

# Effects of exposure conditions on the depletion of antioxidants from high-density polyethylene (HDPE) geomembranes

Henri P. Sangam and R. Kerry Rowe

**Abstract:** Laboratory-accelerated ageing tests have been conducted to examine the depletion of antioxidants from high-density polyethylene (HDPE) geomembranes as a result of their exposure to various environments. Samples of 2.0 mm thick geomembrane were exposed to air, water, and municipal solid waste (MSW) leachate at temperatures of 22, 40, 55, 70, and 85°C. At various time intervals, samples were collected and the oxidative induction time (OIT) was evaluated. The results indicated that the antioxidants are depleted at rates 1.6 to 2.4 times faster for samples in water than for air-exposed samples. For samples in leachate, the depletion is about 4 times faster than that in air and 1.6–3.2 times faster than that in water. Using these rates, it is estimated that if the geomembrane examined were used as an MSW landfill primary liner, it would take at least 40 years to deplete the antioxidants from the geomembrane at a temperature of 33°C and over 150 years at a temperature of 13°C.

*Key words:* ageing, antioxidants, durability, oxidative induction time, HDPE geomembrane, antioxidant depletion time.

**Résumé :** On a conduit des essais de vieillissement accéléré en laboratoire pour examiner la réduction des antioxydants dans les géomembranes de polyéthylène de haute densité (HDPE) résultant de leur exposition à divers environnements. Des échantillons de géomembrane de 2,0 mm d'épaisseur ont été exposés à l'air, à l'eau et au lixiviant de résidus municipaux solides (MSW) à des températures de 22, 40, 55, 70, et 85°C. À différents intervalles de temps, des échantillons ont été prélevés et on a évalué le temps d'induction d'oxydation (OIT). Les résultats ont indiqué que les antioxydants sont réduits à des vitesses de 1,6 à 2,4 fois plus grandes pour des échantillons dans l'eau que pour des échantillons exposés à l'air. Pour des échantillons dans le lixiviant, la réduction est d'environ 4 fois plus rapide que dans l'air et 1,6 à 3,2 fois plus rapide que dans l'eau. En utilisant ces vitesses, on estime que si la géomembrane examinée avait été utilisée comme une membrane primaire MSW de site d'enfouissement, ça prendrait au moins 40 ans pour réduire complètement les antioxydants de la membrane à une température de 33°C, alors qu'à 13°C, le temps de réduction serait de plus de 150 ans.

*Mots clés :* vieillissement, antioxydants, durabilité, temps d'induction d'oxydation, géomembrane HDPE, temps de réduction de l'antioxydant.

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## Introduction

With the increasing use of geomembranes in barrier systems for landfills and other containment applications, there has been an increasing need to address their long-term performance and effectiveness in protecting the groundwater from contamination. There is some field evidence (Schmidt et al. 1984; Hsuan et al. 1991; Brady et al. 1994; Rollin et al. 1994; Rowe et al. 1998) to suggest that these polymer-based materials may experience a change in their properties with time. This raises the following question: How long will these liners adequately perform their design function?

Although the most reliable method of determining the service life of geomembranes would be from exposure under the actual field conditions, this is not presently feasible due to the length of time that would be required to obtain useful results. In addition, there is a paucity of field performance records from which the service life may be deduced. Consequently, several "accelerated ageing" tests have been developed which attempt to simulate long-term exposure of high-density polyethylene (HDPE) geomembranes and to address their durability and degradation issues for landfills and other containment applications. Incubation and immersion media usually used include distilled or tap water (e.g., Duquennoi et al. 1995; Hsuan and Koerner 1995), simulated leachate that is rich in organic solvents (Carraro et al. 1997), simulated leachate containing a surface-active agent (Maisonneuve et al. 1997), and real municipal solid waste (MSW) leachate (Duquennoi et al. 1995; Surmann et al. 1995). Some investigators have also examined the effects of tensile stresses on the degradation of HDPE geomembranes (Surmann et al. 1995; Cazzufi et al. 1995).

Although the degradation of polyethylene geomembranes may take various forms (Koerner et al. 1992; Rowe and

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H.P. Sangam and R.K. Rowe,<sup>1</sup> GeoEngineering Centre at Queen's – RMC, Department of Civil Engineering, Ellis Hall, Queen's University, Kingston, ON K7L 3N6, Canada.

<sup>1</sup>Corresponding author (e-mail: [kerry@civil.queensu.ca](mailto:kerry@civil.queensu.ca)).

Sangam 2002), it is recognized that oxidation has a particularly severe impact on polyethylene materials (Hawkins 1984). It is generally agreed that the fundamental process underlying the oxidation of polymeric material like HDPE is a free radical chain mechanism (Kelen 1983; Grassie and Scott 1985). If oxidation occurs, chain scission leads to a decrease in molecular weight, making the material brittle and thereby prone to environmental stress cracking (Tisinger and Giroud 1993).

Antioxidants and stabilizers added to the geomembrane formulation in proportions of about 0.5–1.0% by weight are often used to retard or halt the oxidation process. These protective agents can be classified in two distinct groups referred to as primary and secondary antioxidants (Chirinos-Padrón and Allen 1992; Fay and King 1994). Primary antioxidants function by trapping the peroxy radical formed in the presence of oxygen, whereas secondary antioxidants reduce the active hydroperoxides to inactive alcohol (Grassie and Scott 1985; Yachigo 1992). The effectiveness of the antioxidants depends on various factors including the total amount, the types, and the combination used and the geomembrane temperature (Chirinos-Padrón and Allen 1992; Fay and King 1994).

The oxidative degradation of HDPE geomembranes appears to proceed in three relatively distinct stages (Hsuan and Koerner 1995, 1998): depletion of antioxidants (stage I), onset of the degradation (stage II), and degradation to failure (stage III). Thus, the service life of the geomembrane will be the sum of the time required for antioxidant depletion, the induction time, and the period during which the physical properties of the geomembrane change to the point that geomembrane failure occurs (stage III). A detailed discussion of these stages has been provided by Hsuan and Koerner (1995, 1998) and Rowe and Sangam (2002).

There are several factors that affect the oxidative degradation of HDPE geomembranes, including the geomembrane properties (branching, tertiary hydrogen, crystallinity, thickness), exposure medium (liquid, soil), exposure conditions (ambient atmosphere, water, leachate, sunlight, temperature), and applied mechanical stress field (tensile stress). During the depletion stage of the antioxidants, they are consumed as a result of chemical reactions with the oxygen, free radicals, and alkyl peroxides and (or) physical loss by diffusion, extraction, or volatilization (Luston 1986). This paper focuses on estimating the length of this antioxidant depletion stage under three different exposure conditions: in air, in water, and in leachate.

### Concepts of laboratory-accelerated ageing tests

The basic concept of the laboratory-accelerated ageing testing is to use a time–temperature shift to estimate the time required for antioxidant depletion based on data from samples aged at different elevated temperatures. The primary assumption is that ageing and degradation are activated processes in which the behaviour of the material within the elevated-temperature incubation range is constant and can be extrapolated to the lower temperature behaviour of practical interest (Koerner et al. 1990). The results obtained at the elevated temperatures can then be extrapolated to representative

service conditions using a time–temperature superposition principle (Arrhenius modelling) to estimate the field service life based on the relationship

$$[1] \quad s = A \exp\left(\frac{-E_a}{RT}\right)$$

where  $s$  is the rate of the reduction in the material property (here antioxidant depletion) considered with respect to time ( $\text{time}^{-1}$ ),  $T$  is the absolute temperature (in K),  $A$  is a constant often called the collisional factor and is material-exposure system dependent,  $E_a$  is the activation energy (in  $\text{J}\cdot\text{mol}^{-1}$ ), and  $R$  is the universal gas constant ( $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ). This extrapolation assumes that  $E_a$  remains relatively constant within the temperature range examined.

Koerner et al. (1992) have described the potential uses of this type of modelling for predicting geosynthetics degradation. The properties to which it is applicable include physical, mechanical, and chemical. The main concerns with this time–temperature superposition approach, however, are as follows: (i) the level of temperature to be used, (ii) the ageing medium, and (iii) the properties to be evaluated and methods of assessing when the geomembrane has reached its service life.

The selection of the elevated temperatures is based on two considerations. First, the temperature should be as high as practical to accelerate the ageing process and allow the evaluation of the degradation in as short a time period as practical. Second, the selected temperatures should not be so high that the polymer tested changes its state compared to that in service. If the temperature is too high and does cause a state change, there will be a change in the reaction rate represented by the activation energy. For example, Wisse and Birkenfeld (1982) showed that the activation energy for a polyester (PET) changes from 65 to 93  $\text{kJ}\cdot\text{mol}^{-1}$  when the incubation temperature is higher than the material glass transition temperature of 80°C. In general, transition temperatures, especially the glass transition and the melt temperatures, define boundaries that should not be passed in an accelerated ageing test (Verdu 1988). In short, both the service and elevated temperatures should be in the same temperature range. For HDPE geomembranes, the glass transition is below –35°C (i.e., below the normal operating temperature for most geomembranes) and the melting point is about 130–137°C (DeLassus and Whiteman 1999).

Another factor to be considered when selecting the incubation temperatures is the type of antioxidants incorporated into the geomembrane. Fay and King (1994) indicated that antioxidants have specific temperature ranges over which they are effective. Thus, the temperature should not be so high as to destroy the antioxidants. In addition, several studies (Smith et al. 1992; Karlsson et al. 1992) have shown that the volatilization of the antioxidants may be very important at temperatures greater than 95°C. Since in landfill applications the operating critical temperature is likely to be less than 95°C, it is important to avoid excessive volatilization by keeping the incubation temperatures below 95°C in the laboratory.

Although the exposure conditions should be identical to those expected in the field, it is practically impossible to simulate such conditions in the laboratory because of the dif-

difficulties associated with maintaining and controlling all of the interacting factors (e.g., stress, leachate strength, bacteria) that are encountered in the field. One practical problem with the use of a real landfill leachate is that its chemical composition is highly variable with time because of variability coming from the landfill and changes that occur in the laboratory with time. To overcome this difficulty, it is more practical to use synthetic leachate wherein the constituents can be controlled.

## Laboratory study

### Material

The geomembrane examined was provided by GSE Lining Technology Inc. (Houston, Tex.). The geomembrane is a 2.0 mm thick smooth HDPE geomembrane manufactured from a copolymer resin and with a density of about  $0.940 \text{ g}\cdot\text{cm}^{-3}$ . The 2.0 mm thickness was selected based on the range of geomembrane liner thicknesses suggested in various regulations worldwide (e.g., Subtitle D in the United States; Germany; Ontario Regulation 238/98) as summarized by Koerner and Koerner (1999). The relevant properties of the geomembrane examined are summarized in Table 1. The initial oxidative induction time (OIT) value is about 133 min greater than the minimum of 100 min suggested in Ontario Regulation 232/98 (Environmental Protection Act 1998).

### Exposure conditions

The three exposure conditions examined were air, water, and leachate. In each case, the geomembrane was immersed in the medium (i.e., exposed to the same conditions on both sides). It is acknowledged that all three exposure conditions represent idealized conditions, since in the field the geomembrane may be exposed to a combination of conditions. Air exposure most closely simulates a geomembrane used as an exposed cover where the soil below is essentially dry. The water-immersion condition most closely approximates a geomembrane in a pond or canal where the soil below is saturated. In many practical situations, the exposure will be different on the two sides of the geomembrane. For example, a geomembrane base liner may be exposed to leachate on one side and water (e.g., near-saturated bentonite in a geosynthetic clay liner) on the other side. Thus, these results are intended to provide an indication of potential times under idealized conditions and their application to practical situations will require engineering judgement.

The leachate used was a synthetic leachate with a composition (Table 2) selected based on data relating to the leachate from the Keele Valley municipal solid waste landfill (Hrapovic 2001). To simulate real leachate, which typically contains surfactants, a particular surfactant (IGEPAL® CA-720) was added to the leachate. This particular surfactant was selected because it is commonly used in environmental stress crack resistance testing.

The incubation temperatures were selected to meet requirements of no modification of the nature of the material, no destruction of the antioxidants present in the material, and minimization of antioxidant losses due to volatilization. Based on these criteria, four elevated temperatures of 40, 55, 70, and 85°C were selected. In addition, a set of samples was conditioned under the three exposure conditions at the

laboratory temperature ( $22 \pm 2^\circ\text{C}$ ) to serve as control for the incubation experiments at elevated temperatures.

### Procedure

The HDPE geomembrane was cut in various coupons having different sizes that were placed in the incubation media at the required temperature. The samples were kept apart (to allow circulation of the immersion media between the coupons) using 5 mm glass rods. The water-immersion tests were conducted in stainless steel containers. The geomembrane did not come into contact with the stainless steel due to the use of glass support rods. For the synthetic leachate exposure, it was important to avoid any leachate interaction with the container material that could affect the degradation processes examined. Thus, glass containers that were known to be inert to the leachate constituents were used. To ensure that the leachate strength remained relatively constant and that reduced conditions were continuously present during the testing period, the leachate was frequently replaced by a freshly prepared leachate. Full details regarding the test procedures are provided by Sangam (2001).

At various time intervals, the incubated samples were retrieved and the amount of antioxidant remaining in the material was evaluated using oxidative induction time tests. Test methods are described in the following section.

### Analytical methods

The OIT is a well-accepted indicator of the amount of antioxidant in the geomembrane (Hsuan and Koerner 1998) and was evaluated according to American Society for Testing and Materials (ASTM 1995) method D3895 (standard OIT) using a differential calorimeter (DSC) and a testing temperature of 200°C and pressure of 35 kPa. The main advantages of the standard OIT are its simplicity, short testing period (about 100 min), and high sensitivity. The main disadvantage associated with this test is that the high temperature of 200°C may destroy some types of antioxidants and hence may bias the results.

A similar test known as high-pressure (HP) OIT was also used for some tests as discussed in the following section. The test follows ASTM (1997) test method D5885 at an isothermal temperature of 150°C and a pressure of 3500 kPa and under conditions similar to those prescribed for the standard OIT. The primary aim of the high-pressure test is to enable the identification of the different types of antioxidants, especially hindered amine antioxidants (Hsuan and Koerner 1998). This test is less sensitive to low OIT values, however, and is inconvenient because of the long duration of the test (about 400 min).

## Experimental results

### Validation of OIT tests

To assess the potential effect of the choice of method for evaluating OIT, two tests (Std-OIT and HP-OIT) were performed on samples incubated at 85°C under different exposure conditions. The gradual decreases in OIT values obtained by the Std-OIT test (ASTM D3895: 200°C, 35 kPa) and the HP-OIT test (ASTM D5885: 150°C, 3500 kPa) are shown in Figs. 1 and 2, respectively, and it can be seen that the trends are very similar. Figure 3 shows the relationship between the

**Table 1.** Properties of the HDPE geomembrane examined.

| Property                                  | ASTM method | Average | COV (%) |
|---|-------------|---------|---------|
| Thickness (mm)                            | D5199       | 2.0     | 1.4     |
| Density ( $\text{g}\cdot\text{cm}^{-3}$ ) | D792        | 0.940   | 0.3     |
| Carbon black content (%)                  | D1603       | 2.54    | —       |
| Carbon black dispersion                   | D3015       | A1–A2   |         |
| Oxidative induction time, OIT (min)       | D3895       | 133     | 3.7     |
| Crystallinity (%)                         | E794        | 44      | 1.2     |
| Melt flow index (g/10 min)                | D1238       | 0.42    |         |
| Stress cracking resistance (h)            | D5397       | 210     |         |
| Initial tear resistance (N)               | D1004       | 354     | 3.6     |
| Puncture resistance (N)                   | D4833       | 736     | 1.3     |
| Tensile strength at yield (kN/m)          | D638        | 35      | 1.4     |
| Tensile strength at break (kN/m)          | D638        | 77      | 3.7     |
| Tensile strain at yield (%)               | D638        | 16      | 3.6     |
| Tensile strain at break (%)               | D638        | 863     | 1.8     |

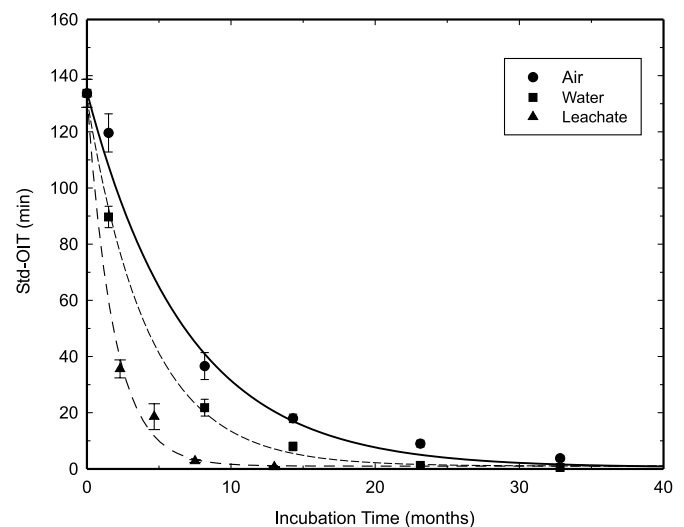
**Note:** COV, coefficient of variation (= (standard deviation)/(mean)  $\times$  100).

**Table 2.** Composition of synthetic MSW landfill leachate (modified from Hrapovic 2001).

| Component   | Conc. ( $\text{mg}\cdot\text{L}^{-1}$ ) <sup>a</sup> |
|---|--|
| <b>Volatile fatty acid</b>  |  |
| Acetic acid   | 4000   |
| Propionic acid  | 3000   |
| Butyric acid  | 500  |
| <b>Inorganics</b>   |  |
| Na <sup>+</sup>   | 1615   |
| K <sup>+</sup>  | 354  |
| NH <sub>4</sub> <sup>+</sup>  | 618  |
| Ca <sup>2+</sup>  | 1224   |
| Mg <sup>2+</sup>  | 473  |
| Cl <sup>-</sup>   | 4414   |
| HCO <sub>3</sub> <sup>-</sup>   | 4876   |
| NO <sub>3</sub> <sup>2-</sup>   | 40   |
| SO <sub>4</sub> <sup>2-</sup>   | 137  |
| HPO <sub>4</sub> <sup>2-</sup>  | 18   |
| CO <sub>3</sub> <sup>2-</sup>   | 156  |
| CO(NH <sub>2</sub> ) <sub>2</sub>   | 772  |
| $E_h$ (adjusted by NaS $\cdot$ 9H <sub>2</sub> O)   | $\sim$ -328 mV                                       |
| pH (adjusted by NaOH)   | $\sim$ 6   |
| <b>Trace metal solution</b>   |  |
| FeSO <sub>4</sub> $\cdot$ 7H <sub>2</sub> O   | 4  |
| H <sub>3</sub> BO <sub>3</sub>  | 0.1  |
| ZnSO <sub>4</sub> $\cdot$ 7H <sub>2</sub> O   | 0.1  |
| CuSO <sub>4</sub> $\cdot$ 5H <sub>2</sub> O   | 0.08   |
| MnSO <sub>4</sub> $\cdot$ H <sub>2</sub> O  | 1  |
| (NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> $\cdot$ 4H <sub>2</sub> O | 0.1  |
| Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> $\cdot$ 16H <sub>2</sub> O                | 0.06   |
| CoSO <sub>4</sub> $\cdot$ 7H <sub>2</sub> O   | 0.3  |
| <b>Surfactant</b>   |  |
| IGEPAL® CA-720  | 5000   |

<sup>a</sup>All concentrations are given as  $\text{mg}\cdot\text{L}^{-1}$  except mV for  $E_h$  and no units for pH.

two sets of test results. The linear variation and the consistency between the data suggest that the use of the high temperature in the Std-OIT test does not destroy the antioxidants used in the formulation of the geomembrane examined. The

**Fig. 1.** Variation of Std-OIT with incubation time at 85°C under different exposure conditions. The data points are means of five replicates and the vertical bars represent standard deviation.

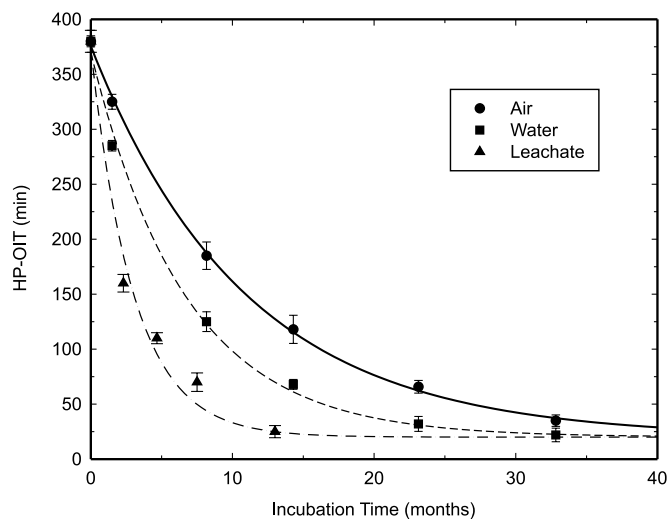
results are similar to those observed by Hsuan and Koerner (1998). Hsuan and Koerner indicate that the linear variation between the two tests suggests that hindered amines or thiosynergists (which have effective temperatures of less than 200°C) are not present in the material and probably the main antioxidants consist of phosphites and hindered phenols that are still effective at 200°C (Hsuan and Guan 1997, 1998).

The observed results also indicate that the Std-OIT test can be used to accurately assess the depletion of the antioxidants in the geomembrane examined. Thus, the Std-OIT test was used for monitoring the OIT for other incubation conditions.

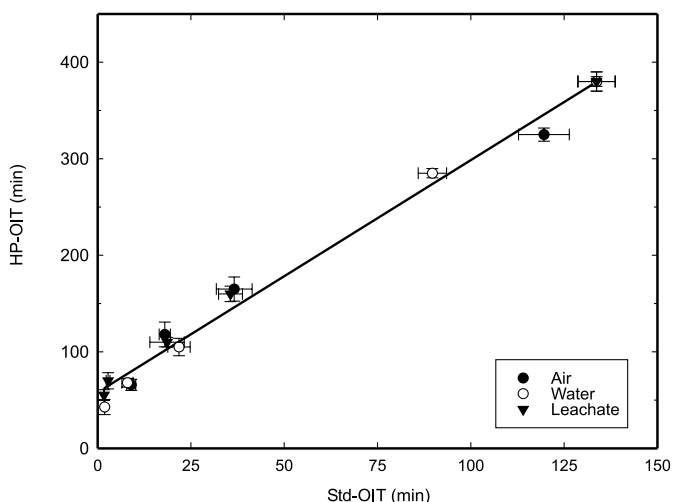
#### Variation of OIT with incubation time

The OIT was measured on incubated samples collected at selected times. Each data point is the average of five replicate samples tested and the vertical bars represent standard deviation. The gradual and continuous decrease of the OIT values with incubation time is evident from the data presented in Fig. 1 for the incubation at 85°C and in Fig. 4 for

**Fig. 2.** Variation of HP-OIT with incubation time at 85°C under different exposure conditions.



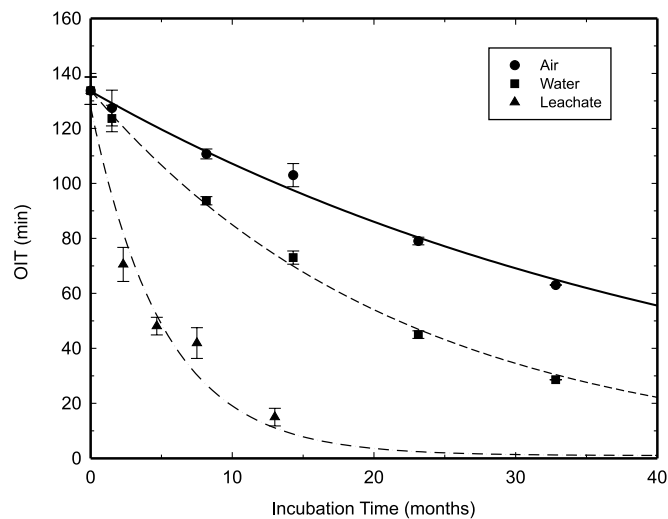
**Fig. 3.** Relationship between Std-OIT and HP-OIT for samples incubated at 85°C.



the incubation at 55°C. Similar plots were obtained at other temperatures (Sangam 2001). The decrease in OIT evident in each case indicates the consumption or removal of the antioxidants originally in the new geomembrane.

The reduction in the OIT appears to be dependent on the exposure conditions. The samples exposed to air had the smallest reduction in the OIT (see Figs. 1, 4) and therefore had lost less antioxidant at a given time than those for the other two exposure conditions (water and leachate). Leachate exposure caused the greatest depletion of antioxidants. For example, relative to an initial OIT value of 133 min at 85°C (Fig. 1), leachate exposure gave rise to a reduction in OIT to less than 3 min after 8 months of incubation, whereas the OIT was 37 and 22 min for air and water exposure, respectively, after 8 months. After 13 months of incubation, the antioxidants were almost completely consumed (OIT = 0.7 min) when immersed in leachate, and some antioxidants remained in samples exposed to water and air with OIT of 8 and 18 min, respectively.

**Fig. 4.** Variation of OIT with incubation time at 55°C under different exposure conditions.



As indicated by Luston (1986), the consumption of antioxidants is attributable to various factors including their chemical reactions with oxygen, free radicals, and alkylperoxides and (or) their physical losses by diffusion, extraction, or volatilization. In the case of air exposure, volatilization and probably chemical reactions are the only processes that can induce the loss of antioxidant, and for water and leachate exposures the extraction of the antioxidants may be dominant. The data also indicate that the decrease of the antioxidant was faster for leachate exposure than for water exposure. As discussed later in the paper, the leachate constituents increased the extraction of antioxidants and (or) their consumption.

The temperature dependence of the consumption of antioxidants can be appreciated by comparing results in Figs. 1 and 4 for a given immersion case (i.e., for air, water, or leachate) for incubation temperatures of 85 and 55°C, respectively. Figures 1 and 4 show that for a given exposure condition there is a greater decrease in the OIT values at a higher temperature. For instance, after 14 months of incubation under air exposure conditions, the OIT of the HDPE geomembrane examined decreased from 133 min to 18 min at 85°C and from 133 min to 103 min at 55°C. This general trend was also observed for other exposure conditions and substantiates the role played by the elevated temperatures in accelerating the depletion of the antioxidants. This suggests that the consumption of the antioxidants under the exposure conditions examined is an activated process.

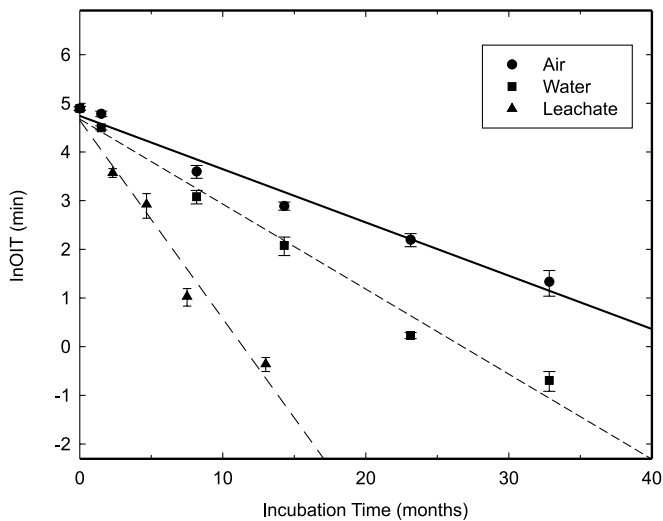
**Rates of antioxidant depletion**

Figure 5 presents a typical plot of ln(OIT) with incubation time yielding straight lines for each exposure condition at 85°C, suggesting that the depletion of antioxidants follows a first-order decay, with the rate represented by the slopes of the lines. At any *t*, the OIT representing the total amount of antioxidants remaining in the geomembrane can be expressed as

$$[2] \quad OIT(t) = OIT_0 e^{-st}$$

where *OIT*<sub>0</sub> is the initial OIT value (in minutes), and *s* is the rate of antioxidant depletion (in month<sup>-1</sup>).

**Fig. 5.** Plot of  $\ln(\text{OIT})$  with incubation time at 85°C and under different exposure conditions.



The inferred rates ( $s$ ) for the incubation conditions examined are summarized in Table 3. The values  $0.1746$  and  $0.0470 \text{ month}^{-1}$  obtained for water bath exposure at 85 and 55°C, respectively, compared well with depletion rates of  $0.1765$  and  $0.0467 \text{ month}^{-1}$ , respectively, reported by Hsuan and Koerner (1995) for an HDPE geomembrane under the same incubation conditions. This suggests that similar antioxidants are present in the HDPE geomembrane investigated here and in that tested by Hsuan and Koerner, as suggested by the Std-OIT and HP-OIT test results previously discussed.

Table 3 shows that the highest depletion rates are obtained for the leachate exposure followed by the water bath exposure and air exposure. A comparison between the rates (Table 3) in terms of a ratio of the rates for each pair of exposure conditions being compared shows that the depletion rates for water immersion vary between 1.6 and 2.4 times the rates when samples are exposed to air. A ratio of about threefold has been reported by Smith et al. (1992) for medium-density polyethylene pipe tested at temperatures of 80, 95, and 105°C with hot water in the pipe and air outside the pipe. The pipe wall thickness was about 2.2 mm, the density of the material about  $0.934 \text{ g}\cdot\text{cm}^{-3}$ , and the main antioxidants were phenolic and phosphites.

The main factors that control the extraction of antioxidants are (i) their dissolution from the geomembrane surface into the immersion solution, (ii) their reaction in the solution (consequently their concentrations), and (iii) the outward diffusion from the polymer matrix (Luston 1986). Antioxidant depletion associated with the synthetic leachate exposure is about 3.8- to 7.0-fold faster than that for air exposure and 2.3- to 3.2-fold faster than that for water exposure. Since the synthetic leachate was highly reduced (redox potential  $E_h \approx -328 \text{ mV}$ ), there was no free oxygen available in the leachate to react with the antioxidants and the loss of antioxidants can be attributed to extraction. The higher rates observed for leachate immersion compared with water immersion, however, suggest that the extraction was accelerated relative to water by the constituents present in the synthetic leachate.

Although the precise reason for the faster removal has not been established, it may be hypothesized to be the result of

some combination of the effect of surfactant and transition metals as noted later in this section. It is well recognized that one of the direct effects of a surfactant like IGEPAL® CA-720 on a geomembrane is the increase of its wettability due to the reduction of the material surface tension. As a consequence, the antioxidants at the surface may have been more quickly dissolved and extracted, thereby inducing a higher concentration gradient of antioxidants between the core of the material and the surface. This increase of the gradient will increase the outward diffusive flux of the antioxidants.

The high antioxidant depletion rates measured in leachate compared with those in water may also be partially attributable to the transition metals and other inorganic compounds present in the synthetic leachate used. It is known (e.g., Osawa and Saito 1978; Wisse et al. 1990) that transition metals increase the consumption of antioxidant by reaction even in relatively anoxic conditions. For HDPE geomembranes, the reaction with the antioxidant will likely predominantly occur at the surface of the material due to the low diffusion coefficient for metals in HDPE as shown by August et al. (1992).

The temperature dependence of antioxidant depletion rates is also evident from Table 3, indicating that the depletion rates are higher at high temperatures than at low temperatures. Based on these data, an Arrhenius equation (eq. [1]) can be established for each exposure condition. The plot of  $\ln(s)$  as a function of the inverse of the incubation temperature (in K) is presented in Fig. 6. The inferred activation energy ( $E_a$ ) and the derived Arrhenius equation for each exposure condition are summarized in Table 4.

### Preliminary application to MSW landfill liners

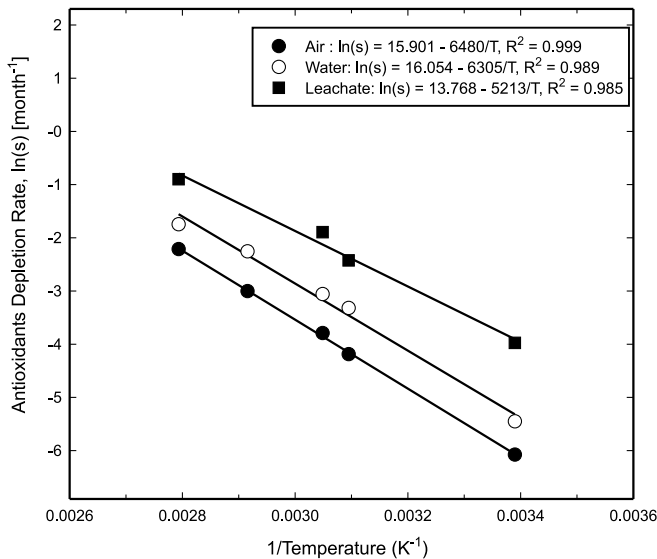
In landfill applications, HDPE geomembranes are used as primary or secondary liners. The conditions that the geomembrane will encounter as a liner are presented in Table 5. The temperatures for the primary liner were selected based on Barone et al. (1997), who reported temperatures monitored for Keele Valley landfill for two different leachate collection systems and stages of construction. The lowest temperature of 13°C was the average temperature measured for a leachate collection system that has a 0.3 m thick continuous stone drainage blanket of 50 mm, uniformly graded, dolomitic limestone over a protective sand layer approximately 0.3 m thick with leachate head varying from 0.1 to 0.4 m. The highest temperature of 33°C corresponds to the average temperature measured at the base of the same landfill, where the leachate collection layer consists of French drains (stone with a nominal diameter of 50 mm) at a spacing of about 65 m sloping towards the collection pipes where there was a leachate mound over 5 m high at the location where the temperature was measured.

In the following estimates, it is assumed that a geomembrane with an initial OIT of about 133 min (i.e., similar to that tested) has been properly designed, selected, and installed with appropriate construction quality control and assurance and was performing adequately after construction was completed. This implies that the eventual failure will occur after oxidative degradation. If this is accepted, then a lower bound estimate of the service life of the geomembrane

**Table 3.** Comparison of the inferred depletion rates,  $s$  ( $\text{month}^{-1}$ ), for different exposure conditions.

| Temp.<br>(°C) | Exposure conditions |               |               | Comparison |              |                |
|---------------|---------------------|---------------|---------------|------------|--------------|----------------|
|               | Air                 | Water         | Leachate      | Water/air  | Leachate/air | Leachate/water |
| 85            | 0.1094 (0.99)       | 0.1746 (0.98) | 0.4074 (0.97) | 1.6        | 4.0          | 2.3            |
| 70            | 0.0497 (0.98)       | 0.1050 (0.99) | —             | 2.0        | —            | —              |
| 55            | 0.0226 (0.99)       | 0.0470 (0.99) | 0.1504 (0.97) | 2.1        | 7.0          | 3.2            |
| 40            | 0.0152 (0.99)       | 0.0362 (0.99) | 0.0886 (0.98) | 2.4        | 3.8          | 2.4            |
| 22 (room)     | 0.0023 (0.86)       | 0.0043 (0.86) | 0.0188 (0.91) | 2.0        | 4.7          | 2.5            |

Note: The numbers in parentheses represent  $R^2$ .

**Fig. 6.** Arrhenius plot of antioxidant depletion rate for different exposure conditions.**Table 4.** Inferred activation energy ( $E_a$ ) and corresponding Arrhenius equation for each exposure condition examined.

| Exposure | $E_a$ ( $\text{kJ}\cdot\text{mol}^{-1}$ ) | Arrhenius equation ( $\text{month}^{-1}$ ) | $R^2$ |
|----------|---|--|-------|
| Air      | 53.9                                      | $\ln(s) = 15.901 - 6480/T$                 | 0.999 |
| Water    | 52.4                                      | $\ln(s) = 16.054 - 6305/T$                 | 0.989 |
| Leachate | 43.3                                      | $\ln(s) = 13.768 - 5213/T$                 | 0.985 |

Note:  $T$ , temperature in K.

can be obtained based on the time for antioxidant depletion. The actual service life may be expected to be longer due to the additional time required for induction and subsequent degradation.

A geomembrane used in a primary composite liner for a landfill will perpetually have leachate on its top surface and soil (e.g., compacted clay liner) in contact with the bottom surface. In this case, the rate of the antioxidant depletion may not be simply determined by the rate obtained from the laboratory-accelerated tests in air, water, or leachate. Since the conditions above and below the geomembrane involve some other material in contact (e.g., geotextile and (or) sand above and clay below), it may be hypothesized that having water or leachate in direct contact represent a worst-case estimate of the time required for antioxidant depletion. An estimate based on these tests represents a lower bound to the antioxidant depletion time and hence the service life under

these exposure conditions (i.e., the time in the field would be expected to be longer than that calculated).

Assuming that the temperature on the liner is about  $13^\circ\text{C}$  (286 K), the estimated rates of antioxidant depletion for air, water, and leachate exposure (using equations in Table 4) are 0.0012, 0.0025, and  $0.0116 \text{ month}^{-1}$ , respectively. When the temperature increases to  $33^\circ\text{C}$ , the estimated rates are about 0.0051, 0.0106, and  $0.0381 \text{ month}^{-1}$  for air, water, and leachate exposure, respectively. As shown in Table 6, the time for complete antioxidant depletion in leachate at a temperature of  $13^\circ\text{C}$  using eq. [2] and considering the OIT of an unstabilized HDPE to be 0.5 min (Hsuan and Koerner 1998) is about 40 years, whereas it is about 190 and 390 years in water and air, respectively. At  $33^\circ\text{C}$ , the estimated times are relatively short, about 12, 44, and 90 years for leachate, water, and air exposure, respectively.

As noted earlier, these inferred depletion times correspond to the test conditions and do not apply directly to the service life of the primary geomembrane liner (PGM) due to the fact that these estimates are based on rates where the exposure conditions are identical on both sides of the geomembrane. In the field, the primary geomembrane is in contact with a leachate at its top and unsaturated (although typically nearly saturated) clay at its bottom. As suggested by Rowe (1998), it is useful to examine the average of the estimates from the conditions that prevail on each side of the liner. This examination is simply for the purposes of identifying the possible effects of mixed conditions and does not represent a prediction of actual field behaviour. In fact, as will be seen, the range of numbers clearly defines the need for future tests that more realistically simulate actual field conditions.

For the primary geomembrane, the condition at its top is fairly well defined to be one of contact with leachate. The conditions for the underlining clay are more difficult to estimate because these conditions depend greatly on water and gas contents. In the limit of a dry soil below the geomembrane, a lower bound estimate of depletion times is obtained by averaging the values calculated for leachate exposure and air exposure alone given depletion times of 210 years at  $13^\circ\text{C}$  and 50 years at  $33^\circ\text{C}$  (see column 5 in Table 6).

In reality, some moisture exists at the bottom of the geomembrane. To approximately account for this condition, the depletion for an "unsaturated" soil on either side of the geomembrane was calculated by averaging the results for air and water exposures. The results are presented in Table 6 (column 7). Using these values, it is estimated that the antioxidant depletion times for conditions of leachate on top and air-water at the bottom are approximately 160 years at  $13^\circ\text{C}$

**Table 5.** Likely conditions encountered by a primary geomembrane liner.

| Exposure                 | Assumed conditions  |
|--------------------------|---|
| Medium                   | Leachate-air; leachate - unsaturated soil; leachate-water |
| Temp. (°C)               | 13-33 <sup>a</sup>  |
| Oxygen concentration (%) | 2-8 <sup>b</sup>  |

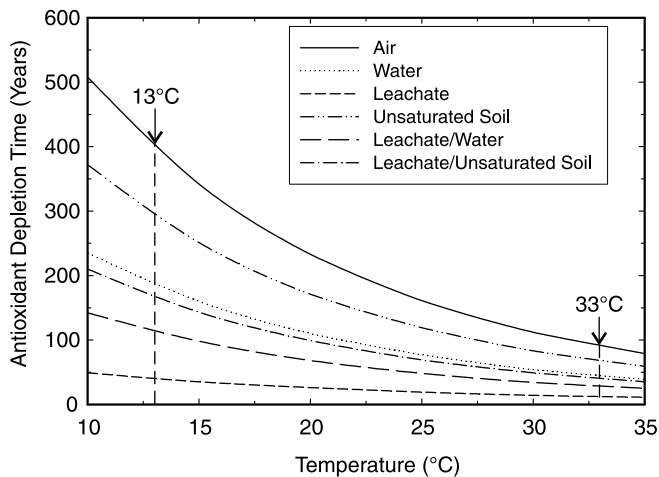
<sup>a</sup>From Barone et al. (1997).<sup>b</sup>From Hsuan (2002).**Table 6.** Estimated antioxidant depletion time (years) for a primary HDPE geomembrane.

| Temp. (°C) |     |       |          | Leachate-water                    |                        | Unsaturated soil [(air + water)/2] | Leachate - unsaturated soil [(leachate + unsaturated soil)/2] <sup>a</sup> |
|------------|-----|-------|----------|-----------------------------------|------------------------|------------------------------------|--|
|            | Air | Water | Leachate | Leachate-air [(air + leachate)/2] | [(water + leachate)/2] |                                    |  |
| 13         | 390 | 190   | 40       | 210                               | 110                    | 290                                | 160  |
| 15         | 330 | 160   | 36       | 180                               | 100                    | 250                                | 140  |
| 20         | 230 | 120   | 26       | 130                               | 70                     | 180                                | 100  |
| 25         | 160 | 80    | 22       | 90                                | 50                     | 120                                | 70   |
| 33         | 90  | 44    | 12       | 50                                | 28                     | 70                                 | 40   |

Note: After completion of all calculations, times greater than 45 years were rounded to the nearest decade. Initial OIT<sub>0</sub> = 133 min and final OIT = 0.5 min.

<sup>a</sup>This is an average of the values of air and water alone and does not really account for the presence of the soil particles (which could have a beneficial effect, since contact with soil particles reduces contact with air and (or) water). This also assumes an oxygen concentration in the air of 21%, whereas in reality it may be lower than 21%.

**Fig. 7.** Variation of estimated (lower bound) antioxidant depletion time with temperature for different exposure media. Data from the corresponding columns in Table 6.



and 40 years at 33°C (see column 8 in Table 6). Figure 7 shows the variation of the time required for the complete depletion of antioxidants from the geomembrane examined as a function of the service temperature for the three test conditions and the approximation for combined conditions discussed earlier.

The results presented are approximate and considered to be conservative for several reasons. First, since extraction is predominantly a diffusion-controlled process, averaging of times for different exposure conditions on both sides of the geomembrane to give an estimate of the case with the different exposure conditions on each side is likely to underestimate the depletion time for the mixed condition. Second, in the laboratory experiments conducted to infer the depletion rates, the leachate strength was essentially constant because it was regularly replaced and so the exposure was essentially constant over the testing period. In the field, the leachate

strength may be expected to decrease with time as noted by Rowe (1995), and the rate of antioxidant depletion might be expected to decrease and be lower than that measured in the laboratory.

## Summary and conclusions

The results from the OIT tests suggest that the depletion of antioxidants follows typical first-order decay kinetics. The results also indicate that the consumption of antioxidants is faster in samples exposed to liquid than in those exposed to air. The depletion rate in water-immersed samples is about 1.6-2.4 times that in air-exposed samples. For leachate-exposed samples, the depletion rate is about four times faster than that in air-exposed samples and 2.3-3.2 times faster than that in water-immersed samples. These observed high rates demonstrate the susceptibility of the antioxidants present in the geomembrane examined to the extraction. In addition, the results demonstrate the role played by the leachate constituents in facilitating the removal of antioxidants from the geomembrane.

The results from these tests were used to provide estimates of the antioxidant depletion times for a geomembrane. These calculations are subject to a number of limitations but do serve to give an indication of the order of magnitude that might be expected for a number of different scenarios. More important, the results and calculations highlight the potentially important role of exposure to leachate in the rate of depletion and the need for future tests that more realistically simulate field exposure conditions than simple immersion tests.

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