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# Research article

# Effects of perfluoroalkyl substances (PFAS) on antioxidant depletion from a high-density polyethylene geomembrane



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|---|--|
| Keywords:<br>Geosynthetics<br>Geomembranes<br>PFAS<br>Antioxidants<br>Landfills<br>Service-life | To safely contain Per-and Polyfluoroalkyl substances (PFAS) in municipal solid waste landfills and contaminated soil monofills, it is necessary to understand how these substances interact with components of engineered systems designed to contain them. This paper examines the interaction between one of the most critical components of the system: a high-density polyethylene (HDPE) geomembrane. The same geomembrane is immersed in PFAS solution and synthetic municipal solid waste leachate containing PFAS for 2.5 years, and the effects of PFAS on antioxidant depletion time is examined. The geomembrane is incubated in ovens at 85-40 °C to obtain data for Arrhenius predictions at typical landfill temperatures. When exposed to PFAS solution alone, the antioxidant depletion times are smaller than when the same geomembrane is immersed in synthetic municipal solid waste leachate alone. The combination of the two has a synergistic effect which leads to an even greater reduction in antioxidant depletion time for this geomembrane, with results showing a 68% decrease in predicted antioxidant depletion time of 25 °C when PEAS is present in leachate. This crudy highlighter |

#### 1. Introduction

# 1.1. PFAS and the environment

Per-and polyfluoroalkyl substances (PFAS) constitute over 9000 chemicals used in a large number of materials over the last half-century (Key et al., 1997) including products like non-stick coatings, firefighting foams, textiles, paper, material for food packaging, insecticides, and a variety of other useful products (Kissa, 1994). PFAS are widely used mainly because of their ability to repel oil and water, and are generally considered surfactants (Dixon-Anderson and Lohmann, 2018).

PFAS are subclassed into polymer and non-polymer PFAS. Under the non-polymer PFAS subclass are the per-fluorinated and the polyfluorinated compounds. The per-fluorinated subclass includes perfluorocarboxylic acids and per-fluoroalkyl sulfonic acids (Bouazza, 2021). Of these, the most studied per-fluoroalkyl acids are per-fluorooctanoic acid (PFOA) and per-fluorooctanesulfonic acid (PFOS). The carbon-fluorine bond is particularly strong, a consequence of this, is the strength, durability, heat resistance and environmental Bouazza, 2021). PFOA and PFOS have been identified as persistent organic pollutants because of their physiochemical characteristics, widespread usage and effects on wildlife and humans (Giesy and Kannan, 2001). The widespread usage of PFAS in everyday life means ultimately,

stability per-fluoroalkyl acids possess (Bartlett and Davis, 2018;

the need to consider the potential impact of PFAS on the service life of geomembranes used to contain them.

the widespread usage of FIAB in everyday incements attimately, they end up as part of our waste from PFAS-bearing consumer goods, industrial activities, sewage sludge, and contaminated site cleanup. Considering the timeline of PFAS usage, it would be fair to assume that all waste materials landfilled since the 1950s are bound to contain significant amounts of PFAS (ITRC, 2017). This makes the study of the interactions between these substances and the consequent effect on the long-term performance of geosynthetic liner components of landfill liners, such as geomembranes, of considerable importance. The need to fill this information gap is highlighted by Bouazza (2021), which gives some information on possible PFAS-geosynthetic liner interactions but concludes by acknowledging the scarcity of research evaluating the effectiveness of geosynthetic liners in containing PFAS and reiterates the need to channel more efforts into understanding the subject.

Abbreviations: PFAS, Per-and Polyfluoroalkyl Substances.

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### 1.2. Brief overview of geomembranes

Geomembranes are used as part of barrier systems for the containment of fluids generated from activities like water treatment, heap-leach mining (a method of mining where crushed ores are stacked over geomembranes in relatively thin lifts and irrigated with solvents to extract metal from ores (Zanbak, 2013).), and landfill storage of waste (municipal solid waste, industrial waste etc.). They are practically impermeable except if they have holes (e.g., Rowe et al., 2003). To minimize the leakage through holes they are often used as part of a composite liner with a clay component (Rowe, 2011). Due to their effectiveness in minimizing the escape of contaminants to the environment they have been widely used in landfills for 50 years and more recently to line specialty disposal areas (monofills) for PFAS contaminated soil. This paper focused on municipal solid waste landfill application. Although geomembranes are manufactured from many different polymers (e.g., polyvinyl chloride, polypropylene, linear low-density polyethylene, medium-density polyethylene, high-density polyethylene, chlorinated polyethylene, chlorosulphonated polyethylene, ethylene propylene rubber and bitumen; Rowe and Sangam, 2002; Scheirs, 2009), high-density polyethylene (HDPE) is most extensively used in landfill applications due to its comparatively high resistance to aggressive leachate components (August and Tatzky, 1984; Haxo and Nelson, 1984; Rowe, 2001, 2020; Rowe and Jefferis, 2022). Thus, HDPE geomembranes are the focus of this paper.

HDPE geomembranes are typically manufactured with 96–97.5 wt% medium-density polyethylene resin with densities ranging from 0.932 to 0.940 g/cc. However, the addition of 2–3 wt% carbon black increases the densities of final products to ranges of 0.941–0.950 g/cc, which is classified as "HDPE" according to ASTM D883. About 0.5 to 1 wt% of the final product is usually made up of other antioxidants/stabilizers (Hsuan and Koerner, 1995, 1998).

#### 1.2.1. Geomembrane service-life

The contaminating lifespan of landfills can be centuries long (Rowe et al., 2004). Hence, it is expected that any geomembrane used as part of a barrier system be able to perform its intended function during, and possibly beyond the contaminating lifespan if good construction and installation practices are employed. The length of time that a geomembrane will perform its design function of minimizing the escape of contaminants to the environment is defined as its service life. In landfills, there are three key factors that influence service life of a geomembrane, namely (i) leachate chemistry (Rowe et al., 2008; Abdelaal et al., 2014a); (ii) temperature (Yoshida, and Rowe, 2003; Rowe and Islam, 2009; Jafari et al., 2014; Rowe, 2020); and (iii) exposure conditions (Rowe et al., 2010, 2013; Abdelaal et al., 2014a, 2014b; Ewais et al., 2014; Abdelaal et al., 2014a, 2014b). During its service life a geomembrane will experience both physical ageing and chemical ageing (Hsuan and Koerner, 1995, 1998).

During physical ageing, the polymer chains of the geomembrane seek to return from an unstable as constructed state to a stable equilibrium state. This process involves rearrangement of fibrils and relaxation of stresses induced during manufacturing and does not involve breakage of covalent bonds within the polymer chains (Petermann et al., 1976). Chemical ageing on the other hand, involves breakage in the backbone of the polymer chains, and formation of weaker intermolecular crosslinks (Scanabel, 1981), which lead to a decrease in geomembrane mechanical properties and eventually failure. This makes chemical ageing worthy of special attention when it comes to assessing the performance of a geomembrane during its service-life (Rowe and Sangam, 2002).

Hsuan and Koerner (1998), categorized the chemical ageing process into three conceptualized stages:

 Stage I (Antioxidant depletion) – Antioxidants are chemical compounds designed to retard or prevent oxidative degradation

of a material (International Geosynthetics Society, 2009). Stage I in the chemical ageing process represents a period where antioxidants and stabilizers put in the geomembrane to protect the polymer resin from oxidative degradation are either completely consumed or deactivated, leaving it exposed to oxidation. The length of this stage is very important in assessing how long a geomembrane will be able to perform its intended function because it controls the length of time that the polymer is protected from oxidative degradation. Antioxidant depletion can be assessed using two laboratory tests, standard oxidative induction time (Std-OIT) test and/or high-pressure oxidative induction time (HP-OIT) test. Oxidative Induction Time (OIT) is defined as a relative measure of a geomembrane's resistance to oxidative decomposition and is obtained by the measurement of the time interval to onset of exothermic oxidation of a geomembrane resin at specified temperature and oxygen atmosphere (ASTM D3895). OIT tests are described in more detail in Section 2.3.

- Stage II (Induction time) At this stage, oxidation of the geomembrane resin begins. However, this occurs at a relatively slow rate and degree of degradation is often immeasurable during this period.
- iii. Stage III (Nominal failure) This stage is often preceded by a rapid rate of geomembrane resin degradation, leading to significant change in mechanical properties. The end of this period is often characterized by loss of 50% of the initial value of a mechanical/engineering property of interest.

This paper focused on Stage I of the chemical ageing process, with emphasis on the following objectives:

- Evaluating the effects of PFAS in water on antioxidant depletion from an HDPE geomembrane.
- Evaluating the effects of PFAS in synthetic municipal solid waste (MSW) leachate on antioxidant depletion from an HDPE geomembrane.

#### 2. Materials and methods

#### 2.1. Geomembrane properties

The smooth black 1.5 mm thick HDPE geomembrane examined was manufactured in 2015 and had initial properties as defined in Table 1.

# 2.2. Incubation media

Studies of the PFAS compounds in landfill leachate indicate that perfluoroalkyl acids with 8 carbons or less tend to dominate, with perfluoropentanoate (PFPeA), per-fluorohexanoate (PFHxA), PFOA, and PFOS among the prominent components found at landfill sites (Huset et al., 2011; Benskin et al., 2012; Simmons, 2019). Although the studies of PFAS in landfill leachate provide insight, the studies are relatively recent, only represent a small proportion of the facilities, and were performed over a very narrow window of time. It is more likely than not that there are landfills with concentrations higher than have been reported. Recognizing the uncertainties, a cautious (conservative) approach was adopted in the selection of the PFAS compounds and the concentrations (i.e., they were selected to represent some of the more critical PFAS compounds at a concentration above that reported to date in the field). The selected PFAS solution contained 20 mg/L (7.5  $\times$   $10^{-5}$ mol/L) of per-fluoropentanoic acid (PFPeA), plus 20 mg/L ( $6.3\times10^{-5}$ mol/L) of per-fluorohexanoic acid (PFHxA), plus 20 mg/L (4.8  $\times$   $10^{-5}$ mol/L) of PFOA, plus 20 mg/L (3.9  $\times$   $10^{-5}$  mol/L) of PFOS and is referred herein as PFAS.

The geomembrane used in this study was immersed in three different solutions:

#### Table 1

Unaged geomembrane properties.

| Nominal Thickness                               | ASTM<br>D5199 | 1.5  | mm           |
|---|---------------|--|--------------|
| Melt Index <sup>a</sup> (sheet) (2.16 kg)       | ASTM<br>D1238 | $\begin{array}{c}\textbf{0.215} \pm \\ \textbf{0.007} \end{array}$ | g/<br>10min  |
| High Load Melt Index <sup>b</sup> (sheet) (21.6 | ASTM          | $12.6 \pm 0.3$   | g/<br>10min  |
| Melt flow rate ratio <sup>c</sup> (sheet)       | ASTM          | 58.6   | -<br>-       |
| Tensile properties (machine direction)          | D1238<br>ASTM |  |              |
|   | D6693         |  |              |
| Strength at yield                               |               | $33.3 \pm 0.2$   | kN/m<br>kN/m |
| Strain at vield                                 |               | $18.8 \pm 0.1$   | %            |
| Strain at break                                 |               | $720\pm3$  | %            |
| Tensile properties (cross machine               | ASTM          |  |              |
| direction)                                      | D6693         | 040 0 7  | 1.5.7./      |
| Strength at yield                               |               | $34.9 \pm 0.7$<br>52 7 ± 1 1                                       | kN/m<br>kN/m |
| Strain at yield                                 |               | $16.9 \pm 0.3$   | %            |
| Strain at break                                 |               | $740\pm 5$   | %            |
| HP-OIT  | ASTM          | $1391 \pm 113$   | minutes      |
| STD OIT   | D5885         | $225 \pm 11$   | minutes      |
| 310-011   | D3895         | $255 \pm 11$   | minutes      |
| Stress crack resistance                         | ASTM          | $5677\pm386$   | hours        |
|   | D3397         |  |              |

<sup>a</sup> Measurement for the mass of molten geomembrane that extrudes from a die over a certain period under a prescribed load of 2.16 kg. The melt index provides an indirect measure of geomembrane sheet molecular weight (ASTM D1238).

<sup>b</sup> Mass of molten geomembrane that extrudes from a die over a certain period under a prescribed load of 21.6 kg.

<sup>c</sup> - Calculated ratio of the average melt index measurements at the higher load to those at the lower load. This ratio is used to infer the molecular weight distribution of the geomembrane sheet (ASTM D1238).

#### Table 2

| Composition of 1 L of synthetic MSW l | eachate used in | this study | (modified f | from |
|---------------------------------------|-----------------|------------|-------------|------|
| Rowe et al., 2008).                   |                 |            |             |      |

| Constituent  | Formula                           | Units    | Concentration |
|--|-----------------------------------|----------|---------------|
| Sodium Hydrogen Carbonate  | NaHCO <sub>3</sub>                | mg∕<br>L | 3012          |
| Calcium Chloride   | CaCl <sub>2</sub>                 | mg∕<br>L | 2882          |
| Magnesium Chloride   | MgCl₂●6H₂O                        | mg∕<br>L | 3114          |
| Magnesium Sulfate Heptahydrate                                       | $MgSO_4 \bullet 7H_2O$            | mg∕<br>L | 319           |
| Ammonium Hydrogen Carbonate  | NH <sub>4</sub> HCO <sub>3</sub>  | mg∕<br>L | 2439          |
| Urea   | CO(NH <sub>2</sub> ) <sub>2</sub> | mg∕<br>L | 695           |
| Sodium Nitrate   | NaNO <sub>3</sub>                 | mg∕<br>L | 50            |
| Potassium Carbonate  | K <sub>2</sub> CO <sub>3</sub>    | mg∕<br>L | 324           |
| Potassium Hydrogen Carbonate   | KHCO <sub>3</sub>                 | mg∕<br>L | 312           |
| Potassium dihydrogenphosphate  | K <sub>2</sub> HPO <sub>4</sub>   | mg∕<br>L | 30            |
| TMS- Trace Metal Solution  |                                   | ml/L     | 1             |
| Sodium Sulphide nonahydrate (3% w/ v) $\rightarrow$ Eh $\sim$ -120mV | Na <sub>2</sub> S                 | ml/L     | 0.68          |
| Surfactant   | Igepal®<br>CA720                  | ml/L     | 5             |
| Sulphuric acid to adjust pH~6  | $H_2SO_4$                         | ml/L     | 0.70          |

- Solution 1 [synthetic MSW leachate]: Synthetic municipal solid waste leachate (no PFAS) with the composition given in Table 2.
- Solution 2 [PFAS + DI water]: The PFAS indicated above and 28 mg/ L of CaCO<sub>3</sub> were added to reverse osmosis water. The 28 ppm CaCO<sub>3</sub> was added to lower the Langelier Index (used as an indirect indicator

of the "aggressiveness" of water) of the reverse osmosis water, thereby curtailing the aggressive nature of reverse osmosis water (Table S1 in supplemental materials). This was done to ensure that interaction between the PFAS and geomembrane was not overshadowed by geomembrane-water interaction and whatever depletion was observed was to a large extent due to the presence of PFAS in the solution.

• Solution 3 [PFAS + synthetic MSW leachate]: the PFAS indicated above was added to the synthetic municipal solid waste leachate (primarily consisting of inorganic salts and surfactant).

# 2.3. Immersion and index testing

The geomembrane sheet was cut into 20 cm  $\times$  10 cm coupons and put in 3.5-Litre jars. Coupons were separated with glass rods in the jars to ensure adequate contact with solutions on both sides of the coupons and were incubated in ovens at 85, 75, 65, 55 and 40  $^\circ C$  for 2.5 years. Specimens were taken out periodically and tested in differential scanning calorimeters (DSCs) to monitor antioxidant depletion with time. As mentioned in the previous section, Std-OIT and HP-OIT tests were both used to assess antioxidant depletion. Std-OIT tests were run at 200 °C. under 35 kPa oxygen pressure as per ASTM D3895 while HP-OIT tests were run at 150 °C, under 3500 kPa oxygen pressure as per ASTM D5885. The two tests are required to obtain a full picture of the depletion of antioxidants and stabilizers which usually involves at least 3 or 4 different chemical compounds. Ideally, antioxidant depletion time predictions are made by assessing both Std-OIT and HP-OIT test results. However, after 2.5 years of incubation, HP-OIT results recorded for this geomembrane had not reached the residual value required to make useful antioxidant depletion time predictions. Hence, predictions made in this paper were based on Std-OIT results only. Std-OIT results presented in this paper are from significant long-term tests with replicates on all samples taken at a given period. Error bars presented in figures represent maximum and minimum values recorded at a specified period.

## 2.4. Uncertainty and repeatability

This study examined the performance of 80 different samples of the same geomembrane. There were 16 samples at each of 5 different temperatures involving the collection of many hundreds of data points. The interpretation is based on hundreds of data points collected over a significant 2.5 years. The 95% confidence levels are indicated for the predictions in Supplementary Material Table S2. Although there is uncertainty in any data set, experience has shown that to the extent that they err, predictions based on 2.5 years of data are likely to underpredict the time to depletion at lower temperatures than we used in obtaining the predictions (i.e., they tend to be conservative and err on the safe side for engineering design).

#### 3. Results and discussion

#### 3.1. Std-OIT depletion curves

The decrease in Std-OIT with time at each temperature for all three solutions examined followed the trend of increasing rate of depletion with increasing incubation temperature and is illustrated for PFAS + DI water in Fig. 1. The depletion of antioxidants normally follows a first order exponential decay model (Hsuan and Koerner, 1998; Sangam and Rowe, 2002; Mueller and Jakob, 2003; Gulec et al., 2004; Rowe and Rimal, 2008a, b; Hsuan et al., 2008; Rowe and Islam, 2009; Rowe et al., 2008, 2009, 2013, 2019, 2020; Abdelaal et al., 2014a, 2014b, Ewais et al., 2018; Abdelaal and Rowe, 2019; Morsy and Rowe, 2020; Morsy et al., 2020), represented by the following expression:

$$OIT_t = OIT_o e^{-st}$$
<sup>(1)</sup>

OIT at given time (OIT<sub>t</sub>), depletion rate (s) and time (t), to reach a



Fig. 1. Plot of Std-OIT depletion with time for PFAS + DI water – error bars indicate minimum and maximum Std-OIT values but are difficult to make out in most cases due to small range of values for a given set of data points.

given OIT value. However, Equation (1) assumes that antioxidants will deplete to a residual OIT value (OIT<sub>r</sub>) of 0.5 min (the OIT value of a pure HDPE resin with no antioxidants; Hsuan and Koerner, 1998). For that scenario, OIT<sub>r</sub> is assumed to be zero and hence the OIT data can be fit to a 2-paramter exponential decay function (Hsuan and Koerner, 1998). Equation (1) provides a relation between the mean OIT value of the unaged geomembrane (OIT<sub>o</sub>).

A different scenario exists for the HDPE geomembrane used in this study because, based on the currently available data, it appears that OIT<sub>r</sub> ~24 min in PFAS + DI water and OIT<sub>r</sub> ~5 min in synthetic MSW leachate and PFAS + synthetic MSW leachate. For OIT<sub>r</sub> > 1.5 min, using the simplified 2-parameter exponential decay function to fit OIT data can lead to misinterpretation OIT depletion times. In this scenario, a 3-parameter exponential decay function based on Equation (2) is adopted (Rowe et al., 2013; Abdelaal and Rowe, 2014a,b; Rowe and Abdelaal, 2016).

$$OIT_{t} = OIT_{r} + (OIT_{o} - OIT_{r}) e^{-st}$$
(2)

Fig. 1 shows the best-fits of the 3-parameter model to the data for PFAS + DI water at all 5 temperatures. The depletion rate can then be inferred from these fits.

Fig. 2 shows the variation in normalized standard OIT versus time for the geomembrane in the three solutions at 65 °C, where the normalized OIT (OIT<sub>t</sub>/OIT<sub>o</sub>) is obtained by dividing the mean Std-OIT<sub>t</sub> value at time t, by the initial Std-OIT<sub>o</sub> of the unaged geomembrane (a complete set of similar normalized curves are given in the Supplementary Material Figs. S3–S5).

The results for the three solutions (Fig. 2) show similar trends for PFAS + DI water, synthetic MSW leachate, and PFAS + synthetic MSW leachate, with the slowest depletion being for PFAS + DI water, and the faster depletion for PFAS + synthetic MSW leachate, with synthetic MSW leachate coming between the two but closer to PFAS + synthetic MSW leachate. Similar trends were observed for OIT reduction curves obtained from incubation at T  $\geq$  75 °C. However, the differences in the relative OIT reduction with time for the 3 solutions becomes apparent from a comparison of the results at 65 °C (Fig. 2) with those at 55 °C (Fig. 3). In contrast to the trend for T  $\geq$  65 °C discussed above, at 55 °C (Fig. 3), the fastest depletion still being for PFAS + synthetic MSW leachate but the slowest now being for synthetic MSW leachate, with PFAS + DI water generally being between the two at any given time.



Fig. 2. Plot of normalized Std-OIT depletion with time for all three solutions at 65  $^\circ\text{C}.$ 

# 3.2. Arrhenius modelling

Rate of antioxidant depletion at typical landfill temperatures (approximately 35 °C for many decades and then decreasing to annual average ambient temperature) is usually slow. Hence the geomembrane used in this study was incubated in the solutions of interest at higher temperatures to help assess changes in geomembrane properties within a few years of testing rather than decades. Extrapolations were then made to typical landfill temperatures ( $T \le 40$  °C). This was achieved by plotting the ln of the rate of antioxidant depletion, *s*, at each temperature versus the inverse of temperature (1/T) in Kelvin to obtain an Arrhenius relationship as described by equation (3) and shown in Fig. 4.

$$ln(s) = \ln A - (E / R)(1 / T)$$
(3)

where s = OIT depletion rate at each incubation temperature, E = activation energy (kJ/mol), R = gas constant (8.314 J mol<sup>-1</sup>. K<sup>-1</sup>), T = incubation temperature in Kelvin (K), and A = constant (intercept). Equation (3) can also be written in the form:



Fig. 3. Plot of normalized Std-OIT depletion with time for all three solutions at 55  $^\circ\text{C}.$ 



Fig. 4. Plot of relationship between OIT depletion rates and temperature for immersion in PFAS + synthetic MSW leachate based on depletion rates at 85 °C, 75 °C, 65 °C & 55 °C.

$$s = Ae^{-E/RT}$$
<sup>(4)</sup>

Using the slope and intercept from the plot in Fig. 4 for PFAS + synthetic MSW leachate (see Figs. S6 and S7 for the other two solutions), depletion rates for relatively lower temperatures of interest can obtained by simply changing the variable, T in Equation (3) or 4.

# 3.3. Std-OIT predicted depletion times

Based on the Arrhenius relationships, the rate of depletion, s, can be predicted at different temperatures (Table 3). At common landfill temperature during the life of a landfill (Rowe and Islam, 2009) the predicted time to depletion of antioxidants detected by the Std-OIT test was fastest for PFAS + synthetic MSW leachate, followed by PFAS + DI water with the slowest rate being for the synthetic MSW leachate (Table 3). It could be hypothesized that combination of surfactant in the synthetic MSW leachate and PFAS, which is also classified as a surfactant, led to an increase in the wettability of the surface of the geomembrane thereby promoting extraction of antioxidants from the geomembrane as hypothesized by Rowe et al. (2008). However, Rowe et al. (2008) also reported that increasing surfactant concentration in synthetic MSW leachate from 5 ml/L to 10 ml/L had no additional effect on antioxidant depletion. Nonetheless, it appears that the addition of PFAS to the 5 ml/L of surfactant in synthetic MSW leachate to produce PFAS + synthetic MSW leachate only constitutes a 0.08 ml/L increase in surfactant

#### Table 3

Predicted Std-OIT depletion times based on Arrhenius Plot for (a) immersion and (b) adjusted for a composite liner (Ra = 3.4). Numbers rounded to 2 significant digits.

| Temp.<br>(°C) | (a) Predicted Depletion Time<br>Immersed in Leachate (years) |  | (b) Predicted Depletion Time In<br>Composite Liner (years)           |                                    |                             |  |
|---------------|--|--|--|------------------------------------|-----------------------------|--|
|               | 1:syntheticMSWleachate $[OIT_d \sim 5]$ min]                 | 2:<br>PFAS<br>+ DI<br>water<br>$[OIT_d]$<br>~ 24<br>min] | 3: PFAS +<br>synthetic<br>MSW<br>leachate<br>$[OIT_d \sim 5$<br>min] | 1:<br>synthetic<br>MSW<br>leachate | 2:<br>PFAS<br>+ DI<br>water | 3: PFAS<br>+<br>synthetic<br>MSW<br>leachate |
| 40            | 50   | 27   | 18   | 170                                | 90                          | 63   |
| 35            | 90   | 45   | 30   | 310                                | 150                         | 98   |
| 30            | 170  | 78   | 46   | 580                                | 270                         | 160  |
| 25            | 330  | 140  | 74   | 1100                               | 460                         | 250  |
| 20            | 640  | 240  | 120  | >2000                              | 830                         | 410  |

concentration, it can be argued that the 5 ml/L to 10 ml/L limit may be specific to particular surfactant (Igepal® CA720) used in the simulated MSW leachate or the HDPE geomembrane studied by Rowe et al. (2008).

Another hypothesis that could be used to explain the shorter antioxidant depletion times observed for PFAS + synthetic MSW leachate compared to synthetic MSW leachate is the synergistic effect of the presence of Igepal® CA720 and functional groups in PFAS chemical structure influencing antioxidant consumption with time. However, the exact reaction mechanism which could be responsible for this increased antioxidant consumption are presently unknown.

The depletion time predictions given Table 3(a) are for a geomembrane immersed in solution and subject to antioxidant depletion on both sides. In practical applications, this may be applicable below wrinkles with a hole. However, over most of the area of the geomembrane, the leachate is only likely to be on one side with the clay liner on the other side. Studies comparing the performance of the geomembrane immersed in solution and the same geomembrane in a composite liner system, with the leachate only above the liner, have shown that there is a substantial difference in the time to antioxidant depletion for the geomembrane in a composite liner configuration (Rowe and Rimal, 2008a,b; Rowe et al., 2009, 2010, 2013). The time to depletion depends on the level of protection above the geomembrane and temperature but based on available data the time to depletion in the simple composite liner with a nominal protection layer is approximately 3.4 times higher than the time to depletion reported for laboratory immersion tests (Rowe and Rimal, 2008a,b; Rowe et al., 2009, 2010,



**Fig. 5.** Variation in predicted antioxidant depletion times for a 1.5 mm-thick HDPE geomembrane in a composite liner containing synthetic MSW leachate, PFAS + synthetic MSW leachate and PFAS + DI water.

2013). Thus, Table 3(b) and Fig. 5 show the expected times to depletion in a composite liner using the geomembrane examined for the 3 different leachate solutions. Table 3b can be used in estimating service life of geomembranes in landfills with a time temperature history (Yoshida and Rowe, 2003; Jafari et al., 2014) as per Rowe and Islam (2009). The effect of PFAS highlights importance of limiting the strains in geomembrane (Tognon et al., 2000; Rowe and Yu, 2019; Abdelaal et al., 2014a, 2014b; Ewais et al., 2014) to avoid premature failure and designing a robust system with redundancy (Rowe, 2011) that includes consideration of the hydrogeological protection as well as the engineering using models that can manage the time and dimensional scales involved (e.g., Rowe, 1988; Rowe et al., 1997: Rowe and Booker, 1995, 2005; Rowe et al., 2004).

#### 4. Conclusions

Based on 2.5 years of testing of an HDPE geomembrane immersed in three solutions including two containing PFAS, the following preliminary conclusions have been reached for the conditions examined:

- 1. The addition of PFAS to either DI water or simulated MSW landfill leachate accelerated the depletion of antioxidants and hence is likely to impact on the service life of the geomembrane for containing PFAS.
- 2. For the conditions examined, the depletion of antioxidants over the range of typical landfill temperatures was slowest in simulated MSW landfill leachate, followed by a solution of PFAS in amended DI water, and fastest in solution of PFAS in simulated MSW landfill leachate.

It is acknowledged that the work reported in this study is limited to a single geomembrane and combination of PFAS compounds over a 2.5year period. Different geomembranes may have different additive packages that respond differently to the solutions examined and hence the specific predictions should not be generalized to other geomembrane products or other solutions containing PFAS. However, this study does provide the first published indication of the importance of considering how PFAS being contained by a geomembrane can affect service life of the geomembrane. It highlights the need for more research into this topic.

### Credit author statement

Author 1: R. Kerry Rowe: Conceptualization, Validation, Resources, Writing – review & editing, Visualization, Project administration, Supervision, Funding acquisition Author 2: Michael Somuah: Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization, Project administration.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data availability

Data will be made available on request.

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2022.116979.

#### References

- Abdelaal, F.B., Rowe, R.K., 2014a. Effect of high temperatures on antioxidant depletion from different HDPE geomembranes. Geotext. Geomembranes. https://doi.org/ 10.1016/j.geotexmem.2014.05.002.
- Abdelaal, F.B., Rowe, R.K., 2014b. Application of a four-parameter exponential decay model for modelling antioxidant depletion in HDPE geomembranes. 10th Int. Conf. Geosynth. ICG 2014.
- Abdelaal, F.B., Rowe, R.K., Islam, M.Z., 2014a. Effect of leachate composition on the long-term performance of a HDPE geomembrane. Geotext. Geomembranes 42, 348–362. https://doi.org/10.1016/j.geotexmem.2014.06.001.
- Abdelaal, F.B., Rowe, R.K., Brachman, R.W.I., 2014b. Brittle rupture of an aged HDPE geomembrane at local gravel indentations under simulated field conditions. Geosynth. Int. 21 (1), 1–23. https://doi.org/10.1680/gein.13.00031.
- Abdelaal, F.B., Rowe, R.K., 2019. Degradation of a HDPE geomembrane without HALS in chlorinated water. Geosynth. Int. 26 (4), 354–370.
- ASTM D883. Standard Terminology Relating to Plastics. American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA.
- ASTM D3895. Standard Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry. American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA.
- August, H., Tatzky, R., 1984. Permeability of Commercially Available Polymeric Liners for Hazardous Landfill Leachate Organic Constituents. Proceedings of the international conference on geomembranes, Denver, pp. 163–168.
- Bartlett, S.A., Davis, K.L., 2018. Evaluating PFAS cross contamination issues. Remediation 28, 53–57. https://doi.org/10.1002/rem.21549.
- Benskin, J.P., Li, B., Ikonomou, M.G., Grace, J.R., Li, L.Y., 2012. Per- and polyfluoroalkyl substances in landfill leachate: patterns, time trends, and sources. Environ. Sci. Technol. 46, 11532–11540. https://doi.org/10.1021/es302471n.
- Bouazza, A., 2021. Interaction between PFASs and geosynthetic liners: current status and the way forward. Geosynth. Int. 28, 214–223. https://doi.org/10.1680/ igein.20.00033.
- Dixon-Anderson, E., Lohmann, R., 2018. Field-testing polyethylene passive samplers for the detection of neutral polyfluorinated alkyl substances in air and water. Environ. Toxicol. Chem. 37, 3002–3010. https://doi.org/10.1002/etc.4264.
- Ewais, A.M.R., Rowe, R.K., Brachman, R.W.I., Arnepalli, D.N., 2014. Service-life of a HDPE GMB under simulated landfill conditions at 85°C. ASCE J Geotech. Geoenviron. 140 (11), 1–13. https://doi.org/10.1061/(ASCE)GT.1943-5606.0001164, 04014060.
- Ewais, A.M.R., Rowe, R.K., Rimal, S., Sangam, H.P., 2018. 17-year elevated temperature study of HDPE geomembrane longevity in air, water and leachate. Geosynth. Int. 25 (5), 525–544.
- Giesy, J.P., Kannan, K., 2001. Global distribution of perfluorooctane sulfonate in wildlife. Environ. Sci. Technol. 35, 1339–1342. https://doi.org/10.1021/es001834k.
- Gulec, S.B., Edil, T.B., Benson, C.H., 2004. Effect of acidic mine drainage on the polymer properties of an HDPE geomembrane, pp. 60–72.
- Haxo, H.E., Nelson, N.A., 1984. Factors in the durability of polymeric membrane liners. In: Proceedings of the International Conference on Geomembranes. IFAI Publishers Denver, CO, pp. 287–292.
- Hsuan, Y.G., Koerner, R.M., 1995. Long term durability of HDPE geomembrane: Part 1 depletion of antioxidant. GRI Rep. 16, 35p.
- Hsuan, Y.G., Koerner, R.M., 1998. Antioxidant depletion lifetime in high density polyethylene geomembranes. J. Geotech. Geoenviron. Eng. 124, 532–541. https:// doi.org/10.1061/(ASCE)1090-0241(1998)124:6(532).
- Hsuan, Y.G., Schroeder, H.F., Rowe, R.K., Müller, W., Greenwood, J., Cazzuffi, D., Koerner, R.M., 2008. Long-term Performance and Lifetime Prediction of Geosynthetics. 4<sup>th</sup> European Conference on Geosynthetics, Edinburgh, September (Keynote paper).
- Huset, C.A., Barlaz, M.A., Barofsky, D.F., Field, J.A., 2011. Quantitative determination of fluorochemicals in municipal landfill leachates. Chemosphere 82, 1380–1386. https://doi.org/10.1016/j.chemosphere.2010.11.072.
- International Geosynthetics Society, 2009. Recommended Description of Geosynthetics Functions, Geosynthetics Terminology, Mathematical and Graphical Symbols, fifth ed., p. 31p
- Interstate Technology Regulatory Council (ITRC), 2017. Environmental Fate and Transport for Per- and Polyfluoroalkyl Substances.
- Jafari, N.H., Stark, T., Rowe, R.K., 2014. Service life of a landfill liner system subjected to elevated temperatures. J. Hazard. Toxic Radioact. Waste 18 (1), 16–26.
- Key, B.D., Howell, R.D., Criddle, C.S., 1997. Critical review fluorinated organics in the biosphere. Environ. Sci. Technol. 31, 2445–2454.
- Kissa, E., 1994. Fluorinated Surfactants: Synthesis, Properties, Applications. Marcel Dekker, New York, NY, USA.
- Morsy, M.S., Rowe, R.K., 2020. Effect of texturing on the longevity of HDPE geomembranes in municipal solid waste landfills. Can. Geotech. J. 57 (1), 61–72. https://doi.org/10.1139/cgj-2019-0047.
- Morsy, M.S., Rowe, R.K., Abdelaal, F.B., 2020. Longevity of twelve geomembranes in chlorinated water. Can. Geotech. J. 58 (4), 479–495. https://doi.org/10.1139/cgj-2019-0520.

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- Mueller, W., Jakob, I., 2003. Oxidative resistance of high-density
- polyethylenegeomembranes. Polym. Degrad. Stabil. 79, 161–172.
- Petermann, J., Miles, M., Gleiter, H., 1976. Growth of polymer crystals during annealing. J. Macromol. Sci. Part B 12, 393–404. https://doi.org/10.1080/ 00222347608019327.
- Rowe, R.K., 1988. Contaminant migration through groundwater: the role of modelling in the design of barriers. Can. Geotech. J. 25 (4), 778–798.
- Rowe, R.K., 2001. Liner Systems, Geotechnical and Geoenvironmental Engineering Handbook. Kluwer Academic, Norwell, USA, pp. 739–788 (Chapter 25).
- Rowe, R.K., 2011. Systems engineering the design and operations of municipal solid waste landfills to minimize leakage of contaminants to groundwater. Geosynth. Int. 16 (6), 391–404.
- Rowe, R.K., 2020. Protecting the environment with geosynthetics the 53rd Karl Terzaghi lecture. ASCE J Geotech. Geoenviron. 146 (9), 04020081, 10.1061/(ASCE) GT.1943-5606.0002239.
- Rowe, R.K., Booker, J.R., 1995. A finite layer technique for modelling complex landfill history. Can. Geotech. J. 32 (4), 660–676.
- Rowe, R.K., Booker, J.R., 2005. POLLUTEv7 Pollutant Migration through a
- Nonhomogeneous Soil,© 1983-2005, vol. 87. Distributed by GAEA Environmental Engineering Ltd.
- Rowe, R.K., Islam, M.Z., 2009. Impact on landfill liner time-temperature history on the service-life of HDPE geomembranes. Waste Manag. 29, 2689–2699.
- Rowe, R.K., Jefferis, S., 2022. Protecting the Environment from Contamination with Barrier Systems: Advances and Challenges, State-Of-The-Art Lecture. Proceedings of the 20th International Conference on Soil Mechanics and Geotechnical Engineering, Sydney, Australia, pp. 187–293.
- Rowe, R.K., Rimal, S., 2008a. Depletion of antioxidants from an HDPE geomembrane in a composite liner. J. Geotech. Geoenviron. Eng. 134, 68–78. https://doi.org/10.1061/ (ASCE)1090-0241 (2008)134.
- Rowe, R.K., Rimal, S., 2008b. Aging of HDPE Geomembrane in Three Composite Landfill Liner Configurations, vol. 134, pp. 906–916. https://doi.org/10.1061/(ASCE)1090-0241 (2008)134.
- Rowe, R.K., Sangam, H.P., 2002. Durability of HDPE geomembranes. Geotext. Geomembranes 20, 77–95. https://doi.org/10.1016/S0266-1144(02)00005-5.
- Rowe, R.K., Sangam, H.P., Lake, C.B., 2003. Evaluation of an HDPE geomembrane after 14 years as a leachate lagoon liner. Canadian Geotechnical Journal 40 (3), 536–550.
   Rowe, R.K., Yu, Y., 2019. Magnitude and significance of tensile strains in geomembrane
- landfill liners. Geotext. Geomembranes 47 (3), 429–458 (R). Rowe, R.K., Abdelaal, F.B., Brachman, R.W.I., 2013. Antioxidant depletion of HDPE
- geomembrane with sand protection layer. Geosynth. Int. 20 (2), 73–89.
- Rowe, R.K., Abdelaal, F.B., 2016. Antioxidant depletion in high-density polyethylene (HDPE) geomembrane with hindered amine light stabilizers (HALS) in low-pH heap leach environment. Can. Geotech. J. 53, 1612–1627. https://doi.org/10.1139/cgj-2016-0026.
- Rowe, R.K., Quigley, R.M., Booker, J.R., 1997. Clayey barrier systems for waste disposal facilities. CRC Press.
- Rowe, R.K., Quigley, R.M., Brachman, R.W.I., Booker, J.R., 2004. Barrier Systems for Waste Disposal Facilities. E & FN Spon, London, p. 587.

- Rowe, R.K., Islam, M.Z., Hsuan, Y.G., 2008. Leachate chemical composition effects on OIT depletion in an HDPE geomembrane. Geosynth. Int. 15, 136–151. https://doi. org/10.1680/gein.2008.15.2.136.
- Rowe, R.K., Rimal, S., Sangam, H., 2009. Ageing of HDPE geomembrane exposed to air, water and leachate at different temperatures. Geotext. Geomembranes 27, 137–151. https://doi.org/10.1016/j.geotexmem.2008.09.007.
- Rowe, R.K., Islam, M.Z., Brachman, R.W.I., Arnepalli, D.N., Ewais, A., 2010. "Antioxidant depletion from an HDPE geomembrane under simulated landfill conditions". ASCE J Geotech. Geoenviron., ASCE 136 (7), 930–939.
- Rowe, R.K., Morsy, M.S., Ewais, A.M.R., 2019. A representative stress crack resistance for polyolefin geomembranes used in waste management. Waste Manag. 100, 18–27. https://doi.org/10.1016/j.wasman.2019.08.028.
- Rowe, R.K., Abdelaal, F.B., Zafari, M., Morsy, M.S., Priyanto, D.G., 2020. An approach to geomembrane selection for challenging design requirements. Can. Geotech. J. 57 (10), 1550–1565. https://doi.org/10.1139/cgj-2019-0572.
- Sangam, H.P., Rowe, R.K., 2002. Effects of exposure conditions on the depletion of antioxidants from high-density polyethylene (HDPE) geomembranes. https://doi. org/10.1139/T02-074.
- Scanabel, W., 1981. Polymer Degradation: Principles and Practical Application.

Scheirs, J., 2009. A Guide to Polymeric Geomembranes: a Practical Approach. John Wiley & Sons.

- Simmons, N., 2019. PFAS Concentrations of Landfill Leachates in Victoria. Australiaimplications for discharge of leachate to sewer, Sardinia.
- Tognon, A.R., Rowe, R.K., Moore, I.D., 2000. Geomembrane strain observed in largescale testing of protection layers. ASCE J Geotech. Geoenviron. 126 (12), 1194–1208.
- Yoshida, H., Rowe, R.K., 2003. Consideration of Landfill Liner Temperature. Proceedings of 8th International Waste Management and Landfill Symposium, S. Margherita di Pula, Cagliari, Sardinia, Italy., p. 9p. October, CD-ROM.
- Zanbak, C., 2013. Heap Leaching Technique in Mining with the Context of Best Available Techniques. 6th international conference- SDIMI, Greece.

#### Glossary

- ASTM: American Society for Testing and Materials
- *DI*: Deionized *HDPE*: High-Density Polyethylene
- *HP-OIT:* High-Pressure Oxidative Induction Time
- MSW: Municipal Solid Waste

OIT: Oxidative Induction Time

PFAS: Per- and Polyfluoroalkyl Substances

PFHxA: Perfluorohexanoic acid

PFPeA: Perfluoropentanoic acid

PFOA: Perfluorooctanoic acid

PFOS: Perfluorooctanesulfonic acid

RO: Reverse Osmosis Std-OIT: Standard Oxidative Induction Time