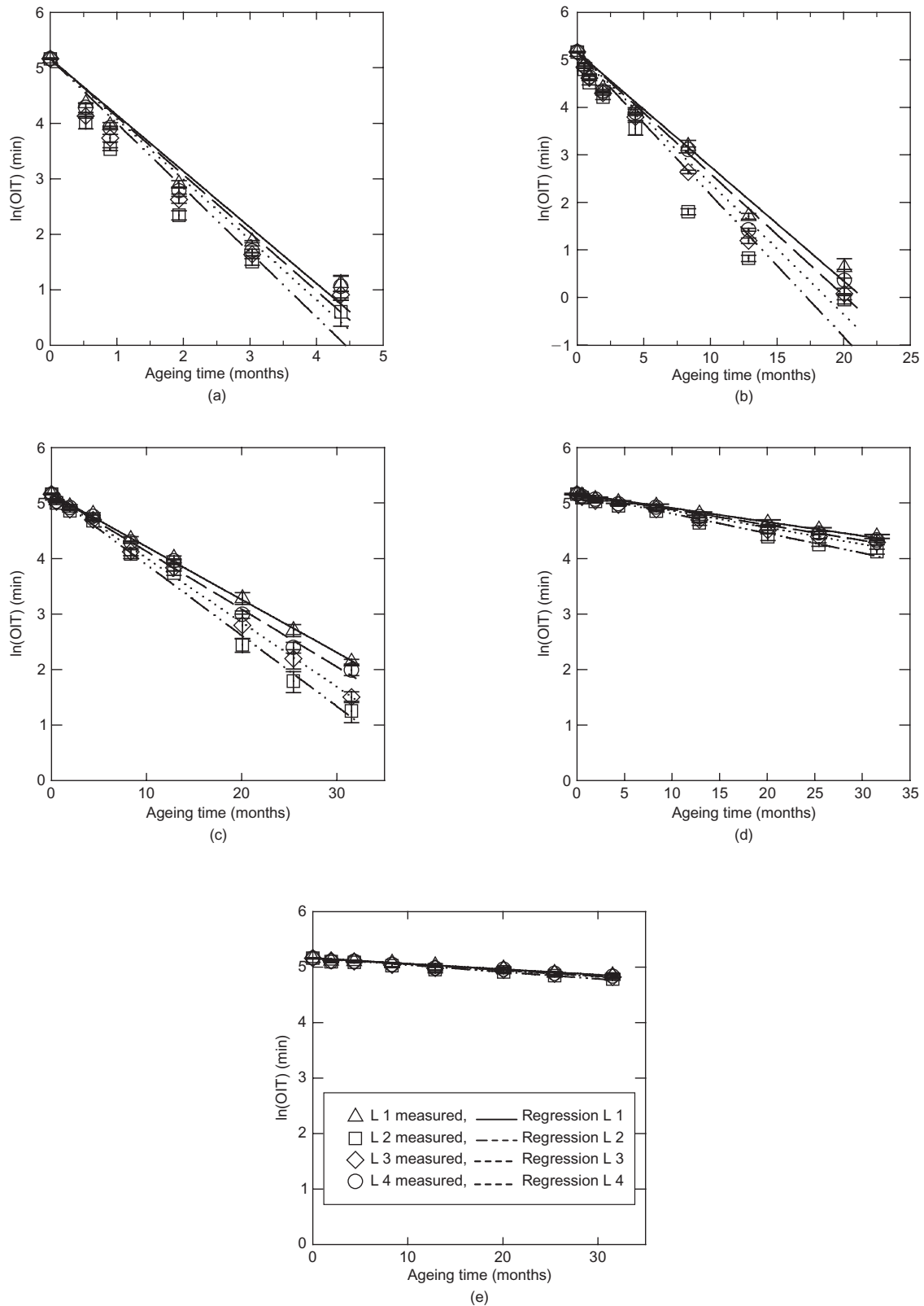


Figure 4. Variation in $\ln(\text{OIT})$ with time at different temperatures in four different leachates (Series 1); R^2 values are given in Table 5: (a) 85°C; (b) 70°C; (c) 55°C; (d) 40°C; (e) 22°C

The depletion rate did not show any additional increase for surfactant concentrations between 5 and 10 ml/l. These results suggest that a small amount of surfactant is sufficient to change the interaction between water and the geomembrane and to increase the rate of antioxidant depletion from HDPE geomembranes. The full effect was

found to occur for a concentration of 5 ml/l of Igepal[®] CA720 in water. Tests with powdered Tide[®] detergent (Test TD) gave a depletion rate of 0.424/month, which is 1.3 times faster than the depletion rate in water, indicating that commercial detergent has the same action as the surfactant used in this study (Igepal[®] CA720). It is

Table 5. Antioxidant depletion rates in four different leachates at five different temperatures: Series 1 tests

Temperature (°C)	Leachate type	Antioxidant depletion rate (month ⁻¹)	R ²
85	Leachate 1	1.012	0.964
	Leachate 2	1.164	0.914
	Leachate 3	1.087	0.930
	Leachate 4	1.045	0.951
70	Leachate 1	0.241	0.977
	Leachate 2	0.299	0.926
	Leachate 3	0.276	0.972
	Leachate 4	0.256	0.974
55	Leachate 1	0.095	0.998
	Leachate 2	0.128	0.993
	Leachate 3	0.119	0.997
	Leachate 4	0.104	0.995
40	Leachate 1	0.025	0.993
	Leachate 2	0.036	0.980
	Leachate 3	0.030	0.970
	Leachate 4	0.028	0.985
22	Leachate 1	0.010	0.984
	Leachate 2	0.013	0.955
	Leachate 3	0.011	0.968
	Leachate 4	0.011	0.944

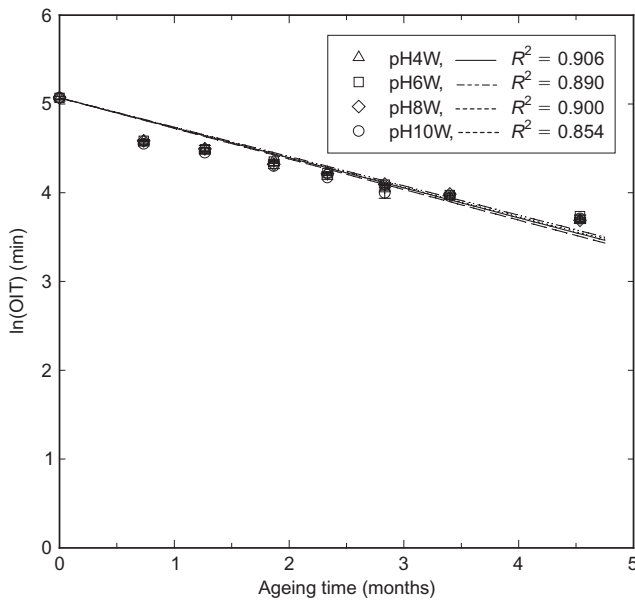


Figure 5. Variation in ln(OIT) with time at 85°C in water, when pH of water changed from 4 to 10 (Series 2)

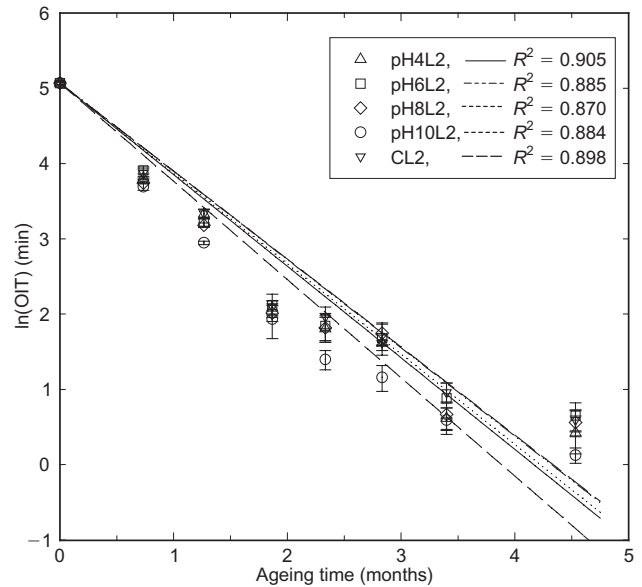


Figure 6. Variation in ln(OIT) with time at 85°C in different leachates, when pH of leachates changed from 4 to 10 (Series 2)

hypothesised that the surfactant increases the wettability of the geomembrane by reducing the surface tension of water and hence increasing the extraction of antioxidants into the water in contact with the geomembrane.

4.4. Prediction of antioxidant depletion time

The results of the Series 1 tests can be used to predict the time required for antioxidant depletion at different temperatures. According to Hsuan and Koerner (1998), the Arrhenius equation is the best tool for the prediction of

antioxidant depletion rate at a temperature of interest. The Arrhenius equation can be written as

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

where *s* is the antioxidant depletion rate (month⁻¹), *E_a* is the activation energy of the depletion process (J/mol), *R* is the universal gas constant (8.314 J/(mol K)), *T* is the absolute temperature (K), and *A* is a constant, often called

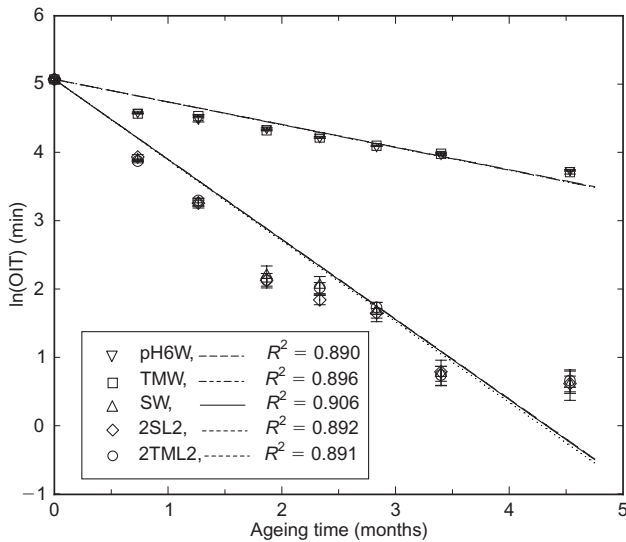


Figure 7. Variation in ln(OIT) with time at 85°C for different combinations of surfactant and trace metals (Series 2); terminology defined in Table 2

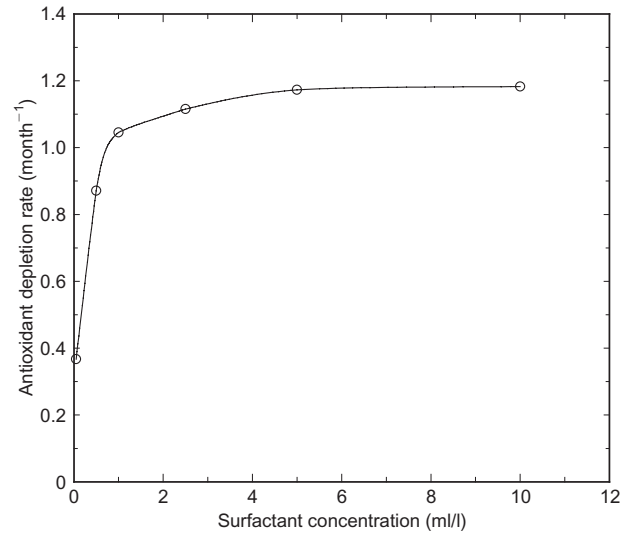


Figure 9. Antioxidant depletion rate against surfactant concentration at 85°C (Series 2)

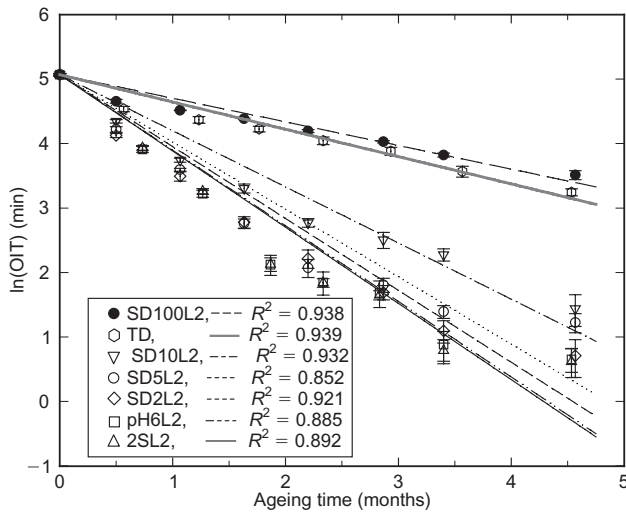


Figure 8. Variation in ln(OIT) with time at 85°C for leachates with different surfactant concentrations (Series 2); terminology defined in Table 2

a collision factor. The Arrhenius equation can also be expressed as

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

Figure 10 shows a linear relationship between ln(s) and 1/T for the four leachates, and the parameters of the Arrhenius equation are given in Table 6. The activation energy is calculated from the slope of the lines (i.e. E_a/R) and found to be between 62.5 and 64.0 kJ/mol. The lowest activation energy was for leachate 2, which comprised trace metals and surfactant in water. Knowing the activation energy for an exposure condition, the antioxidant

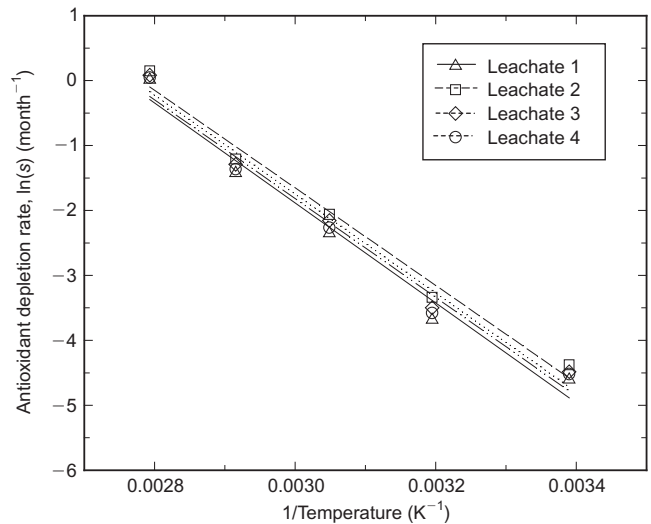


Figure 10. Arrhenius plot of antioxidant depletion in four different leachates (Series 1)

Table 6. Activation energy and Arrhenius equation for four different leachates in Series 1 tests.

Leachate type	Activation energy, E_a (kJ/mol)	Arrhenius equation (s in month ⁻¹ ; T in K)	R^2
Leachate 1 (Full)	64.03	$\ln(s) = 21.22 - 7702/T$	0.977
Leachate 2 (TM + S)	62.49	$\ln(s) = 20.90 - 7516/T$	0.985
Leachate 3 (TM + S + IN + R)	63.34	$\ln(s) = 21.11 - 7618/T$	0.982
Leachate 4 (TM + S + VFA + R)	63.24	$\ln(s) = 21.00 - 7606/T$	0.979

TM = trace metal solution; S = surfactant; IN = inorganic nutrients; R = reducing agent; VFA = volatile fatty acids; Full = TM + S + IN + VFA + R.

depletion rate can be predicted for a site-specific temperature from Equation 3. By substituting the antioxidant depletion rate in Equation 1, the time of antioxidant depletion is calculated for three hypothetical landfill temperatures (60°C, 40°C and 20°C), and the results are shown in Table 7. The details of the basis of selecting the hypothetical landfill base temperatures can be found in Rowe (2005). As noted earlier, there is no statistically significant difference in OIT data between leachate 1 and leachate 4; however, the difference of antioxidant depletion time between these two leachates is 8 years at 20°C (Table 7). Thus the extrapolations based on the Arrhenius plot have some sensitivity to the natural variability of the input data. This sensitivity decreased substantially with increasing temperature.

4.5. Crystallinity

The change in crystallinity of the geomembrane as a function of time at different temperatures in four leachates is plotted in Figure 11. The crystallinity of the geomembrane increased sharply after 1 month of ageing, from its initial value of 37.8% to a value of about 45% at 85°C and 70°C. The crystallinity was relatively constant from 1 month to 13 months, after which time it increased and reached values of 52% and 50% at 85°C and 70°C, respectively, by the end of the testing period (31.5 months). The increase in crystallinity at the initial stage is due to some physical ageing, which enhances the tendency towards re- and/or post crystallisation of the material (Petermann *et al.* 1976; Dörner and Lang 1998a, 1998b). The increase at the later stage is due to chain scission in the material, as verified by the MFI results discussed below. At the three other temperatures (55°C, 40°C and 22°C), the crystallinity of the geomembrane was found to be less than 43%, suggesting that some physical ageing is still occurring in the geomembrane. There was statistically no significant difference in the degree of crystallinity with respect to leachate types.

4.6. Melt flow index

Figure 12 shows the variations in melt flow indices with leaching time at different temperatures. Melt flow index values decreased at the early stage of incubation time at 85°C and 70°C; then it started to increase, and was found still increasing at the end of the tests. At 55°C and 40°C MFI is found to be still decreasing with time, and at 22°C there was no change observed in MFI values. No specific trend was observed with respect to leachate types.

4.7. Tensile properties

Figure 13 shows the variation in four tensile properties (stress and strain at yield and break) as a function of leaching time at 85°C in four leachates. The stress at yield increased by approximately 18% in all four leachates within the testing period. On the other hand, the strain at yield decreased by approximately 10% within the testing period. Similar results were observed by other researchers (Hsuan and Koerner 1998; Sangam 2001). The changes in yield stress and yield strain are probably due to the observed increase in crystallinity of the geomembrane, because the crystalline zone of the geomembrane is generally responsible for its strength (Apse 1989; Lustiger and Rosenberg 1989). No specific trend was observed with respect to leachate type. The behaviour of stress and strain at yield at 70°C and 55°C was the same as the behaviour of samples at 85°C; however, at 40°C and 22°C there was no change in the tensile properties of geomembrane samples over the 31.5 month period of testing.

The break stress and strain decreased by approximately 15% and 10%, respectively, for the samples incubated at 85°C (Figure 13). These decreases were observed after around 20 months of incubation. The decrease in tensile break properties suggests that the geomembrane entered into Stage III of the three-stage degradation model after 20 months. The duration of Stage II (i.e. induction time) was approximately 15 months with respect to tensile break properties. The lower values of break stress and break strain indicate that the geomembrane became more brittle owing to the decrease in molecular weight. It should be noted that there was very little dissolved oxygen (less than 1.5 mg/l) present in the leachates at 85°C, and this may extend the service life relative to what might be expected if more oxygen had been available (e.g. in pipe ageing tests, where there is 85°C water on the inside and air on the outside of the pipe). There was no significant change in tensile break properties at temperatures of 70°C, 55°C, 40°C and 22°C within the 31.5 month testing period. Tensile break properties show similar behaviour in all leachates.

5. CONCLUSIONS

This study describes two series of accelerated ageing tests on 1.5 mm thick HDPE geomembrane immersed in different synthetic leachates. One test series was conducted at five different temperatures (22–85°C) using four different

Table 7. Predicted antioxidant depletion times in four different leachates at three different temperatures by using Arrhenius equation in Series 1 tests

Temp (°C)	Antioxidant depletion time (yrs)			
	Leachate 1	Leachate 2	Leachate 3	Leachate 4
20	77	56	65	69
40	14	11	12	13
60	3.3	2.6	2.9	3.1

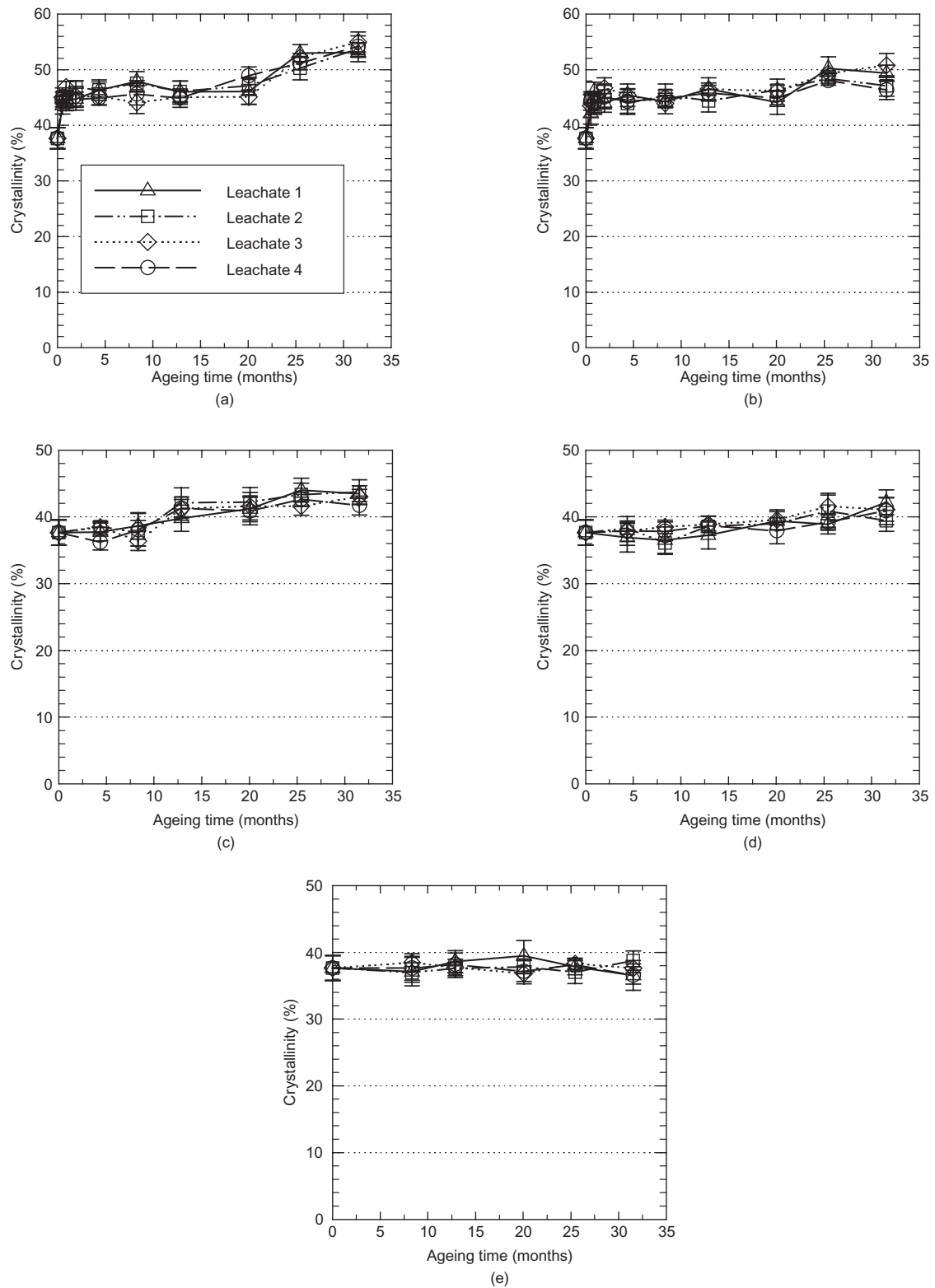


Figure 11. Variation in crystallinity with time in four different leachates at five different temperatures (Series 1): (a) 85°C; (b) 70°C; (c) 55°C; (d) 40°C; (e) 22°C

synthetic leachates. The results showed that to avoid changes in the leachate (e.g. a build-up in antioxidant in the leachate or depletion of available oxygen) impacting on the depletion rate, the leachate should be replaced every two weeks in this type of test. There was only a small difference between the activation energies (62.5 and

64.0 kJ/mol) obtained for the four leachates, which suggests that the OIT depletion mechanisms were very similar in the four leachates. A 15% decrease in tensile break stress and 10% decrease in tensile break strain were observed at 85°C, indicating that the geomembrane reached Stage III of the three-stage degradation model for

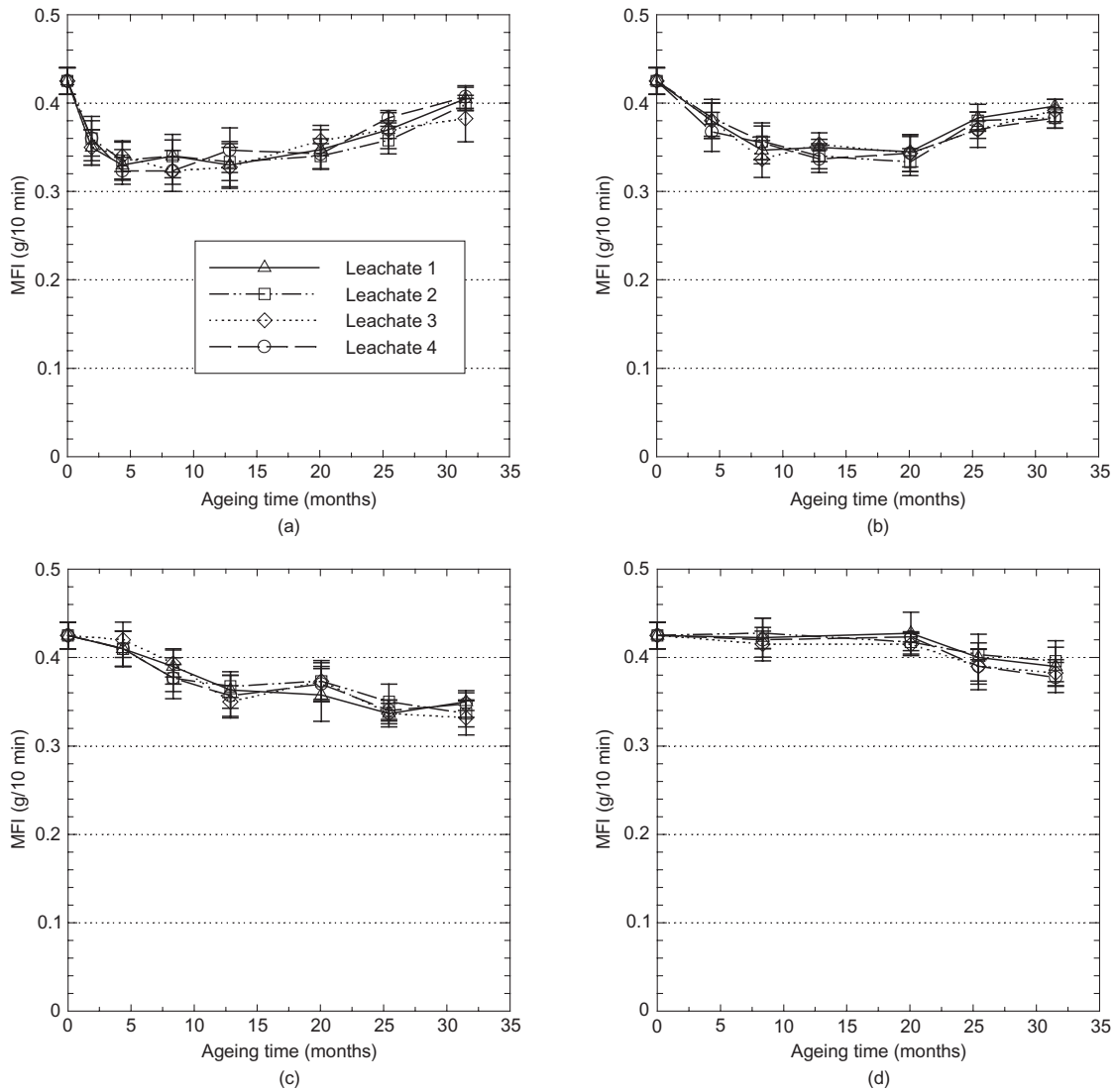


Figure 12. Variation in melt flow index (MFI) with time in four different leachates at four different temperatures (Series 1): (a) 85°C; (b) 70°C; (c) 55°C; (d) 40°C

geomembrane service life at that temperature. The length of Stages I and II were 4.5 and 15 months, respectively, at 85°C. Although the differences were small, the greatest antioxidant depletion rate was observed for the simplest leachate (leachate 2), which is comprised of trace metal solution and surfactant in water.

The second test series examined OIT depletion for 18 different leachates at 85°C. Antioxidants were depleted at a faster rate in relatively acidic or basic immersion mediums (pH 4 and 10) than at typical MSW leachate (pH 6–8). Surfactant was the primary leachate component influencing OIT depletion. A relatively small amount of surfactant was sufficient to influence the depletion of antioxidant substantially. For the surfactant, Igepal[®] CA720, there was no further increase in depletion rate once the concentration reached 5 ml/l water. It appears that the leachate used in Test pH6L2, which is comprised of trace metals, surfactant and a reducing agent, could reasonably and conservatively be used for assessing the potential degradation of HDPE geomembranes in landfill liner applications.

ACKNOWLEDGEMENTS

The research presented in this study was supported by the Natural Science and Engineering Research Council of Canada (NSERC). The authors are grateful to their industrial partners, Solmax International, Terrafix Geosynthetics Inc, Ontario Ministry of Environment, Gartner Lee Ltd, AMEC Earth and Environmental, Golder Associates Ltd, and CTT group, and especially to Terrafix Geosynthetics Inc. (Toronto, Canada) for providing the geomembrane tested.

NOTATIONS

Basic SI units are given in parentheses.

A a constant often called a collision factor (dimensionless)

E_a activation energy of the depletion process (J/mol)

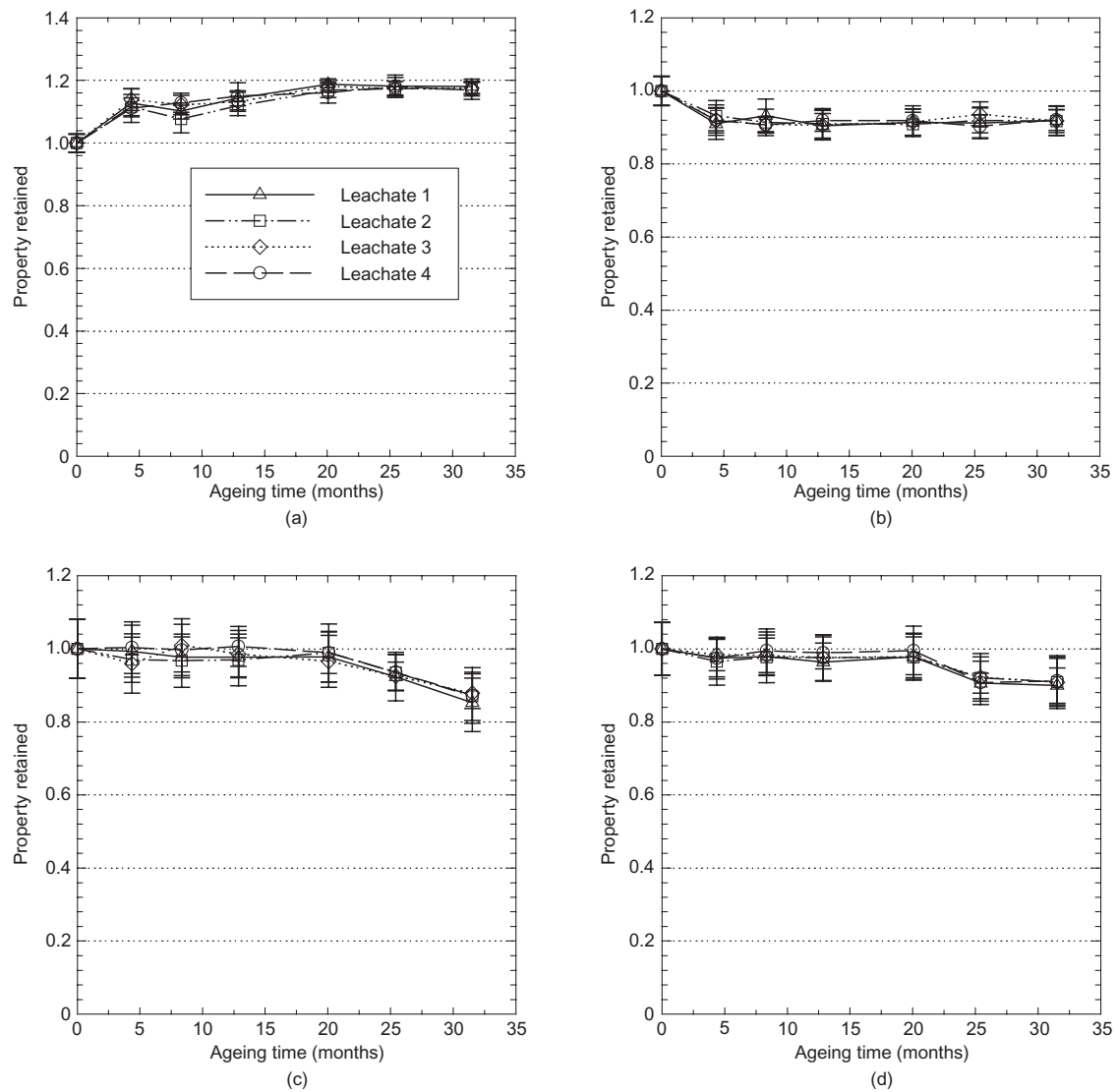


Figure 13. Variation in tensile properties in four different leachates at 85°C (Series 1): (a) yield stress; (b) yield strain; (c) break stress; (d) break strain

- OIT_0 initial OIT in the geomembrane (s)
 OIT_t OIT remaining at any time t in the geomembrane (s)
 R universal gas constant (8.314 J/(mol K))
 s antioxidant depletion rates (s^{-1})
 t leaching time (s)
 T absolute temperature (K)

ABBREVIATIONS

- AMD acid mine drainage
 DSC differential scanning calorimeter
 HDPE high-density polyethylene
 MFI melt flow index
 MSW municipal solid waste
 OIT oxidative induction time
 VFA volatile fatty acid

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