Antioxidant depletion in high-density polyethylene pipes exposed to synthetic leachate and air

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ABSTRACT: Antioxidant depletion rates are reported for samples of one particular high-density polyethylene pipe when immersed in air and a synthetic municipal solid waste leachate, obtained by measuring the oxidative induction time (OIT) at temperatures of 22°C, 40°C, 70°C and 85°C with time. Of the factors examined, the rate of antioxidant depletion was affected most by the ageing temperature, with much faster depletion occurring at higher temperatures. Antioxidant depletion was faster when immersed in the synthetic leachate rather than in air, and faster for the thin pipe examined compared with a thick pipe. No significant difference in antioxidant depletion was found whether the pipe was deflected with a 10% reduction in vertical outside pipe diameter or not deflected. Predictions of the time to deplete antioxidants are then made from Arrhenius extrapolations of the reported data. It is estimated that depletion of antioxidants may take from as long as 600 years at 10°C to as little as 20 years at 50°C when exposed to air, and may reduce to 160 years at 10°C or 10 years at 50°C if exposed to the synthetic leachate. These results are applicable for the particular pipe, antioxidant formulation and conditions examined.

1. INTRODUCTION

Modern solid waste landfills typically include an engineered leachate collection system (e.g. Rowe *et al.* 2004) to help manage the contaminated fluid generated from the solid waste. High-density polyethylene (HDPE) leachate collection pipes are important components in these leachate collection systems. They provide an opportunity to collect and remove leachate from the landfill, and thereby can be used to minimise the hydraulic head at the base of the landfill and remove contaminants from the system. Because the contaminating lifespan of a modern landfill can exceed many decades, or in some cases hundreds of years, the long-term durability of leachate collection pipes is an issue that needs to be examined.

Three major mechanisms that can adversely affect the durability of HDPE pipes are photodegradation, stress cracking, and oxidative degradation (Mruk 1990). Photodegradation is not an issue for leachate collection pipes because they are buried, and because modern HDPE pipe resins include carbon black to protect the pipe from the sun prior to burial (Hsuan and Koerner 1998). Stress cracking is an issue for internally pressurised pipes (e.g. gas lines) where tensile stresses exist through the entire wall of the pipe. It is probably not an issue for leachate collection pipes, because they are not internally pressurised, but are instead subject to gravity loads from burial that result in internal pipe stresses that are a combination of tension and compression through the thickness of the pipe. Over time these stresses may relax once the pipe attains a stable deformed shape (Krushelnitzky 2006). It has been hypothesised that stress cracking is not a major issue for buried pipes, because they may be in a state of relaxing bending stress, as opposed to the constant tensile stresses that internally pressurised pipes experience (Moser 1981; Janson 1996). Janson (1996) wrote:

> [I]t can be said that the constant bending strain the pipe wall is exposed to will not cause failure as long as the pipe material retains its original properties, i.e. as long as the material's stabilization system is intact.

Should the stabilization system be intact forever, a material failure will thus never occur.

Since no stabilisation system will last for ever, an eventual decrease in pipe properties arising from oxidation is be expected to occur. Therefore, out of the major degradation mechanisms, oxidative degradation appears to have the largest potential impact on HDPE leachate collection pipe durability.

It has be postulated by Hsuan and Koerner (1998) that the durability of HDPE can be quantified using three distinct stages (Figure 1):

- t_1, the time required to deplete antioxidants;
- t_2, the time required for the induction of polymer degradation; and
- t_3, the time required for the engineering property of interest to degrade to the extent where it no longer performs its intended design function.

Antioxidants are chemical stabilisers added to HDPE to limit oxidation during the extrusion and long-term service life of the HDPE (Hsuan and Koerner 1998). Thus knowledge of the time to deplete the protective antioxidants in HDPE pipes can be used to obtain first-order estimates of how long they may perform their function (i.e. service life) in a landfill. Depletion of antioxidants for HDPE geomembranes has received considerable attention (e.g. Hsuan and Koerner 1998; Sangam and Rowe 2002; Gulec *et al.* 2004; Jeon *et al.* 2008; Rowe *et al.* 2008, 2009, 2010; Rimal and Rowe 2009); however, there is a paucity of data on antioxidant depletion and oxidative degradation rates of HDPE pipes when exposed to landfill leachate.

The objective of this paper is to quantify the length of the first stage of oxidative degradation for one particular HDPE pipe. Experimental results are presented in which the antioxidant depletion is measured in samples of HDPE pipe when exposed to air and synthetic leachate at temperatures of 22°C, 40°C, 70°C and 85°C. These data are then extrapolated to provide estimates of the time to antioxidant depletion for HDPE leachate collection pipes.
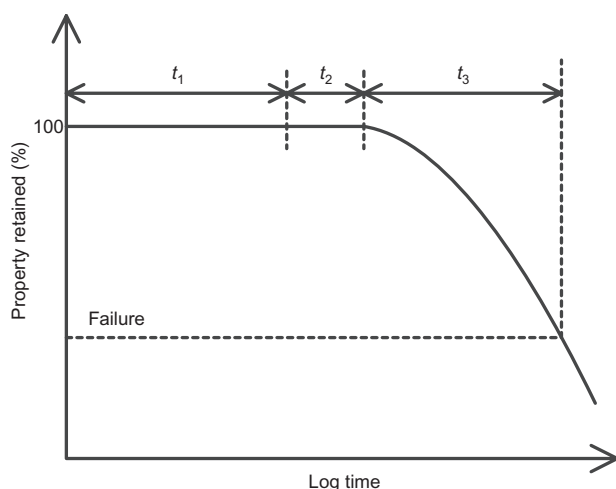

Figure 1. Three-stage conceptual model of chemical ageing of HDPE (modified from Hsuan and Koerner 1998)

2. ANTIOXIDANT DEPLETION AND OXIDATION

The amount of antioxidant in an HDPE pipe decreases as the pipe ages because of two, often simultaneous, mechanisms: chemical reactions and physical loss (Hsuan and Koerner 1998). Chemical reactions occur when the antioxidants react with oxygen, free radicals or alkyl peroxides (Luston 1986). The rate of consumption (progressing from the pipe surfaces inward) depends on the concentration of these chemicals. Physical loss occurs from diffusion, extraction or volatilisation (Luston 1986). Volatility and diffusion of antioxidants are functions of temperature. Increased temperatures result in increased volatilisation of stabilisers from the pipe surfaces, and increased diffusion of stabilisers from the interior to the surfaces of the pipe. Volatility is also a function of the mobility of the antioxidants in the amorphous phase of the polymer, as a greater concentration of antioxidants can be found in the amorphous phase (Hsuan and Koerner 1998). However, volatilisation may not be significant in the field, as temperatures at the base of a landfill rarely exceed 60°C (Rowe 2005; Koerner and Koerner 2006).

Whenever HDPE comes into contact with a liquid, extraction of antioxidants may play an important role. The rate of extraction is controlled by the dissolution of antioxidants from the surfaces of the pipe, and by the rate of diffusion of antioxidants from the interior to the surfaces. Again, both the temperature and the mobility of the antioxidant in the amorphous phase may be expected to play an important role in the amount of extraction that can occur (Hsuan and Koerner 1998). For polyethylene pipes carrying hot water, it has been observed that extraction played a greater role than volatilisation in antioxidant depletion, based upon observations of tests that subjected pipes to water internally and air externally (Gedde and Ifwarson 1990; Karlsson *et al.* 1992, 1993; Smith *et al.* 1992; Viebke and Gedde 1997, 1998; Gill *et al.* 1999). It was found that the consumption of antioxidants was much faster in water than in air.

The rate of oxidation may be expected to depend on the type and structure of the polymer, particularly its crystallinity and number of chain branches (Kelen 1983; Hsuan and Koerner 1995), as well as on the antioxidant formulation. Consequently, lifetime estimates will depend on the specific HDPE material and antioxidant formulation.

The rate of oxidation will also depend on the concentration of oxygen. For landfill leachate collection pipes, the amount of free oxygen may be very small at the base of the landfill, which will reduce the rate of oxidation of the pipes. This is because anaerobic conditions traditionally prevail after 3 to 5 years of waste cover (e.g. Pohland and Harper 1986; Rowe *et al.* 2004). Although low, there may still be sufficient oxygen for oxidation to be an issue, as shown in tests of HDPE geomembranes in reduced-oxygen conditions (Sangam and Rowe 2002; Rowe *et al.* 2008).

The medium in direct contact with HDPE may also be expected to have an impact on the oxidation rate. Recent investigations into antioxidant depletion in HDPE geomembranes have shown that the rate of depletion depends

on the fluids in contact with the geomembrane. For example, antioxidant depletion was found to be 2–4 times faster in municipal solid waste leachate than in water or air (Sangam and Rowe 2002; Rowe *et al.* 2008). The surfactant has been shown to be the constituent of municipal solid waste leachate that has the greatest influence on antioxidant depletion (Rowe *et al.* 2009). This was attributed to reduced surface tension effects with the surfactant, which lead to greater extraction of antioxidants. Further, some soils, if they contain a significant amount of transition metals and moisture, can result in the diffusion of transition metals into the HDPE (Hsuan and Koerner 1995). van Langenhove (1990) showed that certain transition metals (such as Cu, Fe and Mn) resulted in an acceleration of degradation by a factor of 10 (for Cu and Fe) or a factor of 2 (for Mn). For landfill leachate collection pipes, leachate containing transition metals may result in accelerated oxidative degradation.

It is possible that the thickness of the pipe also plays an important role in the rate of oxidation. Karlsson *et al.* (1992) presented results of antioxidant depletion studies in medium-density polyethylene pipes used in hot water applications. Antioxidants were shown to deplete more quickly at the surface of the pipe than in the interior. It can be hypothesised that thicker pipes will take longer periods of time to oxidise, as the outward diffusion of antioxidants will take longer in such pipes. This hypothesis has been supported by observations made on geomembranes in which thinner geomembranes oxidised faster than thicker geomembranes (Kelen 1983).

Oxidative induction time (OIT) is an index test that can be used to measure the amount of antioxidant remaining in a polymer (e.g. Hsuan and Guan 1997). Standard test methods exist for OIT measurement using a differential scanning calorimeter (ASTM D 3895; ASTM D 5885). OIT depletion with respect to time has been expressed as an exponential function of the form (Hsuan and Koerner 1998)

$$OIT_t = OIT_0 e^{-st} \tag{1}$$

where OIT_t is the OIT value in minutes at time t in months, OIT_0 is the initial OIT value in minutes, and s is the rate of antioxidant degradation in 1/months. The data can be represented as a linear function of the natural logarithm of OIT against time, where the slope of the function is the rate of OIT degradation.

3. ACCELERATED AGEING EXPERIMENTS

3.1. Pipe samples

All pipes samples tested were from the same production run and used the same type of HDPE, PE 345464C, when classified in accordance with ASTM D 3350. As detailed in Table 1, two pipe thicknesses were examined, denoted as thick and thin pipes. The thin pipes were machined to size from the thick pipe samples. Unless otherwise noted, the results in this paper refer to the thick pipe. Initial index properties of the particular pipe tested are given in Table 2.

A sample length of 300 mm was used for all tests

Table 1. Pipe diameters and wall thicknesses examined

Type	Outside diameter (mm)	Thickness (mm)
Thick pipe	114.3	10.3
Thin pipe	107	2.5

because Janson (1996) suggested that the sample length should be at least equal to or greater than the pipe diameter in order to avoid excessively low values of residual stress (compared with the values in the field).

A summary of the sample conditions for the thick pipes aged for up to 24 months is presented in Table 3. The thin pipes were aged for a period of up to 10 weeks in synthetic leachate at 85°C without being deflected.

3.2. Exposure media

The thick pipes were exposed to two media: air and a synthetic leachate. The thin pipes were exposed only to the synthetic leachate. Table 4 outlines the composition of

Table 2. Initial and aged index properties of particular HDPE pipe tested; aged values for undeformed pipe samples aged in synthetic leachate at 85°C

Ageing time (days)	Melt flow index[a] (g/10 min)	Crystallinity[b] (%)	Flexural modulus[c] (MPa)
0	0.052	51.8	439
105	0.044	53.7	509
228	0.047	53.1	427
348	0.035	51.5	508
546	0.042	53.2	431
717	0.028	52.6	439

[a]ASTM D 1238.
[b]ASTM E 794.
[c]ASTM D 2412.

Table 3. Test conditions for thick-walled pipe samples

Test series	Deflected (yes/no)	Temperature (°C)	Exposure medium
1	No	22	Air
2	No	40	Air
3	No	70	Air
4	No	85	Air
5	Yes	22	Air
6	Yes	40	Air
7	Yes	70	Air
8	Yes	85	Air
9	No	22	Synthetic leachate
10	No	40	Synthetic leachate
11	No	70	Synthetic leachate
12	No	85	Synthetic leachate
13	Yes	22	Synthetic leachate
14	Yes	40	Synthetic leachate
15	Yes	70	Synthetic leachate
16	Yes	85	Synthetic leachate

Table 4. Synthetic leachate composition

Component	Formula	Amount/litre (mL)
Trace metal solution	See Table 5	1
Sodium sulfide nonahydrate (3% w/v)	$Na_2S.9H_2O$	~0.5–1
$E_h \approx -120$ mV		
Sodium hydroxide (15 M)	NaOH	~0.1
pH 6		
Igepal® CA 720		4.5

the synthetic leachate used for these experiments. It was selected to be consistent with previous studies on HDPE geomembranes. The leachate is composed of a transition metal solution (see Table 5) and a surfactant (Igepal® CA 720) with sodium sulfide to act as a reducing agent (to achieve a reduced electrical potential, E_h, of less than -120 mV) and sodium hydroxide to achieve a pH of 6.0. The leachate was changed every six weeks, except for the samples exposed at 85°C, which were changed every 10 days. This was required because of faster leachate evaporation at 85°C.

3.3. Pipe deflections

Stress might influence the rate of antioxidant depletion (e.g. Bandyopadhyay *et al.* 1985; Rapoport and Zaikov 1986). In order to examine the impact of relaxing bending stresses (the hypothesised stress state acting on leachate collection pipes) on antioxidant depletion, the following conditions were examined: no deflection, and deflected with a 10% reduction in vertical outside pipe diameter. This was imposed by compressing the pipe samples between two parallel stainless steel plates until a 10% reduction in the outside vertical diameter of the pipe occurred. The plates were bolted into place in order to maintain the 10% deflection. This level of deflection was selected because it exceeds the 5–7% (ASTM F 714) maximum allowable deflection criterion, which results in the pipe samples being subjected to more extreme conditions than would typically occur in the field.

3.4. Elevated temperatures

Elevated temperatures were used to accelerate antioxidant depletion. Arrhenius modelling may be used to predict pipe degradation at lower temperatures, based on relatively quick degradation measurements obtained from elevated temperature testing. This is based on the assumption that the material behaviour at the high-temperature range examined can be extrapolated to the lower-temperature behaviour of interest. Arrhenius modelling has been used for similar exposure conditions and similar HDPE geomembrane materials (e.g. Sangam and Rowe 2002). Three elevated temperatures (40°C, 70°C and 85°C) and the ambient laboratory temperature of 22°C were used for ageing. Elevated temperatures were achieved by placing the samples inside forced-air ovens that were electronically controlled to maintain the temperature to within ±0.5°C. When selecting the elevated temperature to use, it was important not to elevate the temperature so high as to change the morphological structure of the material being examined. It was also important that the effective temperature range of the antioxidants used in the pipe was not exceeded, or else the results from OIT tests could possibly be deceiving. The adopted temperatures are believed to be acceptable for use with the HDPE pipe tested, based on a review of the literature dealing with HDPE geomembranes and HDPE pipe elevated temperature tests (e.g. Sangam and Rowe 2002).

3.5. Tests conducted

Specimens cut from the pipe samples were subject to the standard OIT test (ASTM D 3895) and high-pressure OIT test (ASTM D 5885) using differential scanning calorimeters. For the tests presented in this paper, two different differential scanning calorimeters were used: a TA Instruments DSC 2910, and a TA Instruments DCS Q100. *T*-test hypothesis testing showed that there was no significant difference between the results obtained from the two machines at the 95% level of significance.

Table 5. Trace metals solution composition

	Component	Formula	Amount/Litre (mg ± 0.1 mg)
1	Ferrous sulfate	$FeSO_4.7H_2O$	2000
2	Boric acid	H_3BO_3	50
3	Zinc sulfate heptahydrate	$ZnSO_4.7H_2O$	50
4	Cupric sulfate, pentahydrate	$CuSO_4.5H_2O$	40
5	Manganous sulfate monohydrate	$MnSO_4.H_2O$	500
6	Ammonium molybdate tetrahydrate	$(NH_4)_6Mo7O_{24}.4H_2O$	50
7	Aluminium sulfate 16-hydrate	$Al_2(SO_4)_3.16H2O$	30
8	Cobaltous sulfate heptahydrate	$CoSO_4.7H_2O$	150
9	Nickel (II) sulfate	$NiSO_4.6H_2O$	500
10	Sulfuric acid (+96% purity) (ml)	H_2SO_4	1

In addition to monitoring the OIT of the pipes, the melt flow index (ASTM D 1238) and crystallinity (ASTM E 794) of the aged samples were measured with time to assess whether there was any chemical ageing of the polymer. The flexural modulus, obtained by compressing pipe rings following ASTM D 2412, was also measured to track a bulk pipe property with time.

4. OIT TESTING

4.1. OIT test specimens

For the thick pipe samples, the specimens were punched out of two rings 3 to 5 mm in thickness: one cut from the end of the pipe samples, and the other cut from the middle (150 mm from each end) of the pipe samples. Figure 2 shows the location of the specimens that were punched out of the rings. The specimens were punched out of the rings using a 3.175 mm diameter punch. Specimens were typically 1.5 to 2.0 mm in length, with masses between 9 and 15 mg. This exceeds the 5 ± 1 mg specimen mass specified in ASTM D 5885. Validation testing showed there was no discernible difference in OIT values from $9-15$ mg specimens compared with 5 mg specimens. Three specimens were punched from the top of the ring
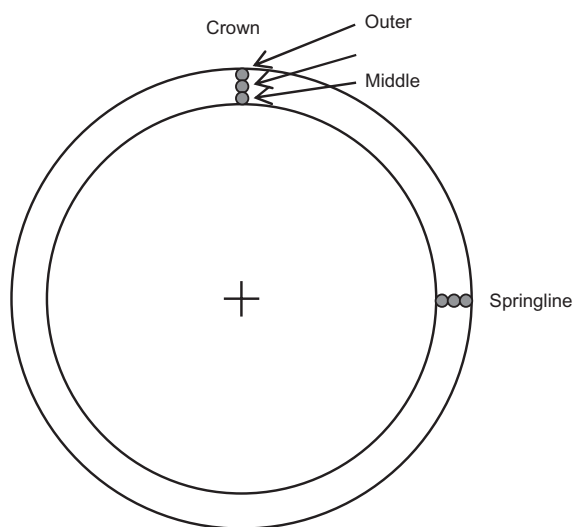
(the crown of the pipe) and three from the side of the ring (the springline of the pipe).

Statistical hypothesis testing showed that there was no significant difference between the OIT values measured between the two rings at the 95% level of significance, for both the deflected and the non-deflected pipe samples.

Table 6 lists various measured OIT values at both the crown and springline for non-deflected pipe samples aged for 26 days, 105 days and 348 days in synthetic leachate at 85°C. OIT values for samples aged in leachate at 70°C, 40°C and 22°C are not shown, but have similar trends. Three different ages were examined to determine whether OIT varied with time between the crown and springline. Statistical hypothesis testing using the data in the table and a *t*-distribution showed that, for non-deflected pipes aged in synthetic leachate, there was no significant difference at the 95% significance level between the specimens taken from the crown and those taken from the springline.

Similar testing was carried out on non-deflected and deflected pipe samples aged in air and deflected specimens aged in leachate. The hypothesis testing showed that there was no significant difference between specimens taken from the crown and the springline at the 95% level of significance.

For the thin pipe samples, the same punch used for the thick pipe samples was used to punch six specimens from the crown and six specimens from the springline of each sample. Statistical hypothesis testing, using a *t*-distribution, showed that there was no significant difference at a 95% level between the specimens taken at the crown and those taken at the springline for the thin pipes.

4.2. High-pressure OIT testing

It is important to ensure that the 200°C testing temperature of the standard OIT test does not destroy the antioxidants used in the formulation of the HDPE (Hsuan and Koerner 1998; Sangam and Rowe 2002). This can be done by comparing the standard OIT measurements with those obtained from a high-pressure OIT test (ASTM D 5885). A linear variation between standard OIT and high-pressure OIT may provide some evidence that hindered amines or thiosynergists (types of antioxidants with effective temperatures less than 200°C) are not present in the polymer (Hsuan and Koerner 1998). If the relationship is linear, the main antioxidants probably consist of phosphates and

Figure 2. Diagram of HDPE ring cut from aged pipe sample, showing specimen locations for OIT testing

Table 6. Measured OIT values at crown and springline, used to test hypothesis that OIT measured at crown and springline are the same. Values are for specimens cut from non-deflected pipe samples aged in synthetic leachate at 85°C

Sample age	Crown			Springline		
	Mean OIT (min)	Standard deviation (min)	Number of data points	Mean OIT (min)	Standard deviation (min)	Number of data points
26 days	47.6	6.1	5	54.5	9.4	5
105 days	32.8	8.0	11	37.3	10.5	12
348 days	9.4	2.6	5	8.1	2.0	6

hindered phenols (types of antioxidants with effective temperatures as great as 200°C) (Hsuan and Guan 1997). Figure 3 is a plot of standard OIT and high-pressure OIT measurements taken from specimens cut from a number of different non-deflected pipe samples aged for different times in leachate at 70°C. The relationship is essentially linear. This indicates that the 200°C testing temperature of the standard OIT test did not prematurely accelerate the degradation of antioxidants, and thus it is reasonable to use the standard OIT test to quantify antioxidant depletion. For the remainder of the paper, unless otherwise noted, OIT results were obtained from the standard OIT test.

4.3. Through-thickness variation of OIT

The variation of OIT through the thickness of the pipe was examined by comparing results from specimens cut from the inside, middle and outside surface of the pipe wall as indicated in Figure 2.

Figure 4 is a plot of the measured OIT for specimens at the inside, middle and outside of the pipe wall, cut from a non-deflected pipe sample aged in synthetic leachate at 85°C. Results from samples aged for 26 days, 105 days, 348 days and 717 days are shown in the figure,
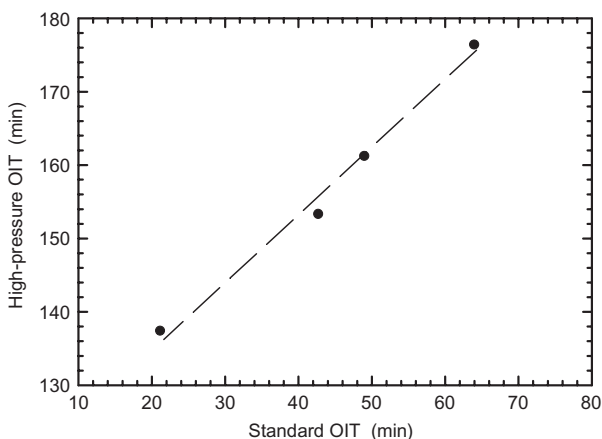

Figure 3. Standard OIT and high-pressure OIT measurements for non-deflected pipe samples aged in leachate at 70°C
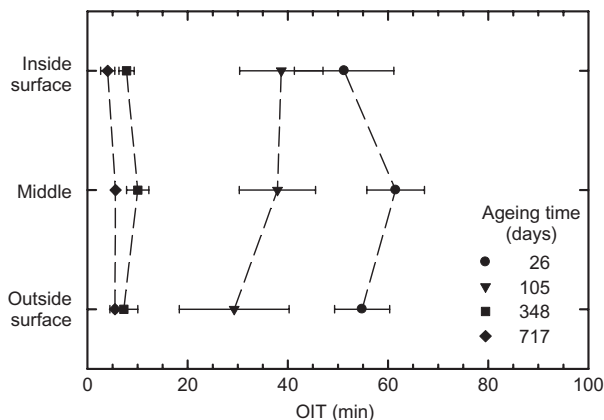
along with error bars indicating the standard deviation of the measurements. Figure 5 is a similar plot, but for specimens cut from a non-deflected pipe sample aged in synthetic leachate at 70°C. Visually, from both plots it appears that the OIT measurements vary somewhat through the thickness of the pipe. At 85°C, in general it appears that the antioxidants on the inside and outside surfaces deplete faster than in the interior of the pipe. As the pipe is exposed to leachate on both the inside and outside surfaces, it could be hypothesised that antioxidants would deplete faster because of greater exposure to leachate. However, this trend is not as apparent with the 70°C samples shown in Figure 5. It was also not visible with specimens cut from samples aged at 40°C and 22°C (Krushelnitzky 2006). Hypothesis testing using a *t*-distribution shows that there is no significant difference at the 95% significance level in OIT measured in specimens collected at the inside, middle and outside of the non-deflected pipe samples aged in synthetic leachate. The large amount of variability in the measurements and the relatively large OIT specimen size relative to the thickness of the pipe account for the lack of a statistically significant through-thickness difference. Variability in the measurements can be a possible result of heterogeneous distribution of antioxidants in the HDPE as a result of manufacturing.

Similarly, for non-deflected pipe samples aged in air, deflected pipe samples aged in air and deflected pipe samples aged in synthetic leachate, there was no statistically significant difference at the 95% level of significance between specimens cut from the outside, middle and inside of the pipe.

This does not necessarily mean that there are no through-thickness variations in antioxidant depletion, but rather that, given the size of the specimen taken for OIT testing (shown to scale in Figure 2), any variation was not discernible with the method used. The reported values of OIT in the rest of this paper represent the overall average for both rings of all the samples illustrated in Figure 2.

4.4. Antioxidant depletion for thick pipe samples

The thick pipe samples had an initial, unaged OIT value of 86 min with a standard deviation of 2.5 min. This value
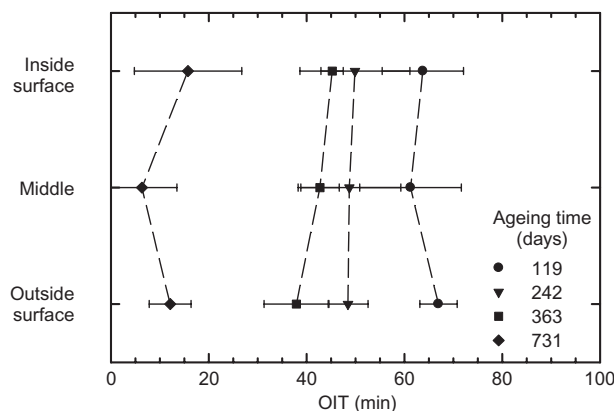

Figure 4. Through-thickness variation of OIT for non-deflected pipe samples in leachate at 85°C

Figure 5. Through-thickness variation of OIT for non-deflected pipe samples in leachate at 70°C

was obtained from 30 specimens cut from five unaged pipes (six specimens per pipe) at the specimen locations indicated in Figure 2.

Figures 6 and 7 are plots showing OIT measurements with time for the series of tests conducted in air on non-deflected (Series 1 to 4) and deflected pipe samples (Series 5 to 8), respectively. The averages of the test results at 22°C, 40°C, 70°C and 85°C are shown as individual data points on the plots, and standard deviations are shown as error bars. Figure 8 is a similar plot for the series (9 to 12) of tests conducted in leachate on non-deflected pipe samples, and Figure 9 is a similar plot for the series (13 to 16) of tests conducted in leachate on deflected pipe samples.

From Figures 6–9 it can be observed that higher temperatures result in greater rates of OIT depletion, and that leachate exposure increases antioxidant depletion relative to air exposure. For the pipes aged in air there was no significant difference in measured OIT between the deflected pipes and the non-deflected pipes, at the 95% significance level using a *t*-distribution. However, the difference between the OIT values measured in the deflected pipes and the non-deflected pipes aged in leachate was statistically significant at the 95% confidence level using a *t*-distribution, with the non-deflected pipes having lower OIT values. Overall, there appears to be no substantial difference in antioxidant depletion whether the
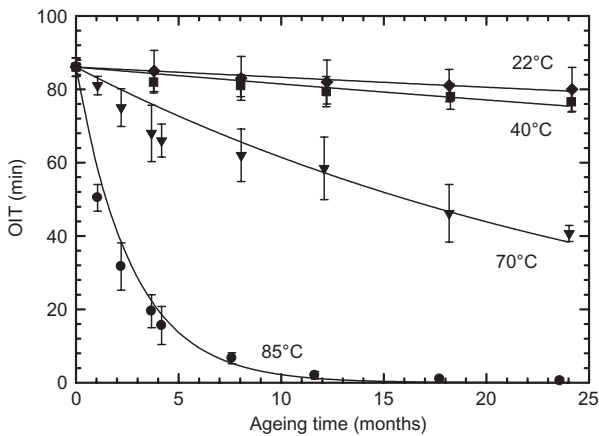

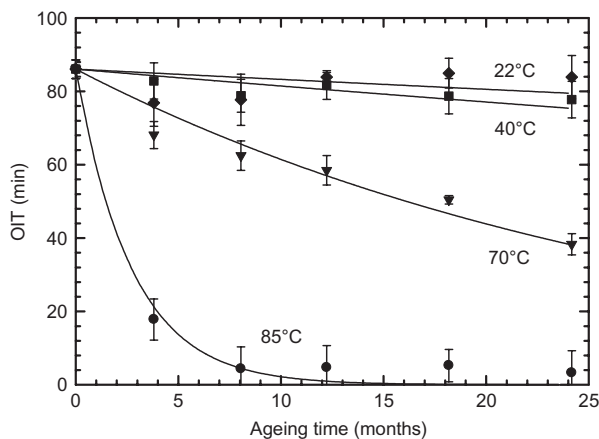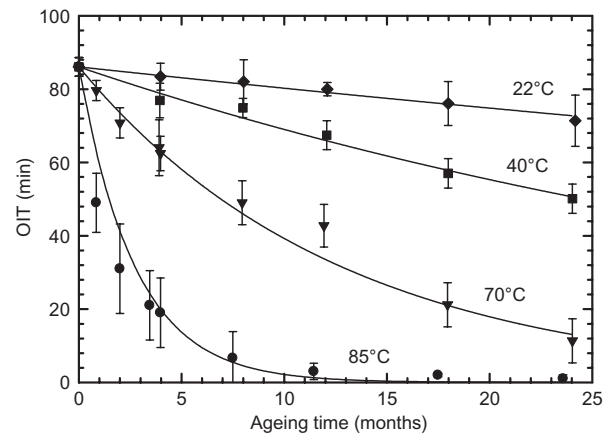**Figure 8. OIT against time for non-deflected pipe in leachate**
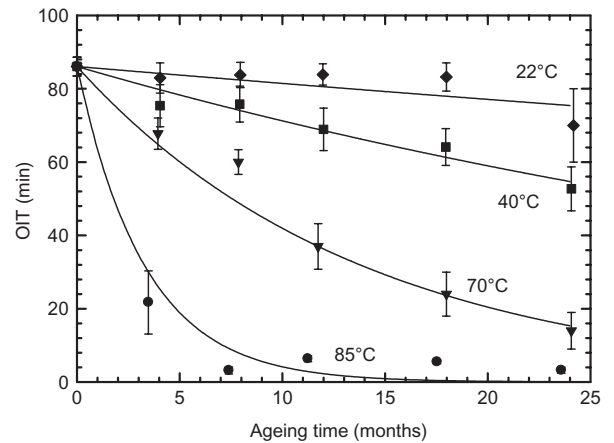

Figure 9. OIT against time for deflected pipe in leachate

pipe was deflected with a 10% reduction in vertical outside pipe diameter or not. Relaxation of the pipe stresses with time when subject to a constant deflection (Krushelnitzky and Brachman 2009) may alleviate any affect from stress.

Best-fit parameters from Equation 1 using the method of least squares for the different temperature and exposure conditions are presented in Table 7. These parameters were then used in Equation 1 to plot the best-fit exponential curves in Figures 6–9.

4.5. Arrhenius modelling of thick pipes

Arrhenius modelling can be used to predict antioxidant depletion rates (Hsuan and Koerner 1998). The basic Arrhenius equation used to predict this depletion is

$$s = A \exp\left(\frac{-E_a}{RT}\right) \qquad (2)$$

where *s* is the rate of antioxidant depletion (per unit area) used in Equation 1; *A* is the collisional factor, which is both material and exposure dependent; E_a is the activation energy (J/mol); *R* is the gas constant (8.314 J/(mol K)); and *T* is the absolute temperature (K).

Based on Fick's first law of diffusion, the collisional factor is a function of the concentration gradient, the surface area of the samples, and the boundary conditions (extraction or volatilisation) acting on the samples. It is
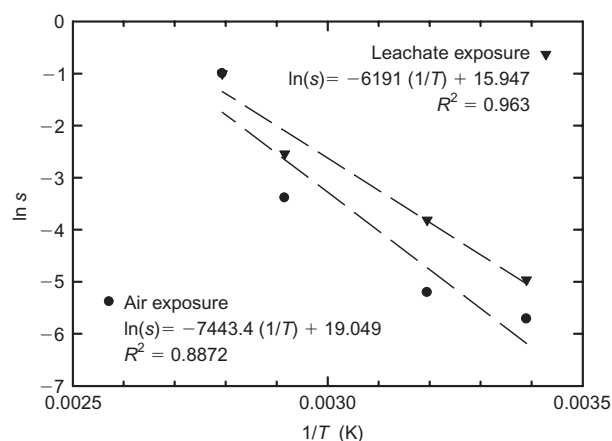

Figure 6. OIT against time for non-deflected pipe in air

Figure 7. OIT against time for deflected pipe in air

Table 7. Antioxidant depletion rates and activation energies

Exposure medium	Antioxidant depletion rate (1/month)				E_a (kJ/mol)
	22°C	40°C	70°C	85°C	
Air (non-deflected and deflected)	0.0033	0.0055	0.0337	0.3676	61.9
Synthetic leachate (non-deflected)	0.007	0.0221	0.0785	0.3677	51.5

assumed that the above Arrhenius equation expresses the depletion of the antioxidants as a result of both the diffusion of antioxidants and the consumption of antioxidants from reactions with oxygen and other transition metals in the leachate. For the air and leachate exposure conditions, the rate of antioxidant depletion at a given temperature has been determined experimentally, and can be found in Table 7. For the two exposure conditions, the values for E_a can be determined from plots of $\ln(s)$ against $1/T$, where the slope of the line is E_a/R. Figure 10 is the Arrhenius plot for the pipe aged in air and the non-deflected pipe aged in leachate, together with the respective least-squares best-fit equations, obtained through linear regression analysis. Activation energies for the two exposure conditions are presented in Table 7. Because the differences between deflected and non-deflected samples in leachate are very small when plotted as an Arrhenius plot (differences in activation energies of 9.5%), only the non-deflected data are presented.

The activation energy for the non-deflected pipes samples aged in synthetic leachate is 51.5 kJ/mol, and is 61.9 kJ/mol for the pipe samples aged in air. It is possible that the differences in activation energy are a function of the differences in consumption of antioxidants by oxygen (in the air), dissolved oxygen (in the leachate) and transition metals (in the leachate). However, given the large variability in the air data, it is also possible that there is no statistical difference between the activation energies in air and leachate. If this is the case, then the major difference between the two exposure conditions is the intercept (the collisional factor), which is a function of the concentration gradient, the exposed area, and the boundary conditions (extraction or volatilisation). Given that these factors varied between the two exposure conditions, the difference in collisional factors, not activation energies, may also be the cause of the increased rate of antioxidant depletion in the synthetic leachate.

Figure 10 shows that pipe samples exposed to synthetic leachate have higher antioxidant depletion rates than those that are exposed only to air for any given temperature. This is thought to be partially a result of both the transition metals and the Igepal in the synthetic leachate accelerating the antioxidant consumption in the HDPE specimens. The Igepal could also impact on the boundary conditions acting on the pipe, resulting in increased wettability and hence in more antioxidants dissolving more quickly from the surface, and consequently resulting in a high antioxidant concentration gradient between the surface of the pipe and the core of the pipe, and in faster extraction (Sangam and Rowe 2002). This mechanism is

Figure 10. Arrhenius plots for air- and leachate-exposed pipes

consistent with the theoretical diffusion and surface partitioning modelling of OIT depletion from an HDPE geomembrane by Rimal and Rowe (2009). Differences in OIT depletions rates may also be caused by differences in the concentration gradient of antioxidants in the different exposure media, resulting in different rates of diffusion of antioxidants. In the air, it is hypothesised that when the antioxidants diffuse out of the pipe, they are carried away by the flowing air in the oven, resulting in no change in the concentration gradient. In the leachate, it is hypothesised that the concentration gradient may decrease with time as the diffused antioxidants build up next to the pipe as they diffuse out of the pipe into the fluid. As discussed previously, the fluid was changed to try to keep the concentration gradient as large as possible. The faster rate of antioxidant depletion in the synthetic leachate could also be attributed to the extraction mechanism that occurs in liquids but not in air. It is possible that the extraction mechanism results in faster diffusion of antioxidants than the volatilisation mechanism would. It is also possible that the exposed areas of pipe are responsible for some of the differences. The non-deflected air-exposed pipes were stored standing on their ends, resulting in a smaller available surface area for the diffusion of antioxidants. However, the deflected air-exposed samples were not stored standing on end, and there was no statistically significant difference between the deflected and non-deflected samples exposed to air. Therefore the differences in exposed area were probably minor compared with the concentration gradients, consumption and boundary conditions (extraction or volatilisation). Given the variability in the data, it is difficult to say exactly which mechanism is

responsible for the differences, but it can be concluded that the leachate results in faster rates of antioxidant depletion than the air exposure.

4.6. Antioxidant depletion for thin pipes

Figure 11 is a plot of the measured OIT over time in the thin pipe samples aged in synthetic leachate, along with the best-fit exponential line. The best-fit parameters were obtained through the use of least-squares linear regression on the plot of the natural logarithm of OIT against time. These parameters were then used in Equation 1 to plot the best-fit exponential curves. From the best-fit line, the rate of antioxidant depletion in the thin pipes is $s = 0.93/$ month. This depletion rate can be compared with that of the non-deflected thick pipes aged in leachate at 85°C, which is 0.3677/month. The rate of depletion in the thin pipe is significantly different from the rate of depletion of the thick pipe at the 95% level of significance using a t-distribution. This seems to indicate that pipe thickness has an impact on the rate of antioxidant depletion in the pipe material. Thicker pipes appear to have slower rates of antioxidant depletion than thinner pipes when exposed to synthetic leachate and aged at 85°C. It is hypothesised that this difference is because the thicker pipes have longer diffusion distances for the antioxidant diffusion, resulting in lower depletion rates.

4.7. Other properties

Other properties that were measured over time included melt flow index, crystallinity and mechanical properties. Table 2 presents these values for undeformed pipe samples aged in synthetic leachate at 85°C. Krushelnitzky (2006) showed that these properties did not change in any statistically significant manner during the two-year test period, which indicates that only the first stage of degradation (i.e. antioxidant depletion) had occurred.

5. DISCUSSION

The time required to deplete antioxidants can be calculated using the OIT degradation results obtained from the experiments presented in this paper. If it is assumed that an OIT value of 0.5 min indicates that all antioxidants have been depleted from the polymer, then Equation 1 can be used to determine the time, t, required for a final OIT value of 0.5 min for different exposure conditions. The initial value of OIT for the pipes is known (86 min), and the rate of antioxidant degradation, s, can be obtained using Equation 2 and the Arrhenius plots in Figure 10 for either air or leachate exposure at the temperature of interest.

Antioxidant depletion estimates were calculated for both air and leachate exposure and a combination of air and leachate exposure at temperatures ranging from 5°C to 50°C, and are plotted in Figure 12. For the calculations involving leachate exposure, the activation energy for the non-deflected pipes exposed to leachate was used for the calculations, as the non-deflected pipes had the fastest rates of antioxidant depletion when exposed to synthetic leachate. The upper range of temperature corresponds to operating temperatures in municipal solid waste landfills, which are commonly up to 30–40°C, but potentially may be as high as 50–60°C (Rowe 2005; Koerner and Koerner 2006). Figure 12 shows that, at 50°C, it is predicted that antioxidants will be depleted after 10 years when exposed to leachate, and after 20 years when exposed to air. The lower range of 5°C corresponds to possible mean ground-water temperature for areas with a local mean temperature range of 8–10°C (Rowe 2005). Figure 12 shows that, at 5°C, it is predicted that antioxidants will be depleted after over 240 years when exposed to leachate, and after 970 years when exposed to air.

Obviously, elevated temperatures have a significant impact on the time for antioxidant depletion of the pipes. It appears that if temperatures approach 50°C for extended periods of time (e.g. for a clogged leachate collection system, or possibly where the landfill is operated as a bioreactor with leachate circulation), the antioxidant depletion time may be of the order of two decades, and consideration should given to evaluating the next two stages of the pipe's service life (i.e. the induction time to polymer degradation, and the time for the engineering properties of interest to degrade to the extent where they no longer perform their design function).
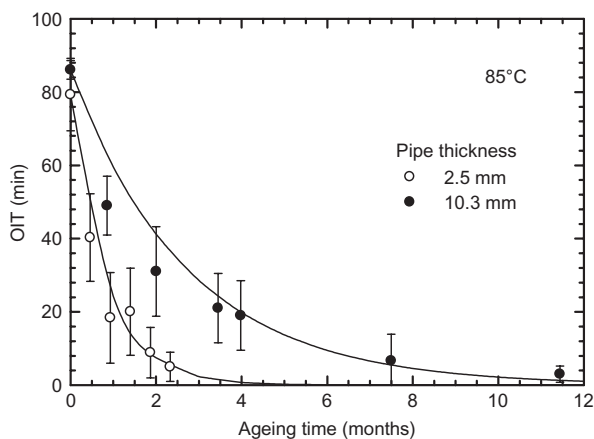
Figure 11. OIT with time for thin and thick non-deflected pipes in leachate at 85°C
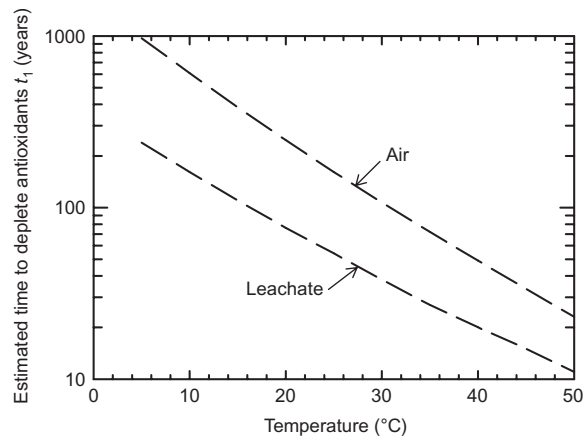
Figure 12. Estimated time to deplete antioxidants for the particular HDPE pipe tested

The antioxidant depletion predictions for the pipes exposed only to synthetic leachate are believed to be somewhat conservative because of a number of limitations in the experimental design. The service life predictions for the synthetic leachate assume that the pipe is fully immersed in full-strength leachate for its entire service life. In reality the pipe is surrounded by gravel, which limits the surface area that is in contact with leachate. Also, in the field the pipes may be drained (depending on the operation of the leachate collection system), so some headspace may exist inside the pipe that is in contact with the atmosphere.

If it is assumed that the pipe is equally exposed to both leachate and air, an estimate of the service life of the pipe can be obtained by taking the average of the air and leachate service lives. This provides antioxidant depletion time predictions of approximately 240 years at 5°C, reducing to around 20 years at 50°C. These values may be expected to underestimate antioxidant depletion rates, since they do not take into account the reduced surface area of the pipe because of contact with soil particles, and they also assume that the atmosphere inside a landfill leachate collection pipe contains oxygen, whereas in reality is it most likely anaerobic, which would result in a slower rate of oxidation than that measured in air. Additionally, the service life predictions for the pipe assume that the leachate does not degrade in strength over time, but the leachate strength in the field most likely decreases with time (Rowe *et al.* 2004), which would result in longer service life predictions.

6. CONCLUSIONS

Antioxidant depletion rates were obtained for samples of one particular high-density polyethylene pipe when immersed in air and a synthetic municipal solid waste leachate. The synthetic leachate consisted mostly of water with trace metals and a surfactant, was reduced to achieve oxygen-deficient conditions, and had a pH of 6. Oxidative induction time (OIT) was measured on pipe specimens that were aged at temperatures of 22°C, 40°C, 70°C and 85°C to quantify the antioxidant depletion with time. OIT values were obtained for specimens taken across the thickness of the pipe. The size of these specimens were too large to be able to discern experimentally a through-thickness variation in OIT, but rather were selected to provide a representative OIT value through the entire wall thickness.

For the particular pipe, antioxidant formulation and conditions examined, the following conclusions may be drawn.

- Antioxidants can deplete even faster under reduced (i.e. oxygen deficient) conditions than in air when immersed in the particular synthetic leachate tested. This shows that oxidative degradation of HDPE leachate collection pipes in landfills may still be significant even in environments where oxygen is limited.
- After ageing the pipe samples for 2 years at temperatures up to 85°C, only the first stage of degradation was observed, based on no statistically significant change in melt flow index, crystallinity or flexural modulus of the pipe.
- Of the factors examined, the rate of antioxidant depletion was affected most by the ageing temperature, with much faster depletion occurring at higher temperatures.
- Antioxidant depletion was faster when immersed in the synthetic leachate rather than in air. This is consistent with previous studies that showed that surfactant in the leachate leads to less antioxidant partitioning at the interface between the pipe and surrounding medium, and hence leads to faster antioxidant depletion.
- Antioxidant depletion was much faster for the thin pipe examined than for a thick pipe. This is consistent with previous studies that showed that the depletion of antioxidants is by outward diffusion: hence the thinner the pipe, the shorter the diffusion path and the faster the antioxidant depletion.
- No significant difference in antioxidant depletion was found whether the pipe was deflected with a 10% reduction in vertical outside pipe diameter or not deflected.
- Predictions of the time to deplete antioxidants from Arrhenius extrapolations of the reported data indicate that depletion of antioxidants may take from as long as 600 years at 10°C to as little as 20 years at 50°C when exposed to air, and may reduce to 160 years at 10°C or 10 years at 50°C if exposed to the synthetic leachate.

NOTATION

Basic SI units are given in parentheses.

A collisional factor in Arrhenius equation (1/s)
E_a activation energy (J/mol)
E_h electrical potential (V)
OIT   oxidative induction time (s)
OIT_t OIT value at time t (s)
R gas constant (J/(mol K))
s OIT degradation rate (1/s)
T temperature (K)
t time (s)
t_s service life of pipe samples (s)
t_1 stage 1 lifetime (s)
t_2 stage 2 lifetime (s)
t_3 stage 3 lifetime (s)

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