Antioxidant Depletion and Service Life Prediction for HDPE Geomembranes Exposed to Low-Level Radioactive Waste Leachate

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Abstract: Antioxidant depletion was evaluated in high-density polyethylene (HDPE) geomembrane (GM) coupons immersed in radioactive synthetic leachate (RSL) representative of leachate in low-level radioactive waste (LLW) disposal facilities operated by the U.S. Department of Energy's environmental restoration programs. Depletion was assessed at four temperatures (25, 50, 70, and 90°C). Comparative tests were conducted with nonradioactive synthetic leachate (NSL) having the same chemistry as RSL, except radionuclides were excluded. Control tests were conducted with deionized (DI) water. One-sided exposure tests were also conducted with the HDPE GM in RSL at 70 and 90°C. Specimens were removed periodically and tested to determine antioxidant depletion, melt flow index (MFI), crystallinity, and stress crack resistance. Standard and high-pressure oxidative induction time (OIT) tests were conducted to measure antioxidant depletion. Antioxidant depletion rates in RSL were only slightly greater than those in NSL, indicating that radionuclides in the LLW leachate had only minor effect on antioxidant depletion. Antioxidant depletion in RSL and NSL occurred 1.1–1.9 times faster than in DI water. Antioxidant depletion in HDPE GMs exposed to RSL and NSL at 90°C was complete after 12 months. MFI decreased systematically after 15 months of immersion, which is indicative of crosslinking due to oxidation. Crystallinity also decreased slightly after 12 months, whereas stress crack resistance (SCR) showed no trend over the immersion period. Arrhenius modeling was used to extrapolate the laboratory data at elevated temperatures to a typical LLW liner at 15°C. Predicted time for antioxidant depletion for a 2-mm-thick HDPE GM in a composite liner in contact with LLW leachate is estimated to be 730 years. The total service life of HDPE GMs in contact with LLW leachate is estimated to be at least 1975 years. **DOI: 10.1061/(ASCE)GT.1943-5606.0001643.**

Author keywords: Radioactive waste; Mixed waste; Geomembrane; Degradation; Antioxidant; High-density polyethylene.

Introduction

Composite barriers consisting of a geomembrane (GM) overlying a compacted clay liner or a geosynthetic clay liner are used in low-level radioactive waste (LLW) and mixed waste (MW) disposal facilities to limit release of leachate (Tian et al. 2016). High-density polyethylene (HDPE) is the most common polymer used for GMs in disposal facilities (Foose et al. 2002; Gulec et al. 2004; Rowe 2005; Take et al. 2007; Bouazza et al. 2008; Saidi et al. 2008; Rowe and Rimal 2008; Rowe et al. 2004, 2010a). A typical HDPE GM is composed of polymer resin (>95%), carbon black (2–3%), and antioxidants (0.5–1%) (Hsuan and Koerner 1998). Carbon black is added to protect the GM from ultraviolet radiation and antioxidants are added to control oxidation.

The long-term service life of HDPE GMs in contact with LLW and MW leachate is of particular importance because the service life of LLW and MW barriers is commonly required to exceed 1,000 years (Tian et al. 2016). Predicting the service life of GMs, defined as the length of time that a GM liner can act as an effective hydraulic barrier (Needham et al. 2006), is essential during design and performance assessments (PAs) for LLW and MW disposal facilities. Without a reliable prediction of service life, most PAs for LLW and MW ignore the ability of GMs to control leachate in the containment system.

HDPE GMs undergo degradation in three stages: antioxidant depletion (Stage I), induction (Stage II), and degradation of polymer properties (Stage III) (Viebke et al. 1994; Hsuan and Koerner 1998; Rowe and Sangam 2002; Gulec et al. 2004; Rowe et al. 2009, 2013, Tian et al. 2014, 2015). The service life of a GM is equal to the total elapsed time from Stages I–III. The duration of Stage I is controlled by the rate of consumption of antioxidants, which involves consumption of antioxidants at the surface of the GM and transmission of antioxidants to the surface by diffusion followed by loss to the surrounding medium (Hsuan and Koerner 1998; Sangam and Rowe 2002; Rimal and Rowe 2009; Rowe et al. 2010a, 2013; Tian et al. 2014). Without antioxidants, a GM would be vulnerable to degradation via oxidation immediately, and progress into Stages II and III (Hsuan and Koerner 1998; Rowe et al. 2009).

The first generation of modern GMs was installed ca. 1980 (Hsuan and Koerner 1998), making long-term field data relevant

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to LLW and MW disposal (100+ years) nonexistent. Consequently, accelerated aging tests conducted in the laboratory are used to estimate the service lifetime of HDPE GMs. Studies have been conducted with HDPE GMs exposed to municipal solid waste (MSW) leachate (Sangam and Rowe 2002; Rowe and Rimal 2008; Rowe et al. 2010a), acidic mine drainage (AMD) (Gulec et al. 2004), and synthetic LLW leachate (Tian 2015; Abdelaal and Rowe 2015). These studies have shown that antioxidant depletion in HDPE GMs is affected by the leachate composition (e.g., heavy metals and surfactants) (Gulec et al. 2004; Rowe et al. 2008). Heavy metals in the leachate can catalyze decomposition of hydroperoxides, leading to generation of free radicals and increasing consumption of antioxidants (Osawa and Ishizuka 1973; Gulec et al. 2004). Surfactants in leachate accelerate loss of antioxidants to the surrounding medium by increasing the wetting ability of the GM (Rowe et al. 2008).

LLW leachate contains inorganic macrocomponents, trace heavy metals (e.g., Fe, Cu), and radionuclides (e.g., uranium, ^{226}Ra, and ^{99}Tc) (Tian 2012; Tian et al. 2014; Abdelaal and Rowe 2015) that may alter rate of depletion of antioxidants relative to other leachates. Tian (2012) describes an analysis of LLW leachate collected from four LLW disposal facilities operated by the U.S. Department of Energy for environmental restoration activities. The LLW leachate described in Tian (2012) contains uranium (6.4–$3{,}060\ \mu g/L$), ^{99}Tc(0.3–28 Bq/L), and tritium (0.6–$4{,}629$ Bq/L) at concentrations above the detection limit. The average pH of the four LLW leachates was 7.2 with a range from 5.7 to 9.1. Abdelaal and Rowe (2015) report that LLW leachate contains ^{226}Ra(3.9–50 Bq/L) and ^{238}U(6–$1{,}500\ \mu g/L$) based on an analysis of six LLW disposal facilities. The pH of the six LLW leachates they evaluated ranged from 8.0 to 12.3. The uranium, ^{226}Ra, ^{99}Tc, and tritium in LLW leachates emit α and β particles, which can cause radiation-induced oxidation of a HDPE GM (Klemchuck 2000). Consequently, antioxidant depletion in HDPE GMs installed in LLW waste disposal facilities cannot be inferred directly from exposure data for MSW or AMD leachates.

Studies examining the service life of HDPE GMs exposed to LLW leachate with α and β radiation are limited. Abdelaal and Rowe (2015) examined antioxidant depletion in HDPE GMs exposed to synthetic LLW leachate with high pH (9.5–13.5), but without radionuclides. Increasing pH from 9.5 to 13.5 increased the antioxidant depletion rate. Whyatt and Farnsworth (1989) investigated degradation of the mechanical properties of a HDPE GM exposed to a solution with high pH after exposure to γ radiation with a dosage up to 389 kGy (38.9 Mrad). The break strength and break elongation of the GM decreased after irradiation, whereas the yield strength, yield elongation, and hardness increased. Whyatt and Farnsworth (1989) also report that the HDPE GM did not become more vulnerable to chemical degradation after irradiation. However, their study evaluated γ irradiation, whereas α and β particles are common in LLW and MW leachates.

The objective of this study was to estimate the service life of a commercially available 2-mm-thick smooth HDPE GM exposed to synthetic LLW containing radionuclides (^{238}U, ^{99}Tc, and tritium) that is representative of leachates found in LLW and MW disposal facilities operated by the U.S. Department of Energy for environmental restoration activities. The primary focus of the study was on quantifying the duration of antioxidant depletion (Stage I). Estimates of the duration of Stages II and III were also made based on analogous data in the literature. A conservative estimate of the total service life (i.e., likely underestimation of life span) is obtained from the Stage I data from this study and the Stage II and III data from the literature.

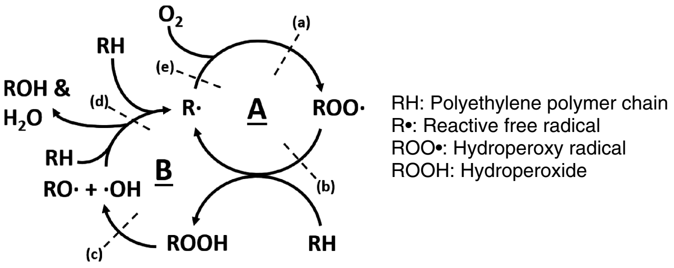

Fig. 1. Oxidation loops for polyethylene [reprinted from Geotextiles and Geomembranes, Vol. 20, No. 2, R.Kerry Rowe and Henri P Sangam, "Durability of HDPE geomembranes," pp. 77–95, Copyright (2002), with permission from Elsevier]

Background

Degradation of HDPE

Degradation of polymers is controlled primarily by oxidation reactions associated with free radicals. Oxidation of polyethylene (PE) follows the free-radical reactions shown in Fig. 1 (Grassie and Scott 1985; Hsuan and Koerner 1998; Rowe and Sangam 2002). Loop A consists of the formation of hydroperoxides (ROOH) and free radicals. Loop B is an autoaccelerating process associated with the decomposition of ROOH, which increases availability of free radicals to attack the original polymer chain and accelerate the chain reactions. Loop A is initiated when sufficient activation energy (e.g., via radiation or heat) is available for the polymer chain (RH) to form a free radical polymer chain (R•) and hydrogen (H•). Oxygen (O_2) reacts with a free radical in the polymer (R•), forming a hydroperoxy free radical (ROO•) that can attack the polymer chain and form ROOH. ROOH molecules are unstable, oxidizing rapidly into RO• and OH•, which react with the original polymer chain to form more free radicals (Grassie and Scott 1985; Hsuan and Koerner 1998; Rowe and Sangam 2002). Consequently, the decomposition of ROOH is autoaccelerating. Antioxidants are added to interrupt these processes.

Effect of Radiation on Polymer Degradation

HDPE GMs installed in LLW disposal facilities may be exposed to radiation due to decay of radionuclides (e.g., uranium, ^{226}Ra, ^{99}Tc) in LLW leachate (Tian 2012; Tian et al. 2014; Abdelaal and Rowe 2015). Radiation can break polymer chains (e.g., C─C and C─H), forming free radicals (e.g., C• and H•) (Klemchuck 2000). These free radicals can react with oxygen, forming ROOH, which is defined as radiation-induced oxidation (Klemchuck 2000). Mason et al. (1993) investigated the impact of gamma radiation on the antioxidant depletion in cross-linked PE materials. Antioxidant depletion was measured using oxidative induction time (OIT) followed ASTM D3895 (ASTM 2007b). OIT of the PE decreased exponentially as a function of exposure dosage, indicating that antioxidants were consumed as a result of radiation.

Polymer degradation due to radiation depends on the type of radiation (Phillips 1988; Klemchuck 2000; Czvikovszky 2004). Charged α particles penetrate a polymer on the order of micrometers, whereas charged β particles can penetrate on the order of millimeters. In contrast, γ rays, which are uncharged, can penetrate meters. Therefore, α and β particles potentially may affect the surface of GM, whereas γ rays can affect the overall thickness of a GM.

The energy of α and β particles typically is high enough to be categorized as ionizing radiation. Ionizing radiation with sufficient energy to exceed the dissociation energy of covalent bonds in the polymer chain results in scission of carbon-carbon bonds (e.g., main chain rupture) and carbon-hydrogen bonds (e.g., side chain rupture), and the formation of the free radicals (R• and H•) (Klemchuck 2000). For example, the average bond energy of the carbon-carbon bond in a polymer typically is 5–10 eV (Czvikovszky 2004); thus, α and β particles carrying energies beyond this dissociation energy can be characterized as ionizing radiation, resulting in radiation damage. These broken bonds with an excited electron can form a new chemical bond with an adjacent free radical, defined as cross-linking (Phillips 1988; Peacock 2000). Chain scission and crosslinking alter the polymer structure, resulting in changes in engineering properties. Moreover, in the presence of oxygen, free radicals formed by irradiation can react with oxygen to form ROOH, resulting in the accelerating degradation process in Fig. 1 (Phillips 1988; Bracco et al. 2006; Costa et al. 2008).

The predominant radiation from LLW leachate is associated with α particles (from the decay of uranium and ^{226}Ra) and β particles (from decay of ^{99}Tc and tritium). The peak energy of α particles emitted from uranium and ^{226}Ra exceeds 4.2 MeV, and the peak energy of β particles emitted from ^{99}Tc and tritium is 294 and 12.3 keV, respectively. These α and β particles emitted from LLW leachate have peak energies that exceed the dissociation energy of the carbon-carbon bond (e.g., 5–10 eV) in the polymer, providing opportunity for degradation of polymer through radiation-induced oxidation.

Depletion of Antioxidants

Antioxidants are added to polymeric materials to prevent oxidation (Grassie and Scott 1985; Hsuan and Koerner 1998). Antioxidant packages with a combination of two or more types of antioxidants are used to provide overall stability from low to high temperature (0–300°C). Primary antioxidants intercept the reactions in Loop A in Fig. 1, indicated as (b) and (d) using dashed lines in Fig. 1. These antioxidants donate an electron that reacts with the free radicals (ROO•, RO•, and OH•), converting them to ROOH, ROH, and H_2O (Hsuan and Koerner 1998; Rowe and Sangam 2002; Gulec et al. 2004). Primary antioxidants also function as electron acceptors that break the links (a) and (e) in Loop A (Fig. 1) by converting alkyl free radicals (R•) to a stable polymer chain. Secondary antioxidants intercept link (c) in Loop B (Fig. 1) by converting the ROOH to a stable alcohol (ROH), thereby preventing ROOH forming free radicals (Grassie and Scott 1985; Hsuan and Koerner 1998; Rowe and Sangam 2002). Antioxidants are consumed as these reactions occur.

Effect of Leachate on Antioxidant Depletion

Previous studies have evaluated antioxidant depletion in HDPE GMs exposed to MSW leachate (Sangam and Rowe 2002; Rowe and Rimal 2008; Rowe et al. 2009, 2013) and AMD (Gulec et al. 2004) using OIT tests. Heavy metals in leachate catalyze decomposition of hydroperoxide, leading to generation of free radicals and increasing consumption of antioxidants (Osawa and Ishizuka 1973; Hsuan and Koerner 1998; Gulec et al. 2004). Surfactants in leachate increase the wetting ability of the GM (Rowe and Rimal 2008), which promotes mass transfer of antioxidant from the GM to the surrounding medium, resulting in greater loss of antioxidants via diffusion. GM thickness has a significant impact on diffusion loss, with thinner GMs having a shorter diffusion path from the center to the surface, resulting in a higher antioxidant depletion rate (Rowe et al. 2010b).

Materials and Methods

Geomembrane

A commercially available 2-mm-thick smooth HDPE GM with a density of 0.946 kg/m^3 was used in the experimental program. The initial standard oxidative induction time (Std-OIT) was 197 min per ASTM D3895 (ASTM 2007b), and the high-pressure oxidative induction time (HP-OIT) was 831 min per ASTM D5885 (ASTM 2006). Crystallinity of the new HDPE GM was 42.6% per ASTM E794 (ASTM 2012) and the melt flow index (MFI) was 0.081 g/10 min per ASTM D1238 (ASTM 2013a). The initial stress crack resistance of the HDPE GM was 4,241 ± 934 h per ASTM D5397 (ASTM 2007a).

Exposure Liquids

Two different synthetic leachates were used in the study: radioactive synthetic leachate (RSL) and nonradioactive synthetic leachate (NSL). RSL is representative of leachates in LLW disposal facilities operated by the U.S. Department of Energy and is based on analysis of field data, as described in Tian (2012). The composition of RSL is in Table 1. NSL is identical to RSL, but has no radionuclides. Deionized (DI) water was used as a reference liquid.

Mean concentrations reported by Tian (2012) were used for all chemical components in RSL, except for radionuclides, which had concentrations near the upper bound, thus representing a worst-case scenario radiologically. The RSL and NSL solutions were prepared by mixing salts in Type II DI water per ASTM D1193 (ASTM 2011) as described in Tian et al. (2016). Major cations and anions were prepared by adding $CaCl_2$, $MgSO_4$, $NaNO_3$, $NaHCO_3$, Na_2SO_4, and $KHCO_3$ salts in Type II DI water (Table 1), trace metals were added as sulfur salts (e.g., Al, Fe, and Mn) and chloride salts (e.g., Li and Ba), and arsenic was added from an arsenic standard solution used for instrument calibration. ^{238}U was added as uranyl acetate, tritium was added as water molecules, and ^{99}Tc as sodium pertechnate. The leachate was replaced monthly to maintain constant leachate composition. Metal concentrations were analyzed periodically by inductively coupled plasma-optical emission spectroscopy (Vista MPX, Varian, Palo Alto, California) following U.S. Environmental Protection Agency (USEPA) Method 6010B to confirm that target concentrations were maintained.

Immersion Test

Insulated stainless steel tanks (381 × 381 × 840 mm) filled with DI water were used for immersing the test specimens. The tanks were equipped with heaters and stirrers to maintain constant and uniform temperature in excess of the ambient environment to accelerate aging (Sangam and Rowe 2002; Gulec et al. 2004; Rowe et al. 2009; Tian et al. 2014). Temperatures were set at 25, 50, 70, and 90°C and controlled to within ±0.1°C. GM coupons (120 × 240 mm in size) cut with a die using a Clicker C10617 cutting press (International Industrial Products Corporation, Nashville, TN) were placed in polypropylene (PP) boxes (150 × 150 × 300 mm) sealed with a rubber gasket and filled with synthetic leachate or DI water. Three PP boxes were placed in one stainless steel tank to age HDPE GM specimens at a specific temperature. The small PP boxes reduced the volume of radioactive leachate used in the testing program, isolated the tanks from radionuclides, and prevented evaporation of leachate at the high aging temperatures that were employed.

Table 1. Composition of Radioactive Synthetic Leachate (RSL)

Group	Components	Formula	Concentration	Units
Major cations and anions	Calcium chloride dihydrate	$CaCl_2 \bullet 2H_2O$	4	mM
	Magnesium sulfate heptahydrate	$MgSO_4 \bullet 7H_2O$	6	mM
	Sodium nitrate	$NaNO_3$	1.5	mM
	Sodium bicarbonate	$NaHCO_3$	2.8	mM
	Sodium sulfate	Na_2SO_4	1.35	mM
	Potassium bicarbonate	$KHCO_3$	0.7	mM
Trace metals	Aluminum sulfate hexadecahydrate	$Al_2(SO_4)_3 \bullet 16H_2O$	0.015	mM
	Arsenic	Arsenic Standard for AAS (1,000 mg/L)	0.001	mM
	Barium chloride	$BaCl_2$	0.002	mM
	Copper(II) sulfate pentahydrate	$CuSO_4 \bullet 5H_2O$	0.0002	mM
	Iron(III) sulfate hydrate	$Fe_2(SO_4)_3$	0.05	mM
	Lithium chloride	LiCl	0.02	mM
	Manganese sulfate monohydrate	$MnSO_4 \bullet H_2O$	0.01	mM
	Nickel(II) sulfate hexahydrate	$NiSO_4 \bullet 6H_2O$	0.0003	mM
	Strontium sulfate	$SrSO_4$	0.02	mM
	Zinc sulfate heptahydrate	$ZnSO_4 \bullet 7H_2O$	0.0005	mM
Radionuclides	Uranyl acetate	$UO_2(CH_3COO)_2 \bullet 2H_2O$	1,500	μg/L
	sodium pertechnate	$NaTcO_4$	29.6	Bq/L
	Tritium	H_2O	4,440	Bq/L

Note: The leachate has pH 7.2, Eh = 120 mV, and total organic carbon = 8 mg/L. H_2SO_4 used to adjust pH $\approx$ 7.2, Na_2S used to adjust oxidation reduction potential (ORP) to $\approx$120 mV. Total organic carbon (TOC) comprised of 5 mg/L added as carbon fraction in surfactant (Igepal CA-720), and 3 mg/L is as carbon fraction in acetate.

One-Sided Exposure Test

One-sided exposure tests were conducted to examine antioxidant depletion in the HDPE GM in contact with LLW leachate under a scenario more representative of a liner. HDPE GM specimens were installed in the base of aluminum columns having a diameter of 102 mm and a height of 152 mm. The columns were filled with RSL and placed in a stainless steel tank filled with water maintained at 70 or 90°C (five tests conducted at each temperature). Specimens were removed after 1, 2, 3, 5, and 7 months of exposure for OIT testing.

Oxidative Induction Time

Oxidative induction time was measured with differential scanning calorimetry (DSC) following the procedures in ASTM D3895 and D5885 (ASTM 2007b, 2006a; Hsuan and Koerner 1998; Sangam and Rowe 2002; Gulec et al. 2004; Rowe et al. 2010a, 2013; Tian et al. 2014). OIT is proportional to the total amount of antioxidant remaining in the HDPE GM and is a measure of antioxidant content. Std-OIT tests were conducted in accordance with ASTM D3895 (ASTM 2007b) and HP-OIT tests were conducted in accordance with ASTM D5885 (ASTM 2006a).

Std-OIT was measured using a TA Instruments Q100 DSC (TA Instruments, Schaumburg, Illinois). A 5-mg specimen was heated to 200°C at 20°C/min in a nitrogen atmosphere. After reaching 200°C, the specimen was maintained isothermally for 5 min. The gas was then changed to oxygen, and the change in enthalpy was recorded. The test was terminated when an exothermal peak was detected. The initial Std-OIT of the HDPE GM was 197 ± 5 min. Comparative tests were also conducted on the same GM specimens by a commercial laboratory for comparative purposes. The commercial laboratory reported a Std-OIT of 187 ± 4 min for unexposed HDPE GM, which is comparable to the Std-OIT measured at the University of Wisconsin.

HP-OIT tests were conducted to investigate whether antioxidants in the GM may have been destroyed and ignored in the Std-OIT tests because of the higher temperature of the Std-OIT test (Hsuan and Guan 1997; Hsuan and Koerner 1998). HP-OIT testing is similar to Std-OIT testing, except higher gas pressure (3500 kPa) and lower temperature (150°C) are applied during testing. The HP-OIT tests were also conducted by the commercial laboratory.

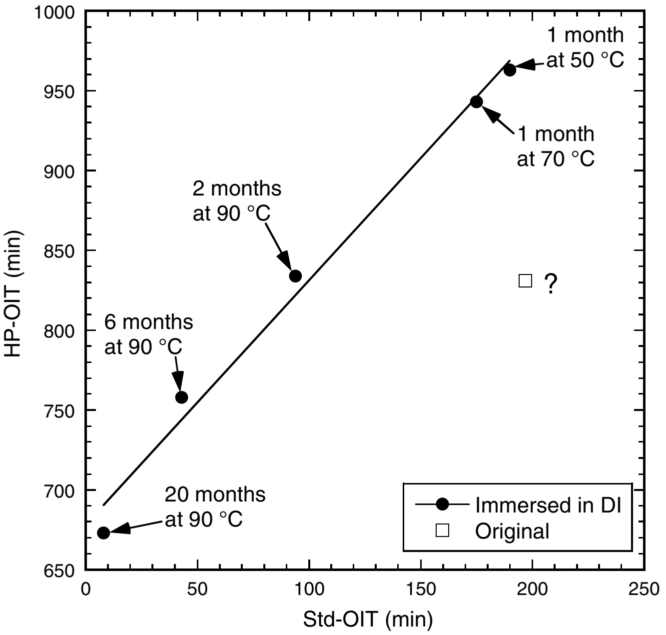

Fig. 2. Std-OIT versus HP-OIT for HDPE geomembranes immersed in DI water and initial condition; anomalous data point marked with question mark

The relationship between HP-OIT and Std-OIT is shown in Fig. 2. A linear relationship exists between Std-OIT and HP-OIT, except for the one point corresponding to the original GM. Hsuan and Koerner (1998), Sangam and Rowe (2002), and Gulec et al. (2004) report similar linear relationships, indicating that the high temperature of the Std-OIT test did not destroy or mask the antioxidants. This finding also suggests that the antioxidant package used in the GM is likely phosphite-based and phenol-based (effective temperature ranges of 150–300°C and 0–300°C), rather than

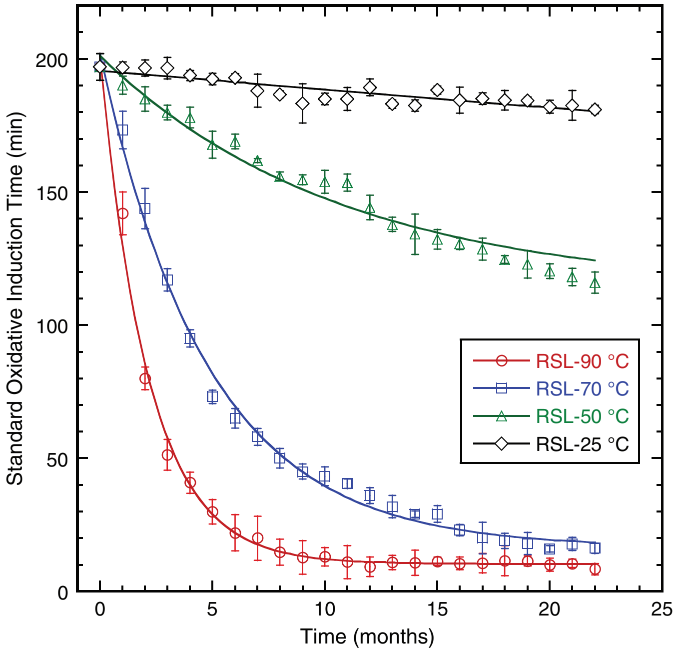

Fig. 3. (Color) Standard oxidative induction time (Std-OIT) of GM immersed in radioactive synthetic leachate (RSL) versus immersion time

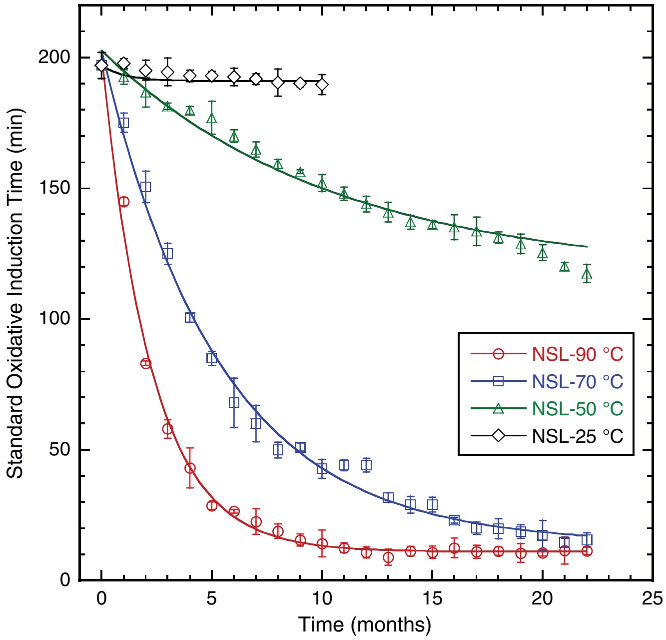

Fig. 4. (Color) Standard oxidative induction time (Std-OIT) of GM immersed in nonradioactive synthetic leachate (NSL) versus immersion time; tests with HDPE GMs immersed in NSL at 25°C were conducted one year later than tests conducted at 50, 70, and 90°C, and thus the total testing time is shorter

hindered amines (Hsuan and Koerner 1998). Consequently, the Std-OIT test was used in subsequent analyses.

Melt Flow Index Test

Melt flow index (MFI) was measured using the procedures in ASTM D1238 (ASTM 2013a) with a Dynisco LMI 4001 Model (Dynisco, Franklin, Massachusetts). MFI corresponds to the amount of molten polymer extruded through a standard orifice in 10 min under a constant load of 2.16 kg at elevated temperature (190°C).

Crystallinity

Crystallinity of the HDPE GM was measured using the TA Instruments Q100 DSC following the procedures in ASTM E794 (ASTM 2012). GM specimens with mass between 10 and 15 mg were placed in the DSC and heated at a rate of 10°C/min through the melting range until the baseline reoccurred above the melting endotherm.

Stress Crack Resistance

Stress crack resistance (SCR) of the HDPE GM was monitored using single point-notched constant tensile load tests following the procedure in ASTM D5397 (ASTM 2007a). Dumbbell-shaped specimens were prepared using the Clicker cutting press, notched 20% of the total thickness, and immersed in a solution containing 10% Igepal CO630 and 90% water at 50°C. The notched specimens were loaded to 30% of the tensile yield stress. Tests were conducted using a Model AA-S-AA-000 manufactured by BT Technology (Rushville, Illinois). Independent tests were conducted by the same commercial laboratory used for the OIT tests.

Results and Discussion

Depletion of Antioxidant

Antioxidant depletion is shown in terms of OIT in Figs. 3–5. The antioxidant depletion rate was quantified using a first-order model with a residual OIT (Hsuan and Koerner 1998; Mueller and Jakob 2003; Gulec et al. 2004; Rowe et al. 2009, 2010a, 2013):

$$\mathrm{OIT}_t = \mathrm{OIT}_r + (\mathrm{OIT}_0 - \mathrm{OIT}_r)\exp(-st) \qquad (1)$$

where OIT_t = OIT at time t; OIT_0 = initial OIT; OIT_r = residual OIT; s = antioxidant depletion rate (month^{-1}); and t = time (month).

Fits of Eq. (1) to the OIT data obtained by least-squares regression are shown in Figs. 3–5. Antioxidant depletion rates for each immersion liquid and temperature are summarized in Table 2. Residual OIT in Eq. (1) is the relatively constant OIT at the end of testing, when the remaining antioxidants are no longer effective in preventing oxidation (Rowe et al. 2013). OIT_r in Eq. (1) was determined to be 11 min by simultaneous least-squares fitting of the OIT depletion data for the HDPE GM exposed to RSL, NSL, and DI at 25, 50, 70, and 90°C (Fig. 6). Individual fits to each data set yielded OIT_r from 9 to 12 min for the 2-mm-thick HDPE GM immersed in RSL, 8 to 13 min for NSL, and 9 to 14 min for DI water.

OIT decreases with immersion time and decreases at a higher rate at higher temperature (Figs. 3–5, Table 2). Hsuan and Koerner (1998), Sangam and Rowe (2002), Gulec et al. (2004), and Rowe et al. (2010a, 2013) report similar results for other leachates. The depletion rate for RSL at 90°C is 0.4569 month^{-1}, which is 2.5 times higher than the rate at 70°C (0.1862 month^{-1}), 16 times higher than that at 50°C (0.0277 month^{-1}), and 97 times higher than that at 25°C (0.0047 month^{-1}). The fastest depletion occurs in RSL, followed by NSL, and DI (Fig. 6 and Table 3). At 90°C, the antioxidant depletion rate in RSL (0.4569 month^{-1}) is 1.06 times faster than the rate in NSL (0.4319 month^{-1}), and 1.50 times faster than to the rate in DI water (0.3047 month^{-1}). A paired t-test was used to evaluate whether the rate of OIT depletion differed statistically for RSL, NSL, and DI water at a significance level (α) = 0.05. The p-values obtained from the four

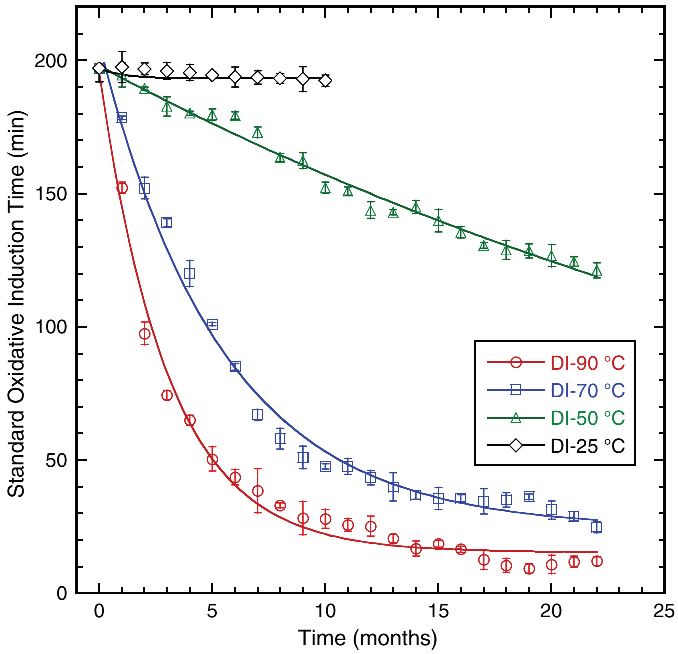

Fig. 5. (Color) Standard oxidative induction time of GM immersed in DI water versus immersion time; tests with HDPE GMs immersed in NSL at 25°C were conducted one year later

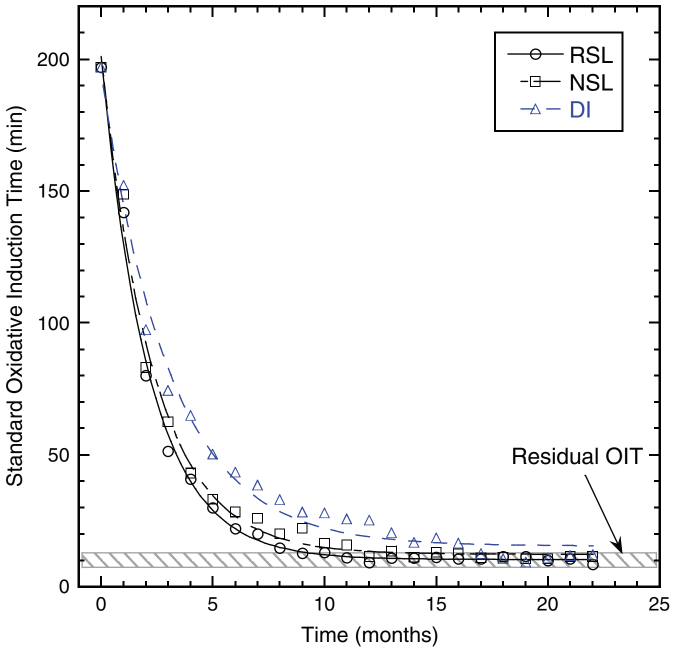

Fig. 6. (Color) Standard oxidative induction time depletion of HDPE GM immersed in RSL, NSL, and DI water at 90°C as a function of immersion time

Table 2. Antioxidant Depletion Rates in DI, NSL, and RSL

	Antioxidant depletion rate (s) (month^{-1})			Ratio of antioxidant depletion rates		
Temperature (°C)	DI	NSL	RSL	RSL/NSL	RSL/DI	NSL/DI
25	0.0025	0.0043	0.0047	1.09	1.88	1.72
50	0.0244	0.0278	0.0277	1.00	1.14	1.14
70	0.1344	0.1789	0.1862	1.04	1.38	1.33
90	0.3047	0.4319	0.4569	1.06	1.41	1.50

Table 3. Arrhenius Equations and Activation Energies for HDPE GMs Immersed in RSL, NSL, and DI Water

Immersion liquid	Arrhenius equation $\ln(s) = \ln(A) - (E_a/R)/T$	R^2	Activation energy (E_a) (kJ/mol)
RSL	$\ln(s) = 20.043 - 7{,}879/T$	0.99	65.4
NSL	$\ln(s) = 20.193 - 7{,}922/T$	0.99	65.8
DI	$\ln(s) = 21.623 - 8{,}203/T$	0.99	68.1

aging temperatures in RSL and DI water ($p = 6.8 \times 10^{-8}$ to 0.015) and in NSL and DI water ($p = 3.8 \times 10^{-7}$ to 0.0011) were less than 0.05, indicating a statistically significant difference between the OIT depletion rate in RSL and NSL compared to DI water.

The higher depletion rate for the GM immersed in NSL or RSL relative to that for DI water is attributed to the metals and surfactant in the leachate. Transition metals (e.g., Mn, Cu, and Fe) in RSL and NSL can breakdown ROOHs via redox reactions, creating additional free radicals and additional consumption of antioxidants (Gale et al. 1972; Osawa and Ishizuka 1973). For example, Gulec et al. (2004) report an antioxidant depletion rate for a 1.5-mm HDPE GM that is 1.3 times higher in synthetic acid mine drainage containing a variety of metals than in acidic water without metals, illustrating that transition metals in AMD (e.g., Fe = 1,500 mg/L) accelerate the antioxidant depletion rate. Similarly, Rowe and Rimal (2008) report that surfactants can increase the wetting ability of the GM, resulting in more rapid loss of antioxidants via diffusion into the leachate. Increasing the surfactant concentration from approximately 1.1 g/L (1 mL/L) to 5.5 g/L (5 mL/L) in experiments conducted by Rowe et al. (2008) led to an increased antioxidant depletion rate.

The ratio of antioxidant depletion rates in RSL and NSL to DI water (1.1–1.9 times) is similar to the ratio (1.8 times) reported by Gulec et al. (2004) for AMD and lower than the ratio (2.5–4.0 times) reported by Rowe et al. (2009) for MSW leachate. This probably reflects the lower surfactant concentration in RSL or NSL (e.g., 12 mg/L) relative to synthetic MSW leachate [e.g., ~5.5 g/L (5 mL/L)] (Rowe et al. 2009). Rowe et al. (2008) reported that a small amount of surfactant can increase the antioxidant depletion rate significantly. The AMD in Gulec et al. (2004) had a lower pH (e.g., 2.1) and higher concentration of transition metals than RSL and NSL, but contained no surfactants. Consequently, the similar ratios observed in this study and by Gulec et al. (2004) probably reflect compensating effects of the differences in metals and surfactant concentrations. The HDPE GMs used in previous studies may have contained different antioxidants, as reflected by the differences in initial Std-OIT [e.g., 133 min for Rowe et al. (2009); 204 min for Gulec et al. (2004); 197 min for the current study], which may also lead to different antioxidant depletion rates.

Effect of Radiation from RSL on Antioxidant Depletion

The antioxidant depletion rate in RSL was 9, 4, and 6% faster than in NSL when immersed at 25, 70, and 90°C (Table 3), respectively. At 50°C, the antioxidant depletion rates were the same. A paired t-test was used to determine whether the rates of OIT depletion differed statistically between RSL and NSL at each aging temperature. *P*-values of 0.00046, 0.0050, and 0.000049 were obtained for 50, 70, and 90°C, indicating a statistically significant difference

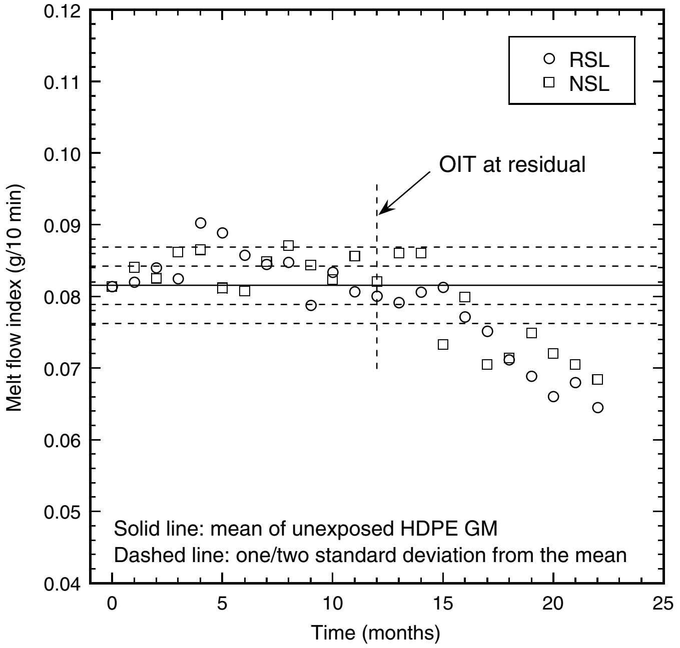

Fig. 7. Melt flow index of HDPE GM exposed to RSL and NSL at 90°C as a function of immersion time

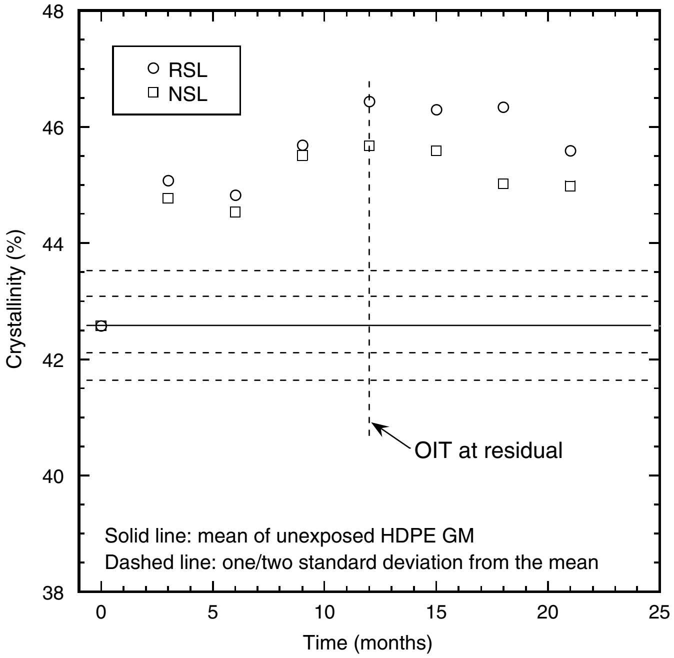

Fig. 8. Crystallinity of HDPE GM exposed to RSL and NSL at 90°C as a function of immersion time

between antioxidant depletion rate in RSL and NSL at these temperatures. For 25°C, the p-value was 0.12, indicating no statistically significant difference. Consequently, while the effect of radionuclides in RSL generally is statistically significant, the effect on antioxidant depletion in HDPE GM relative to NSL is subtle.

The small increase in antioxidant depletion rate of the HDPE GM in RSL relative to NSL is attributed to the low radiation dosage from exposure to the LLW leachate. An α particle form ^{238}U with peak energy of 4.2 MeV will penetrate only 25 μm in water, and a β particle from ^{99}Tc with peak energy of 294 keV will penetrate approximately 0.5 mm in water (Turner 2007). Thus, only those α and β particles emitted within a narrow zone adjacent to the GM may reach the surface of a HDPE GM. Penetration of α and β particles is strongly affected by the density of materials being penetrated (Turner 2007), and HDPE GMs have a density (942 kg/m^3) close to water. Therefore, the penetration of α and β particles in a HDPE GM is likely to be similar range to that in water and only impact the surface of the GM. Further study is ongoing to investigate the effect of higher levels of α and β radiation on antioxidant depletion in HDPE GMs.

Melt Flow Index

The MFI for the GM immersed in RSL and NSL at 90°C is shown in Fig. 7. The mean MFI of the unexposed GM is shown as the solid line in Fig. 7 and the dashed lines are one and two standard deviations from the mean. For both RSL and NSL, the MFI data fall within the band corresponding to two standard deviations until 14 months of aging. After 15 months, the MFI begins decreasing systematically, which is indicative of increasing molecular weight, suggesting crosslinking associated with oxidation. The decrease in MFI at 15 months at 90°C is consistent with completion of Stage I (antioxidant depletion) at 12 months and the onset of Stage III degradation at 15 months, as described in Rowe et al. (2009). The delay between the end of Stage I (12 months) and the initiation of Stage III (15 months) is representative of Stage II (Hsuan and Koerner 1998; Rowe et al. 2009).

Crystallinity

Crystallinity is a measure of the relative abundance of crystalline and amorphous regions in a polymer, and is an indicator of change in polymer structure (Sperling 1992; Kong and Hay 2002). Higher crystallinity generally corresponds to HDPE GMs with greater stiffness and lower stress crack resistance (Rowe et al. 2009). Crystallinity of the GMs immersed in RSL and NSL at 90°C is shown in Fig. 8 as a function of immersion time. The crystallinity increased abruptly from 42.6 to 44.7–45.1% during the first three months of immersion, and then increased more gradually to 45.6–46.4% from 3 to 12 months of immersion. A very gradual decrease in crystallinity (approximately 1%) occurred during the final next nine months.

The increasing crystallinity during the first 12 months is attributed to recrystallization and/or postcrystallization as the polymer established equilibrium from a nonequilibrium state (Petermann et al. 1976; Wrigley 1989; Dörner and Lang 1998). Similar increases in crystallinity of HDPE GMs immersed in leachate at 85°C have been reported by Dörner and Lang (1998) and Rowe et al. (2009). The slight decrease in crystallinity after 12 months, when the antioxidants were depleted, is indicative of less freedom of molecular segments to form crystallinities (Peacock 2000; Rowe et al. 2009) and is consistent with the crosslinking in response to oxidation suggested by the decrease in MFI. Rowe et al. (2009) also observed a drop in crystallinity for HDPE GMs immersed in MSW leachate after antioxidants were depleted completely. Consequently, the MFI data and the crystallinity data are consistent with the HDPE GM completing Stage I (antioxidant depletion), and progressing into Stage III, when changes in polymer structure occur in response to oxidation.

Stress Crack Resistance

SCR measurements for the HDPE GM samples immersed in RSL at 90°C are shown in Fig. 9. The SCR for original HDPE GM was 4,241 ± 934 h based on the measurements at the

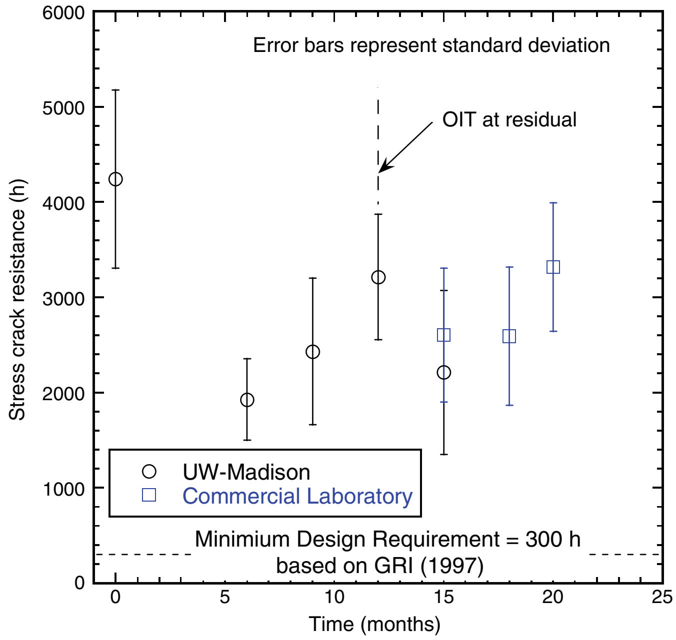

Fig. 9. (Color) Stress crack resistances of HDPE GM exposed to RSL at 90°C; minimum design requirement is based on GRI (1997)

University of Wisconsin. The large standard deviation in the SCR data is likely due to imperfections in the notch.

Except for the drop between initial condition and SCR at 6 months, there is no trend and no measurable change in SCR for up to 20 months, even though the antioxidants were depleted after 12 months.

One-Sided Exposure Test

One-sided exposure tests were conducted to provide a more representative condition for antioxidant depletion compared to an immersion test (Rowe and Rimal 2008; Rowe et al. 2010a, 2013; Tian et al. 2014). In immersion tests, both sides of the GM are exposed to leachate, whereas only one side of a GM is exposed to leachate in a liner in a waste containment facility (Rowe et al. 2010a; Tian et al. 2014). Antioxidants diffuse to and are released from both sides of the GM during an immersion test, reducing the diffusion path to one-half thickness of the GM. In contrast, the diffusion path is the entire thickness of the GM in one-sided exposure. This is directly analogous to the longer time required for pore water pressure dissipation during consolidation with single drainage versus double drainage (Budhu 2011). Because diffusion loss is a significant mechanism for antioxidant depletion (Rimal and Rowe 2009), immersion tests underestimate the antioxidant depletion time that occurs in one-sided exposure scenario.

Ten one-sided exposure tests were conducted using RSL as the contacting liquid. Five tests were conducted at 70°C and five at 90°C. The tests were disassembled periodically and OIT was determined. OIT depletion as a function of aging time from these tests is shown in Fig. 10. Antioxidant depletion rates were calculated using Eq. (1) and $\mathrm{OIT}_r = 11$ min obtained from the immersion tests. Antioxidant depletion rates for one-sided exposure to RSL were 0.0542 and 0.1352 month^{-1} at 70 and 90°C, respectively, 3.44 and 3.38 times slower than obtained from the immersion tests. Rowe et al. (2010a) also report antioxidant depletion rates approximately three times lower for one-sided exposure tests relative to immersion tests.

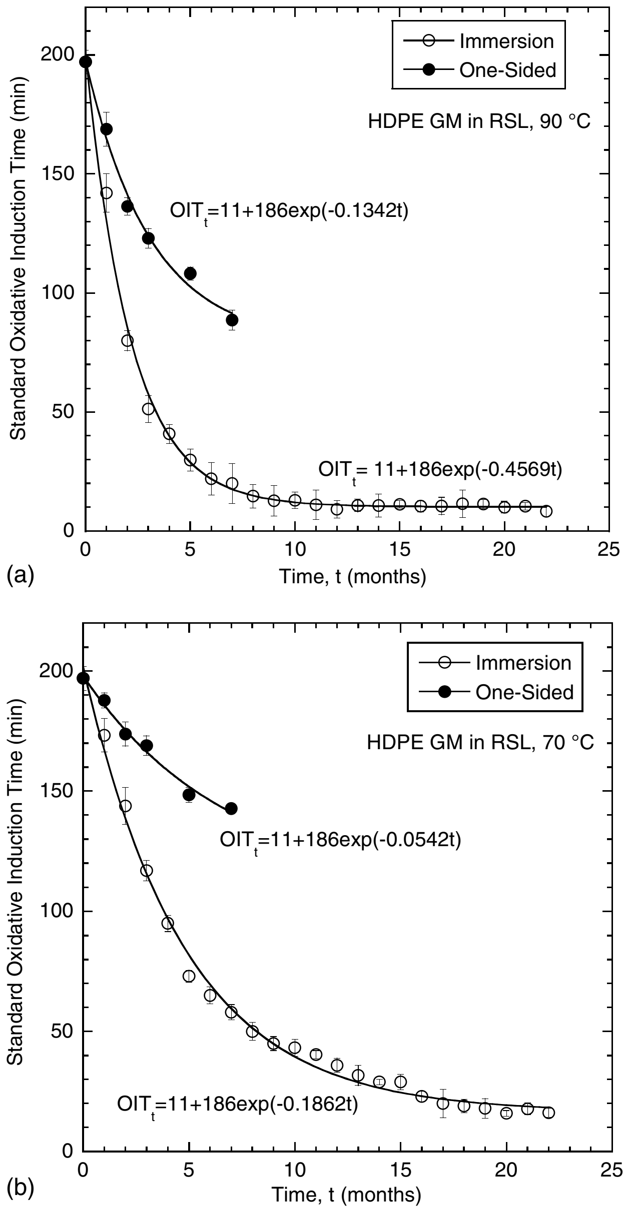

Fig. 10. Standard oxidative induction time as a function of immersion time of HDPE GM in RSL from immersion tests and one-sided tests: (a) 90°C; (b) 70°C

Practical Implications—Service Life Estimation

Stage I—Antioxidant Depletion

Arrhenius modeling was used to estimate the time for antioxidant depletion in a HDPE GM installed in the field using procedures similar to those described in Hsuan and Koerner (1998), Sangam and Rowe (2002), Gulec et al. (2004), Rowe and Rimal (2008), and Rowe et al. (2009, 2010a). The depletion rate (s) is scaled to field temperature using the Arrhenius equation

$$s = Ae^{-E_a/(RT)} \tag{2}$$

where A = constant; E_a = activation energy; R = universal gas constant; and T = absolute temperature (°K).

Arrhenius graphs [ln(s) versus 1/T] for the HDPE GM immersed in DI water are shown in Fig. 11(a) along with data from immersion

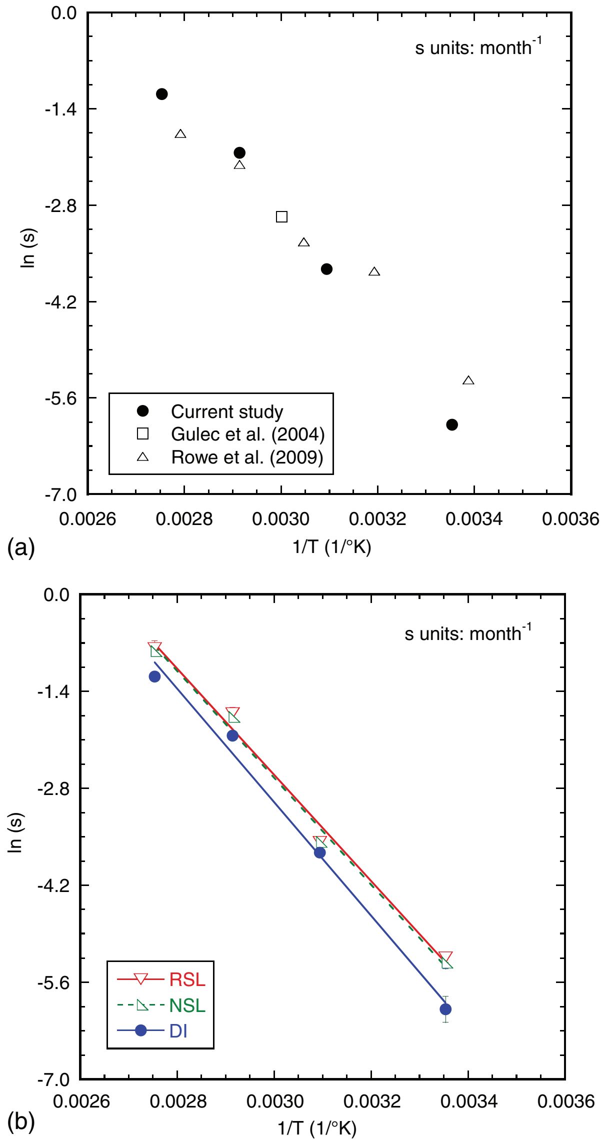

Fig. 11. (Color) Arrhenius plot of antioxidant depletion for (a) DI water (current and other studies); (b) RSL, NSL, and DI water

tests with DI water reported in Gulec et al. (2004) and Rowe et al. (2009). ANCOVA analysis was used to compare the data sets in Fig. 11(a) at a significance level (α) = 0.05 (Gulec et al. 2004) to assess whether the data collected in this study are comparable to those obtained by others for a similar immersion solution and GM. A p-value of 0.68 ($\gg 0.05$) was obtained, indicating no statistically significant difference between the Arrhenius equation fit to the data from this study and the data from Rowe et al. (2009). That is, even though a fit by eye or by regression might suggest that the trends are modestly different, there is no statistically significant difference between the regression relationships for the data from Rowe et al. (2009) and the data from this study. Gulec et al. (2004) only reported an antioxidant depletion rate in HDPE GM exposed to DI water at 60°C. Consequently, no statistical analysis was conducted using the data from Gulec et al. (2004). Nevertheless, as indicated in Fig. 11(a), the rate reported by Gulec et al. (2004) for DI water is similar to the rates reported in this study for DI water.

Arrhenius graphs are shown in Fig. 11(b) for tests conducted with RSL, NSL, and DI water with fits of Eq. (2) obtained by least-squares regression. Activation energies and the constant A in Eq. (2) obtained by least-squares regression are summarized in Table 3. The activation energy was obtained from the slope (E_a/R). The highest activation energy was obtained for GM immersed in DI water (68.1 kJ/mol), followed by NSL immersion (65.8 kJ/mol), and by RSL immersion (65.4 kJ/mol). The lowest activation energy corresponds to highest antioxidant depletion rate obtained for the HDPE GM immersed in RSL.

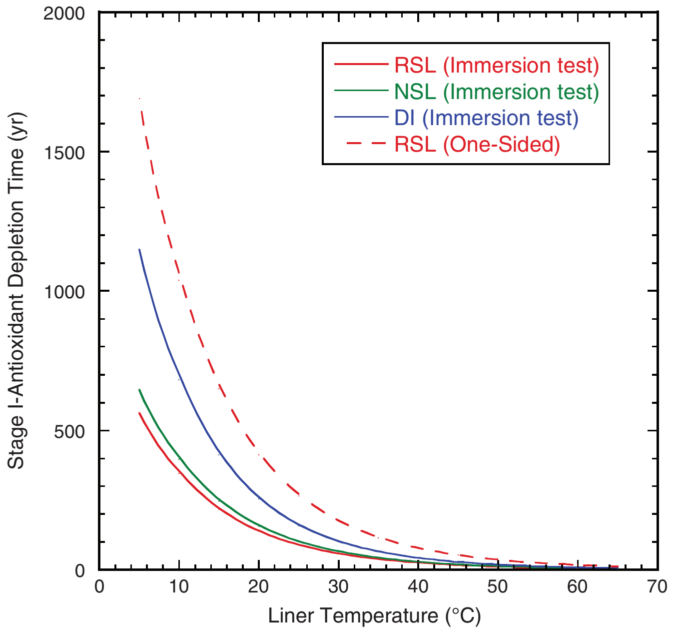

Fig. 12. (Color) Predicted antioxidant depletion time as a function of temperature, immersion liquid, and exposure condition

The parameters in Table 3 were used to predict the antioxidant depletion rate (s) at different temperatures ($\mathrm{OIT} = \mathrm{OIT}_r$) and the time for Stage I antioxidant depletion. For one-sided exposure representative of field condition, depletion rates obtained from the immersion test were scaled by factor of 3.4 (obtained from the one-sided exposure tests).

Stage I antioxidant depletion times for immersion are shown in Fig. 12 as a function of temperature for each of the immersion liquids. At a field temperature of 15°C, which is typical of liner temperatures at LLW facilities operated by the U.S. Department of Energy (Tian 2012), the predicted time to antioxidant depletion is 215 years under immersion conditions. For a liner condition in a LLW or MW disposal facility with one-sided exposure, the predicted antioxidant depletion time is 730 years (Fig. 12).

Stages II and III

The data collected in this study are not sufficient to use the Arrhenius methodology to predict the durations of Stages II and III, or the entire service life (sum of durations for Stages I, II, and III) of a HDPE GM in a LLW or MW facility. However, performance assessments for LLW and MW facilities require that service life predictions be made. Thus, a conservative approach was followed using data from a long-term study (10 years) conducted by Rowe et al. (2009) using MSW leachate. Using the data from Rowe et al. (2009) as a surrogate is reasonable, as antioxidant depletion in MSW leachate occurs more quickly than in LLW or MW leachate. Moreover, once antioxidant depletion occurs, oxidation is the predominant mechanism causing polymer degradation. Metals are catalysts to oxidation of GMs (Gulec et al. 2004), and

Table 4. Estimates of Duration of Stages II and III (Data from Rowe et al. 2009)

	Stage II			Stage III		
Property	E_a (kJ/mol)	s_T at 15°C (month^{-1})	Duration Stage II (year)	E_a (kJ/mol)	s_T at 15°C (month^{-1})	Duration Stage III (year)
Break strength	71.4	0.00049	200	80.0	0.000032	2,585
Break strain	28.7	0.0037	25	80.0	0.000056	1,495
SCR (50%)	74.7	0.00035	235	80.0	0.000068	1,220

Note: s_T = depletion rate at temperature T. Activation energy for Stage III was set at 80 kJ/mol per Rowe et al. (2009). SCR = 50% represents a 50% reduction in SCR. Predicted lengths of Stages II and III rounded to nearest 5 years.

MSW leachates have higher metal concentrations and higher ionic strength than LLW leachates (Tian 2012; Tian et al. 2016). Thus, oxidation in MSW leachate is expected to be more rapid than in LLW and MW leachate.

Lower bound predictions of the durations of Stages II and III based on break strength, break strain, and SCR [50% remaining per GRI (1997)] using the data in Rowe et al. (2009) are summarized in Table 4. These predictions were made using the same approach employed in Rowe et al. (2009), except the temperature was set at 15°C to represent a liner in a LLW or MW facility. In addition, predictions were made with parameter sets in Rowe et al. (2009) yielding the shortest possible durations for Stages II and III and without an adjustment to account for the lower rate occurring in a liner scenario than in the immersion conditions. That is, the most conservative possible approach when making the estimates. For these assumptions, the shortest duration is 25 years for Stage II and 1,220 years for Stage III. Thus, for a Stage I duration of 730 years, the total service life is estimated to be 1975 years.

The authors acknowledge that this prediction is only an estimate of the actual service life. Additional study is needed to quantify the duration of Stages II and III with greater precision for LLW and MW leachates.

Summary and Conclusions

The effects of synthetic LLW leachate on antioxidant depletion, melt flow index, crystallinity, and stress crack resistance of a high-density polyethylene geomembrane have been described. GM specimens were exposed to radioactive synthetic leachate (RSL), nonradioactive synthetic leachate (NSL), and DI water (control) at 25, 50, 70, and 90°C for up to 22 months. NSL had the same chemical composition as RSL, but without radionuclides. Immersed samples were periodically removed to determine the oxidative induction time, MFI, crystallinity, and SCR. One-side exposure tests in columns were used to relate antioxidant depletion rates obtained from the immersion tests to conditions more representative of field conditions. Arrhenius modeling was used to predict the time for Stage I (antioxidant depletion), Stage II, and Stage III degradation. On the basis of experimental data and analyses, the following conclusions are drawn:

- Radiation from LLW leachate has a statistically significant, but subtle impact on antioxidant depletion. Antioxidant depletion occurred up to 9% more rapidly in RSL than in NSL. The antioxidant depletion rates in RSL and NSL were up to 88% greater than in DI water, most likely because of metals (e.g., Fe and Mn) and surfactants in the leachate. Antioxidants in the HDPE GM exposed to RSL or NSL were depleted completely after 12 months of aging at 90°C.
- MFI of the HDPE GM immersed in RSL and NSL at 90°C was unchanged for the initial 14 months, and then decreased systematically, indicating degradation of polymer after antioxidant depletion was complete at 12 months. These data suggest that Stage II occurred between 12 and 14 months and Stage III began at 15 months at 90°C.
- Crystallinity of the HDPE GM increased during the first 12 months of immersion, and then decreased gradually over the next nine months after the antioxidants were depleted. The decreasing crystallinity suggests that crosslinking occurred in the HDPE GM.
- No trends were observed in the SCR data except for a drop after the first six months of immersion, indicating no significant degradation affecting SCR occurred during the 20 months of the aging test.
- Predictions made with Arrhenius modeling for a typical liner temperature of 15°C in a LLW disposal facility indicate that antioxidant depletion in HDPE GM will occur in approximately 730 years with one-sided exposure to leachate. Conservative lower bound estimates of the durations of Stages II and III were made using rate parameters reported by Rowe et al. (2009) from long-term immersion tests (two-sided exposure). Using this approach, the total service life is estimated to be at least 1975 years. Additional long-term study is needed to define the total service life of HDPE GMs in LLW and MW leachate with greater precision.

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