



Durability of fluorinated high density polyethylene geomembrane in the Arctic

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ABSTRACT

A series of fluorinated high density polyethylene (f-HDPE) geomembrane (GM) samples of different thickness (1, 1.5 and 2.5 mm) was exhumed from the backfill immediately upstream of a barrier system constructed to contain a hydrocarbon spill in the Canadian Arctic. The samples were tested for oxidation induction time (OIT), crystallinity, melt index (MI) and tensile properties. The results of these tests are reported and it is shown that the durability of the GM was maintained well beyond the initial 3-year design life of the barrier system. Based on 7 years of field data, the std-OIT depletion time for the 1.5 mm thick GM used in the barrier system was inferred to be over 140 years while the antioxidant depletion time based on the HP-OIT is estimated to be about 200 years. No significant temporal changes in the crystallinity, MI or tensile properties of the exhumed GM samples were detected.

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1. Introduction

High density polyethylene geomembranes (HDPE GM) are commonly used as part of composite liner systems to limit the migration of contaminants (Rowe et al., 2004) and have been the subject of much recent research (e.g. Rowe et al., 2007; Take et al., 2007; Brachman and Gudina, 2008a,b). The HDPE GM should not only have chemical resistance and low permeability to the contaminants but also remain chemically and mechanically stable (durable) over the design life. Prior field studies and laboratory tests have demonstrated that HDPE GMs age with time (Hsuan et al., 1991; Tisinger et al., 1991; Hsuan and Koerner, 1998; Sangam and Rowe, 2002; Rowe et al., 2004; Rimal et al., 2004; Rowe, 2005). The severity of ageing depends on the exposure media (e.g. air, water, leachate, hydrocarbons, acid mine drainage) and temperature (Hsuan and Koerner, 1998; Sangam and Rowe, 2002; Rimal et al., 2004; Gulec et al., 2004; Rowe et al., 2009).

At Brevoort Island in the Canadian Arctic, a composite barrier system comprised of a fluorinated HDPE geomembrane (f-HDPE GM) and a geosynthetic clay liner (GCL) was selected to control the advective and diffusive migration of a hydrocarbon spill and hence allow time for future site remediation (Li et al., 2002; Bathurst et al., 2006). The f-HDPE GM was selected because it is more resistant to diffusion of aromatic hydrocarbons than the conventional (untreated) HDPE GM (Sangam et al., 2001; Sangam and Rowe, 2005).

In the field application under investigation, a key question is the long-term durability of f-HDPE GM and the time that is potentially available for the clean-up of the spill. Recently, laboratory tests on samples immersed in jet fuel have indicated slower antioxidant depletion rates for f-HDPE GM than the conventional HDPE GM (Rimal et al., 2004). However, it is not possible to precisely simulate realistic field conditions in the laboratory and so there is still an outstanding question regarding how the synergistic effects of contact with hydrocarbons and climatic conditions in the Arctic will impact the durability and service life of the f-HDPE GM in the field. Thus the objectives of this paper are to (1) assess the durability and performance of f-HDPE GM installed at the field site on Brevoort Island, and (2) compare the antioxidant depletion time observed in the field with that expected based on laboratory tests.

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2. Background

At a North Warning System long-range radar installation located at 63°20'23"N, 64°08'45"W on Brevoort Island, Nunavut Territory in Canada, Arctic diesel (jet fuel) spills and leaks have occurred. The site is located 225 km east of Iqaluit. The site (known as BAF-3) was re-built in 1987. The site has a zone of continuous permafrost at a depth of 1–2 m, which provides a natural barrier to downward migration of contaminants. But the shallow permafrost depth contributes to lateral spreading of the hydrocarbons, especially after rainfall or snow thaw events.

There are two large petroleum tanks approximately 75 m north of the ocean. The existing tanks replace older tanks dating back to the original Brevoort Island distant early warning line communication site. Contamination due to leaks from the old corroded tanks or fuel spilled during reconstruction activities was first investigated in 1998 (Bathurst et al., 2006). The presence of hydrocarbons was confirmed in the sloped area between the tanks and the ocean at levels up to 14,000 ppm total petroleum hydrocarbons (TPH). Additional sampling was conducted in 2000 by the Environmental Sciences Group (2001). Laboratory analysis of samples from the site indicated that most of the surface samples were uncontaminated but the samples collected at depths beneath the surface had TPH levels that exceeded acceptable criteria. It was concluded from the contaminant distribution at the site that the hydrocarbon plume was moving down slope from the site of the decommissioned tanks towards the ocean.

The Canadian Department of National Defence initiated a clean-up of the site. Site remediation by excavation and exsitu treatment was planned. However a short-term strategy was needed to contain the hydrocarbon plume until the site remediation could be undertaken. The strategy involved the installation of a subsurface geosynthetic composite barrier system comprised (from bottom up) of a needle-punched GCL, f-HDPE GM, and a needle-punched geotextile protection layer in a trench constructed down-gradient of the plume and excavated to permafrost in 2001 (Li et al., 2002; Bathurst et al., 2006). The area above the contaminant plume was covered with a GM and the surface graded to minimize future infiltration. The barrier was designed to intercept the jet fuel contaminant plume. The plume migrates predominantly at the water table since it is less dense than water.



Fig. 1. Photograph of frames supporting f-HDPE GM coupons during installation and prior to complete soil burial and placement of GM surface cover.

3. Materials

During the construction of the barrier system a set of vertical wooden frames supporting coupons of f-HDPE GMs was buried in the backfill immediately up-gradient of the barrier system (Li et al., 2002) with the objective of allowing the monitoring of changes in the barrier materials with time. Each frame holds six 0.25×3.0 m samples (as depicted in Fig. 1). The coupons were extended to reach the permafrost to maximize the probability of contact with contaminants. Six sets of f-HDPE coupons were installed. Each set consisted of four samples.

Two sets of f-HDPE GM of each thickness (1.0 mm, 1.5 mm and 2.5 mm) were buried. The properties of the virgin f-HDPE GMs are summarized in Table 1. There were differences in oxidative induction time (OIT) and crystallinity between 1.5 mm thick Set 3 and Set 4 GMs. The Set 4 GM used in the barrier wall had higher initial OIT and lower crystallinity than Set 3 GM. All GMs were manufactured by GSE Lining Technology Inc., Houston, Texas, USA as smooth black-surfaced HDPE GM that was then treated using the fluorination process by Fluoro-Seal Inc., Texas, USA. This process involves application of elemental fluorine gas to both sides of the untreated GM. The fluorine atoms chemically substitute the hydrogen atoms in the carbon–hydrogen (C–H) bond in the

Table 1
Initial properties of f-HDPE GM placed in field at BAF-3.

Property	Method	1.0 mm, Set 1 and 2		1.5 mm, Set 3		1.5 mm, Set 4		2.5 mm, Set 5 and 6	
		Avg.	COV	Avg.	COV	Avg.	COV	Avg.	COV
Std-OIT (min)	ASTM D3895	128	2.4	118	1.7	174	1.8	125	2.6
HP-OIT (min)	ASTM D5885	254	1.8	246	2.9	335	1.4	886	4.0
Crystallinity (%)	ASTM E794	59	0.72	63	1.3	47	2.4	41	5.7
Melt index (g/10 min)	ASTM D1238	0.098	7.3	0.170	11	0.130	10	0.365	3.1
Tensile strength (MD)	ASTM D6693								
Tensile strength at yield (kN/m)		20.5	3.1	32.1	2.0	30.5	1.7	48.3	1.7
Tensile strain at yield (%)		20.5	1.85	19.6	2.5	19.9	2.81	20.6	1.26
Tensile strength at break (kN/m)		29.6	10.7	47.6	8.1	51.6	6.5	84.5	13.8
Tensile strain at break (%)		672	9.8	757	9.7	798	5.7	852	11.3
Tensile strength (CD)	ASTM D6693								
Tensile strength at yield (kN/m)		21.8	3.1	31.4	3.5	32.2	1.9	47.2	2.9
Tensile strain at yield (%)		17.5	0.86	19.3	4.2	18.1	0.9	20.2	2.0
Tensile strength at break (kN/m)		31.6	10.0	54.4	6.7	47.8	7.8	91.6	9.8
Tensile strain at break (%)		767	8.6	903	6.6	779	7.2	958	11.3

Note: Avg. = average, COV = coefficient of variation (%), MD = machine direction, CD = cross machine direction. For each set average Std-OIT, HP-OIT, Crystallinity and Melt Index values obtained from 3–5 specimens per sample. Average tensile properties obtained from 5 specimens per sample in MD and CD.

Table 2
Time of retrieval from BAF-3.

From set	Thickness (mm)	During summer of
1	1.0	2002, 2004
2	1.0	2002, 2004, 2008
3	1.5	2002, 2004
4	1.5	2002, 2004, 2007, 2008
5	2.5	2002, 2004, 2007, 2008
6	2.5	2002, 2004

polyethylene chain to form carbon–fluorine (C–F) covalent bonds. Thin carbon–fluorine layers of 0.31–0.37 μm (as measured in some of the samples of f-HDPE by Scanning Electron Microscope/Energy Dispersive X-Ray) are created on the two sides of the GM.

4. Methods

4.1. Oxidative induction time

Small quantities of antioxidants are added to the polyethylene resin used to manufacture HDPE GM to minimize oxidative degradation of the polymer and hence extend the service life of the GM. The OIT test provides an index measure of the amount of antioxidant present in the GM and is useful in monitoring the depletion of antioxidants from the GM. Many prior studies have used OIT as an indicator of the amount of antioxidant in the GM (Hsuan and Koerner, 1995; Hsuan and Koerner, 1998; Sangam and Rowe, 2002; Müller and Jakob, 2003; Rimal et al., 2004; Gulec et al., 2004; Rowe, 2005; Rowe et al., 2008; Rowe et al., 2009, Rimal and Rowe, in press, 2009). Standard OIT tests were carried out following ASTM D3895 with differential scanning calorimeters (DSC): TA Instruments 2910 and Q100. For the evaluation of standard oxidative induction time (std-OIT) the testing temperature of 200 °C was used at a pressure of 35 kPa and flow of ultra high pure nitrogen and oxygen of 50 ml/min.

High pressure oxidative induction time (HP-OIT) (ASTM D5885) was also evaluated using test temperature of 150 °C at pressure of 3500 kPa in an oxygen environment using TA Instruments 2910 DSC with a special pressure cell. The HP-OIT test is useful in measuring OIT if hindered amine light stabilizers (HALS) are present in the GM. HALS are ineffective at 200 °C and have shown to be active at 150 °C in HP-OIT tests (Thomas and Ancelet, 1993; Hsuan and Koerner, 1998).

4.2. Degree of crystallinity

The degree of crystallinity influences some of the important physical and mechanical properties of a GM such as yield stress, elastic modulus, density, impact resistance, melting point, and

Table 3
Properties of 1 mm thick f-HDPE GM recovered from BAF-3 in 2002, 2004 and 2008.

Property	Method	Initial 2001		2002		2004		2008	
		Avg.	COV	Avg.	COV	Avg.	COV	Avg.	COV
Std-OIT (min)	ASTM D3895	128	2.4	125	3.9	130	4.2	93	1.0
HP-OIT (min)	ASTM D5885	254	1.8	254	2.2	253	0.4	259	0.7
Crystallinity (%)	ASTM E794	59	0.7	60	4.6	60	2.8	59	2.2
Melt index (g/10 min)	ASTM D1238	0.098	7.3	0.105	7.3	0.110	10.2	0.099	5.1
Tensile strength (average MD and CD)	ASTM D6693								
Tensile strength at yield (kN/m)		21.2	4.5	20.6	3.6	20.1	6.9	20.4	2.5
Tensile strain at yield (%)		19.0	8.4	19.1	8.6	20.9	8.4	20.8	7.5
Tensile strength at break (kN/m)		30.6	10.4	31.2	9.4	32.9	9.3	34.1	5.9
Tensile strain at break (%)		720	11.1	744	10.4	790	8.4	813	7.5

Note: Avg. = average, COV = coefficient of variation (%), MD = machine direction, CD = cross machine direction.

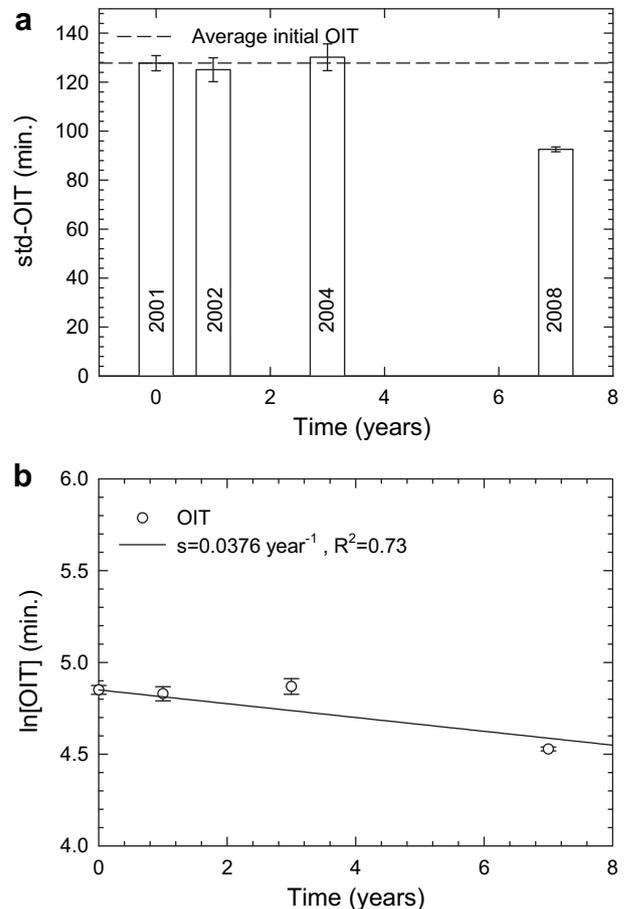


Fig. 2. (a) Std-OIT of virgin and exhumed 1.0 mm thick f-HDPE GM samples. (b) Logarithm of Std-OIT versus time for the 1.0 mm thick f-HDPE GM. Note: 3–5 specimens per sample for each set, error bars represent ± 1 standard deviation.

permeability (Kong and Hay, 2002; Sperling, 1992). In a semi-crystalline polymer like HDPE, a slow change in crystallinity may be attributed to the physical ageing where the material attempts to establish equilibrium from its as-manufactured nonequilibrium state (Petermann et al., 1976; Hsuan and Koerner, 1995; Rowe and Sangam, 2002).

Crystallinity tests were performed according to ASTM E794 using a differential scanning calorimeter. The GM specimen was heated at the rate of 20 °C/min to 200 °C in nitrogen atmosphere. The percentage crystallinity was calculated by dividing the measured heat of fusion with the heat of fusion of 100% crystalline HDPE, 290 J/g (Flory and Vrij, 1963).

Table 4
Properties of 1.5 mm thick f-HDPE GM (Set 3) f-HDPE GM recovered from BAF-3 in 2002 and 2004.

Property	Method	Initial 2001		2002		2004	
		Avg.	COV	Avg.	COV	Avg.	COV
Std-OIT (min)	ASTM D3895	118	1.7	118	1.2	123	5.6
HP-OIT (min)	ASTM D5885	246	2.9	246	3.6	244	0.9
Crystallinity (%)	ASTM E794	63	1.3	60	7.9	59	4.5
Melt index (g/10 min)	ASTM D1238	0.170	11	0.156	4.3	0.168	8.8
Tensile strength (average MD and CD)	ASTM D6693						
Tensile strength at yield (kN/m)		31.8	2.9	27.1	2.0	29.9	5.1
Tensile strain at yield (%)		19.5	3.4	17.4	5.9	20.2	7.7
Tensile strength at break (kN/m)		51.0	9.9	44.3	16.0	45.3	14.9
Tensile strain at break (%)		830	12.0	810	17.3	769	16.6

Note: Avg. = average, COV = coefficient of variation (%), MD = machine direction, CD = cross machine direction.

4.3. Melt index (MI)

The MI is useful in examining the changes in molecular weight of the polymer. Oxidative degradation (chemical ageing) of polymer results in either a cross-linking or chain-scission reaction. Cross-linking increases the molecular weight and chain scission decreases the molecular weight (Peacock, 2000). MI is inversely proportional to molecular weight (Shah, 2002). The MI test was conducted in accordance with ASTM D1238 for condition E at 190 °C at a load of 2.16 kg.

4.4. Tensile properties

Changes in tensile properties are a useful means to assess the durability of the GM. Polymer degradation due to ageing leads to decreases in strength and strain at break while tensile modulus and yield stress increase (Rowe and Sangam, 2002). The tensile properties of the GM were obtained in accordance with ASTM D6693 using Instron Model 3396 and Zwick Roell test machines equipped with load cell, crosshead measurements, and self-aligning wedge grips. Dumbbell-shaped specimens (ASTM D638 Type IV) were tested at a speed of 50 mm/min. Tensile properties at yield and break were recorded.

5. Results and discussion

5.1. Sample collection

The f-HDPE coupons buried in 2001 were retrieved from the field site in summer of 2002, 2004, 2007 and 2008 and returned to

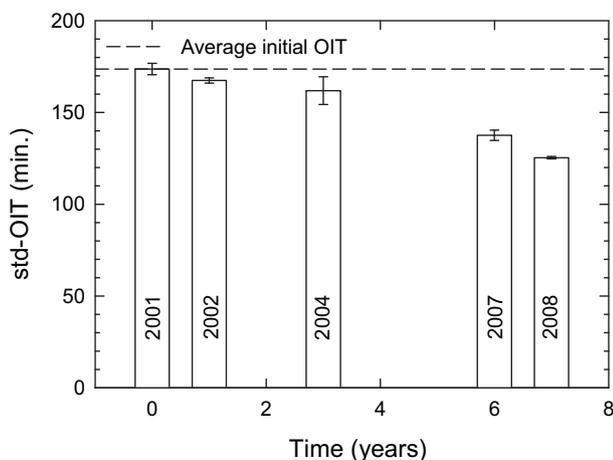


Fig. 3. Std-OIT of virgin and exhumed Set 4, 1.5 mm thick f-HDPE GM samples. Note: 3–5 specimens per sample, error bars represent ± 1 standard deviation.

the laboratory for analysis 1, 3, 6 and 7 years after burial. Table 2 shows the time of exhumation of each set of samples from BAF-3. The properties of the GM noted in the previous section were monitored and quantified to assess their durability and field performance.

6. 1.0 mm Thick f-HDPE GM

Std-OIT test results on virgin and exhumed samples of 1.0 mm thick GM (Set 1 and 2) are illustrated in Fig. 2a and Table 3. The vertical bars represent average std-OIT value and the error bars represent ± 1 standard deviation. The horizontal dashed line represents the initial std-OIT of the virgin GM sample. Two tailed *t*-tests were used to check for any statistical difference between the two averages. For all *t*-test results described in this paper the conventional 95% confidence level (i.e. significance level $\alpha = 0.05$) was used. The probability (referred to as *p*-value) of falsely rejecting the null hypothesis (H_0 : average value for virgin GM = average value for exposed GM) was computed. Average std-OITs of the virgin GM and GM from the field after 7 years exposure were compared using the *t*-test (Rimal, 2009). There was statistically significant difference between the std-OIT value of the virgin GM and the 1.0 mm thick f-HDPE samples exhumed after 7 years with the Std-OIT retained after 7 years being only 72% of the original value. It was observed that the std-OIT value remained steady for the first three years (from 2001 to 2004). The significant decline in std-OIT value in 2008 could be attributed to the GM being in contact with higher concentration of jet fuel after 2004.

Since the depletion of antioxidants follows a first-order decay model, the OIT value at time *t* can be expressed as (Hsuan and Koerner, 1998)

$$\text{OIT}_t = \text{OIT}_0 \cdot \exp(-st) \quad (1)$$

or taking logarithm of both sides,

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

where OIT_0 is the initial OIT (in min), *s* is the antioxidant depletion rate (in year⁻¹) and *t* is the time (in year).

The time for depletion of OIT (t_d) is represented by the following equation.

$$t_d = \frac{\ln(\text{OIT}_0) - \ln(\text{OIT}_f)}{s} \quad (3)$$

where OIT_f is the final residual value of 0.5 min for a pure HDPE resin without any antioxidant (Hsuan and Koerner, 1998).

For the 1.0 mm GM the plot of logarithm of std-OIT versus exposure time at BAF-3 is shown in Fig. 2b. The calculated antioxidant depletion rate was 0.0376 year⁻¹ and the corresponding

Table 5
Properties of 1.5 mm thick f-HDPE GM (Set 4) f-HDPE GM recovered from BAF-3 in 2002, 2004, 2007 and 2008.

Property	Method	Initial 2001		2002		2004		2007		2008	
		Avg.	COV	Avg.	COV	Avg.	COV	Avg.	COV	Avg.	COV
Std-OIT (min)	ASTM D3895	174	1.8	167	0.9	162	4.7	138	2.8	125	0.5
HP-OIT (min)	ASTM D5885	335	1.4	326	1.5	315	0.7	305	2.1	310	1.5
Crystallinity (%)	ASTM E794	47	2.4	48	6.4	48	7.1	45	18.4	51	11.9
Melt index (g/10 min)	ASTM D1238	0.130	10	0.133	13.8	0.143	8.2	0.132	6.4	0.100	0
Tensile strength (average MD and CD)	ASTM D6693										
Tensile strength at yield (kN/m)		31.3	3.4	27.5	5.5	30.3	5.9	30.2	4.8	29.5	2.2
Tensile strain at yield (%)		19.0	5.3	17.0	5.7	19.5	3.3	19.9	6.6	20.7	4.4
Tensile strength at break (kN/m)		49.7	7.8	44.1	10.7	47.5	12.0	42.0	29.3	47.8	13.4
Tensile strain at break (%)		788	6.2	795	10.0	785	11.9	715	22.0	802	12.6

Note: Avg. = average, COV = coefficient of variation (%), MD = machine direction, CD = cross machine direction.

calculated complete antioxidant depletion time was about 150 years.

There was no statistically significant difference in HP-OIT of the 1 mm thick GM over the 7 year period. This suggested that the primary component of the antioxidant package giving rise to the stable HP-OIT had not depleted in 7 years. In contrast the significant decline in std-OIT may be due to the depletion of a component of the antioxidant package that is not evident in the HP-OIT test but is more readily leached out of the GM when GM is in contact with jet fuel. Therefore, the estimates of antioxidant depletion time for the GM based on std-OIT may be conservative (i.e. may underestimate the antioxidant depletion time in the field).

Results of crystallinity and MI tests are given in Table 3. Based on the *t*-test, there was no significant difference in the degree of crystallinity and MI of 1.0 mm thick f-HDPE GM samples after 7 years in the field.

Conventional tensile tests were performed on virgin and exhumed f-HDPE GM samples and the results are given in Table 3. Results of *t*-tests showed that there was a statistically significant difference between the yield strength of virgin and exhumed GM after 7 years in the field. However, the difference in yield strength was very small (0.8 kN/m). This difference cannot be attributed to oxidative degradation as sufficient amount of antioxidants are still present to protect the GM. The difference could be due to a small variability in tensile properties at different locations along the GM roll. To check if any temporal trend existed in the data, a regression analysis was performed on the yield strength data with respect to time. The zero slope test was conducted to evaluate if the slope of the regression line is significantly different from zero (Kleinbaum

et al., 1998). The results of the zero slope test (Rimal, 2009) indicated that at a significance level of 0.05, there was no linear temporal change in yield strength (i.e. the slope was not significantly different from zero) over 7 years in the field. Thus the yield strength has remained essentially constant. Likewise, although the average yield strain of the virgin GM changed from 19.0% to 20.8% after 7 years in the field, the zero slope test results suggested that there was no linear temporal trend in the data over 7 years. Similar conclusions were reached with respect to the break strength and strain (Rimal, 2009). The tensile properties of polyethylene are closely related to the degree of crystallinity and density (Peacock, 2000). Since there was no change in crystallinity of the GM it is not surprising that there was no significant temporal trend in strength or strain over the period examined. The small observed variation in tensile properties is considered to be the effect of variability in specimens from different parts of the GM roll that occurs during manufacturing and not due to degradation of the GM.

6.1. 1.5 mm Thick f-HDPE GM

For Set 3 GM there was no statistically significant difference between the std-OIT value of the virgin GM and the sample exhumed after 3 years at BAF-3 (Table 4). Similarly there was no significant difference in HP-OIT values for these GMs. For Set 4, std-OIT test results on virgin and exhumed samples of 1.5 mm thick GM are illustrated in Fig. 3 and Table 5. Std-OIT values for the virgin GM and 3, 6 and 7 years of exposure at BAF-3 were compared using the *t*-test. Although the std-OIT value did drop to 93% of initial std-OIT in 3 years, this drop was not statistically significantly different from

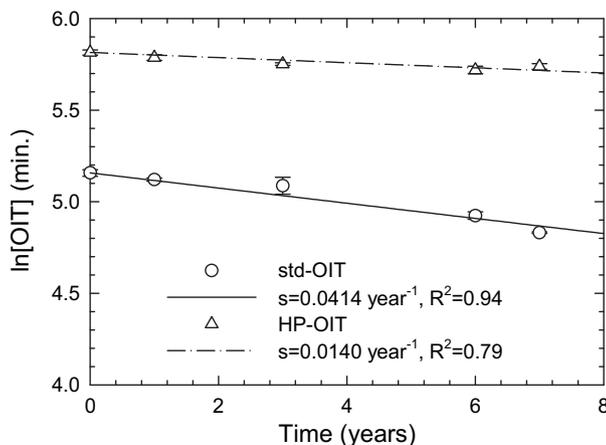


Fig. 4. Logarithm of std-OIT and HP-OIT versus time for Set 4, 1.5 mm thick f-HDPE GM samples. Note: 3–5 specimens per sample, error bars represent ± 1 standard deviation.

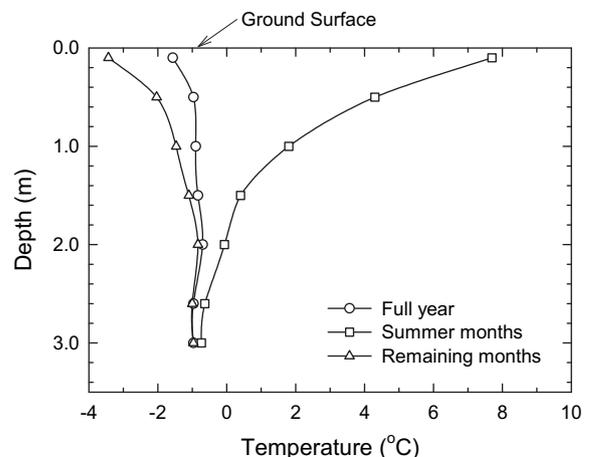


Fig. 5. Average temperatures with depth at barrier on Brevoort Island.

Table 6
Properties of 2.5 mm thick f-HDPE GM recovered from BAF-3 in 2002, 2004, 2007 and 2008.

Property	Method	Initial 2001		2002		2004		2007		2008	
		Avg.	COV	Avg.	COV	Avg.	COV	Avg.	COV	Avg.	COV
Std-OIT (min)	ASTM D3895	125	2.6	121	6.1	124	3.8	75	8.7	74	2.9
HP-OIT (min)	ASTM D5885	886	4.0	887	0.8	891	5.4	876	3.1	850	4.5
Crystallinity (%)	ASTM E794	41	5.7	39	5.1	38	6.9	39	2.6	44	2.7
Melt index (g/10 min)	ASTM D1238	0.365	3.1	0.363	6.2	0.369	6.3	0.369	0.6	0.370	1.2
Tensile strength (average MD and CD)	ASTM D6693										
Tensile strength at yield (kN/m)		47.7	2.5	43.4	4.1	48.2	5.0	47.6	2.6	46.3	1.4
Tensile strain at yield (%)		20.4	1.8	19.1	2.2	20.8	1.9	21.4	2.2	21.4	2.0
Tensile strength at break (kN/m)		88.1	11.9	75.0	14.4	81.0	22.8	87.0	9.1	85.3	14.0
Tensile strain at break (%)		905	12.3	846	12.3	852	16.8	870	8.7	892	13.2

Note: Avg. = average, COV = coefficient of variation (%), MD = machine direction, CD = cross machine direction.

that of the virgin GM. However, the drop to 79% and 72% of the initial std-OIT after 6 and 7 years, respectively, was statistically significant and is consistent with the trend noted at 3 years.

For the 1.5 mm thick GM the plot of logarithm of OIT versus exposure time at BAF-3 is shown in Fig. 4 for Set 4 GM. The regression line is represented by Equation (2). The slope of the line (i.e. std-OIT depletion rate, s) is 0.0414 year^{-1} . Based on the 7 years of data, the calculated t_d for Set 4, 1.5 mm thick f-HDPE GM at BAF-3 was about 140 years. The HP-OIT of the Set 4 GM gradually decreased over time (Table 5, Fig. 4). The HP-OIT depletion rate was 0.0140 year^{-1} and the HP-OIT depletion time based on OIT_f of 20 min for pure unstabilized polyethylene resin (Hsuan and Koerner, 1998) was 200 years. Thus the std-OIT gave a shorter (more conservative) antioxidant depletion time than the HP-OIT.

Temperature at the field site was monitored below ground surface (from 0.1 to 3 m). Full year temperature data was available for years 2003–2005. The full year average temperature, two summer months average temperature and the remaining 10 months average temperatures are shown in Fig. 5. The annual average temperature ranged from $-1.6 \text{ }^\circ\text{C}$ at 0.1 m to $-1.0 \text{ }^\circ\text{C}$ at 3 m. There was a more significant seasonal variation than is evident from these annual average values, as shown in Fig. 5. At 0.1 m depth the average summer temperature was $7.7 \text{ }^\circ\text{C}$ and average temperature for the remaining 10 months of the year was $-3.4 \text{ }^\circ\text{C}$. Below 0.5 m the annual average temperature was approximately $-1 \text{ }^\circ\text{C}$. Thus $-1 \text{ }^\circ\text{C}$ was selected as the subsurface temperature applicable to the jet fuel spill containment site at BAF-3.

One of the objectives of this study was to compare the antioxidant depletion time observed in the field with that based on laboratory tests. In the field the GM was partially exposed to jet fuel from one side and water from the other side. Thus the values of std-OIT depletion time at $-1 \text{ }^\circ\text{C}$ in jet fuel immersion tests can be taken as a reference (Rimal, 2009). At $-1 \text{ }^\circ\text{C}$ the std-OIT depletion time ranged from 26 to 33 years for 1.5 mm thick fluorinated GM immersed in jet fuel (Rimal and Rowe, in press) and in the range of 100–130 years for a sample exposed to jet fuel on one side and water on the other. This suggests that the conditions in the field which gave a std-OIT depletion time of 140 years for the Set 4 samples at BAF-3 were less severe than the laboratory tests with neat jet fuel. This may arise, in part, from variations in water level adjacent to the GM (which limit the time the GM is exposed to neat jet fuel that floats on the top of the groundwater) and in part due to spatial variation in the distribution of hydrocarbon at the site. Hence the better performance of the field exhumed samples with regard to std-OIT depletion was expected.

The results from OIT tests implied that the GM is still in the first stage of ageing i.e. (1) the antioxidant depletion time. The other two stages that follow after the depletion of antioxidants are (2) induction time to the onset of polymer degradation and (3) polymer degradation stage as described by Hsuan and Koerner (1998).

Variation in crystallinity and MI versus time for the Set 3 and Set 4 GM are given in Tables 4 and 5. Neither changed significantly over the periods monitored.

For Set 3 GM (Table 4) there was a small but statistically significant difference in tensile yield strength (32–30 kN/m in 3 years). Other tensile properties showed no statistically significant change. There was a small but statistically significant difference in tensile properties at yield of the virgin and the exhumed Set 4 GM exposed for 7 years in the field (Table 5). However, the difference between the tensile break properties of the virgin and exhumed Set 4 GM exposed for 7 years in the field were still not statistically significant at the 95% confidence level. A regression analysis and zero slope test suggested no linear temporal changes in the yield or break properties of the GM over 7 years in the field.

6.2. 2.5 mm Thick f-HDPE GM

The results of std-OIT test on virgin and exhumed 2.5 mm thick GM (Set 5 and 6) are summarized in Table 6 and plotted in Fig. 6. Std-OIT values were compared using the t -test. There was no statistically significant change in std-OIT value of the 2.5 mm thick GM after 3 years in the field. However, the std-OIT was only 60% of the initial std-OIT of the GM after 6 years with a sharp decline in std-OIT being observed between 2004 and 2007.

A plot of logarithm of std-OIT versus exposure time is shown in Fig. 7. The regression line yields the overall std-OIT depletion rate of 0.0721 year^{-1} . Which is higher than that obtained for the 1.5 mm thick f-HDPE GM. The higher depletion rate was not expected for the thicker GM. The sharp decrease in std-OIT value during 3 years

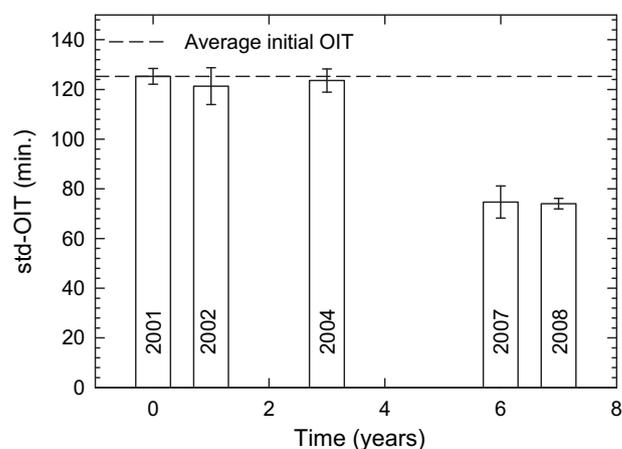


Fig. 6. Std-OIT of virgin and exhumed 2.5 mm thick f-HDPE GM samples. Note: 3–5 specimens per sample for each set, error bars represent ± 1 standard deviation.

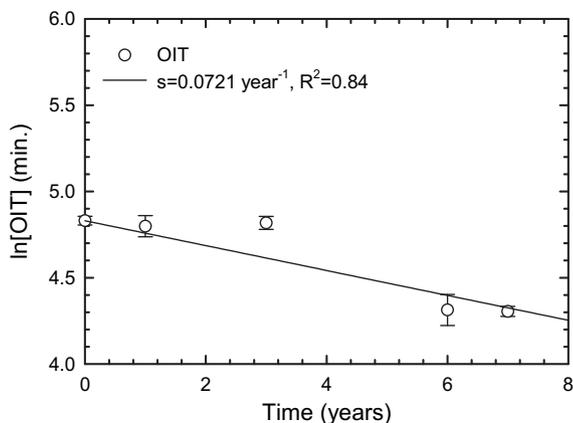


Fig. 7. Logarithm of std-OIT versus time for 2.5 mm thick f-HDPE GM samples. Note: 3–5 specimens per sample for each set, error bars represent ± 1 standard deviation.

between 2004 and 2007 could have occurred due to spatial variability of hydrocarbons in the field. The sharp decline in std-OIT may be attributed to the sample being in contact with higher concentration of jet fuel after 2003. The calculated t_d for Set 5 GM in the field was about 80 years based on 7 years of data. However, this result should be taken with caution due to the sharp decline in std-OIT for this GM between 2004 and 2007. It is noted that this GM had a much higher HP-OIT value (886 min) than the other GMs examined in this study (Table 6). It was found that there was no statistically significant change in HP-OIT of this GM between 2001 and 2008. This suggests that the primary component of the antioxidant package giving rise to the HP-OIT result had not depleted in 7 years and that the decrease in std-OIT may be due to a component of the antioxidant package that is not detected in the HP-OIT test but is more readily leached out of the GM when the GM is in contact with jet fuel. Since the HP-OIT gives a better measure of the antioxidants available for some antioxidant packages, the prediction of antioxidant depletion time based on std-OIT value should be applied with caution for this GM.

The crystallinity and MI of the 2.5 mm thick f-HDPE GM (Table 6) did not change significantly over 7 years. Crystallinity results are presented in Fig. 8. The tensile properties of 2.5 mm thick f-HDPE GM samples are given in Table 6. There was a small but statistically significant difference between the yield strength of virgin and exhumed GM exposed for 7 years in the field. There was a small increase in tensile strain (from 20.4% to 21.8%) at yield that was

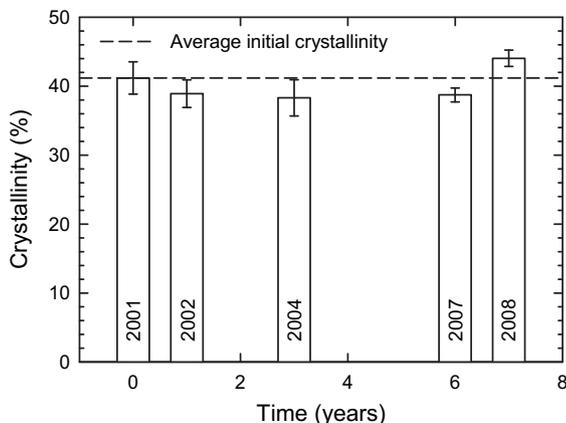


Fig. 8. Crystallinity of virgin and exhumed 2.5 mm thick f-HDPE GM samples. Note: 3–5 specimens per sample for each set, error bars represent ± 1 standard deviation.

noted for GM samples exhumed after 7 years; however, the zero slope test results did not support the hypothesis that there was a linear temporal trend in the yield strain data. No statistically significant changes were observed for tensile properties at break.

7. Conclusions

A series of f-HDPE GMs samples buried in the backfill immediately upstream of a barrier system constructed to contain a hydrocarbon spill in the Arctic was retrieved. The exhumed samples were tested for OIT, crystallinity, MI and tensile properties. Based on the test results the following conclusions were reached.

- The chemical and mechanical durability of the GM installed at the site was maintained well beyond the initial 3-year design life of the barrier system.
- For 1 mm thick GM, the std-OIT depletion time in the field was about 150 years based on 7 years of data. However, this value is likely conservative since the HP-OIT remained stable for 7 years.
- For the same 1.5 mm thick GM as used in the barrier system, the antioxidant depletion time observed was inferred to be over 140 years. This result is a little more than would be expected based on laboratory tests reported by Rimal and Rowe (in press) assuming that the GM is exposed to jet fuel on one side and water on the other. Based on the decrease in HP-OIT, the time to complete antioxidant depletion was estimated to be about 200 years.
- The calculated std-OIT depletion time for 2.5 mm thick GM in the field was about 80 years. However, since the HP-OIT remained stable for 7 years, the predicted antioxidant depletion time based on std-OIT may be very conservative (low) for this GM.
- No significant temporal changes were noted in the crystallinity, MI or tensile properties of the exhumed GM. These results implied there was no degradation apparent at the molecular level. This indicated that the polyethylene molecules have remained essentially unchanged and no oxidation has occurred. The antioxidants remaining in the GM continue to provide required protection.
- The difference in ageing between the field samples and samples immersed in jet fuel in the laboratory, as reported by Rimal and Rowe (in press), is attributed to the less extreme exposure conditions in the field with the geomembrane at most only partly exposed to hydrocarbon given the variable distribution of hydrocarbons (e.g. in part due to variation in water level adjacent to the geomembrane and in part due to spatial variation in the distribution of hydrocarbons at the site).
- The actual service life of the 1.5 mm thick f-HDPE GM used in the BAF-3 barrier system may be expected to be longer than the more than 140 years inferred from OIT testing for the first stage of GM ageing due to the additional time required for the subsequent two stages of polymer degradation.

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