Effect of Low-Level Radioactive Waste Leachate on Antioxidant Depletion in HDPE Geomembranes – 15135

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ABSTRACT

Low-level radioactive waste (LLW) and mixed waste (MW) disposal facilities in the US are required to have a service life in excess of 1000 yr. Understanding the rate of degradation of high-density polyethylene (HDPE) geomembranes (GMs) used in barriers of LLW and MW facilities is necessary to assess their service life. HDPE GMs undergo degradation in three stages: antioxidant depletion (Stage I), induction time (stage II), and polymer degradation (Stage III). For LLW and MW facilities, these degradation mechanisms must be assessed with the GM in contact with leachates representative of LLW or MW. This paper focuses on antioxidant depletion in LLW leachate. HDPE GM coupons (2-mm thick) were immersed in radioactive synthetic leachate (RSL) with chemistry representative of leachate in LLW disposal facilities operated by the US Department of Energy's environmental restoration programs. Depletion was assessed at four temperatures (25, 50, 70, and 90 °C). Comparative tests were conducted with non-radioactive synthetic leachate (NSL), which has the same chemistry as RSL except radionuclides are excluded. Control tests were conducted with deionized (DI) water. Specimens were removed periodically and tested to determine their mechanical and chemical properties. Antioxidant depletion was measured by both standard and high-pressure oxidative induction time (OIT) tests. The rate of antioxidant depletion in RSL is statistically no different than depletion in NSL. Extrapolating the laboratory data at elevated temperatures to a typical LLW liner at 15 ^{o}C via Arrhenius modeling showed that the time for antioxidant depletion for a GM in a composite liner is approximately 650 yr when exposed to LLW leachate. Actual service life of the GM will be longer.

INTRODUCTION

Composite barrier systems are used in low-level radioactive waste (LLW) and mixed waste (MW) disposal facilities due to their ability to limit contaminant transport to very low rates. Composite barriers consist of a thin polymeric sheet referred to as a geomembrane (GM) overlying a geosynthetic clay liner or a compacted clay liner. High-density polyethylene (HDPE) is the most common polymer used for GMs in LLW and MW facilities. Understanding degradation of HDPE GMs is important when conducting performance assessment for LLW and MW disposal facilities.

GM degradation is largely controlled by polymer type and environmental factors, such as UV light, radiation, elevated temperatures, chemical corrosion, and oxidation degradation [1]. Identification of one dominant factor that governs the degradation of GM installed in a LLW disposal facility is difficult because, typically, more than one effective factor is encountered *in situ* [2]. For example, oxidation degradation, chemical corrosion, and radiation effects may impact the degradation of GM installed in LLW facilities because the LLW leachate consists of numerous metal components (e.g., Ca, Mg, Na, Fe, and Mn) and radionuclides (e.g., U, ^{99}Tc and ^{3}H) [3]. Metals in LLW leachate can accelerate the decomposition of hydroperoxide, resulting in more rapid consumption of antioxidants [4]. In addition, the ionizing radiation energy by radioactive decay of U and ^{99}Tc can generate additional free radicals (e.g., broken carbon-carbon bond or carbon-hydrogen bond) in GM [5], accelerating depletion of antioxidants.

The most reliable way of assessing non-mechanical degradation of GMs is to exhume samples from the field at different time intervals during the service life. However, first generation GMs were installed ca. 1980, making long-term (100+ yr) field data non-existent. Consequently, accelerated aging tests conducted in the laboratory typically are used to estimate the service lifetime of GMs [6, 7, 8, 9, 10].

GMs undergo non-mechanical degradation in three stages: antioxidant depletion (Stage I), induction time to the onset of polymer degradation (Stage II), and polymer property degradation (Stage III). Antioxidant depletion involves oxidation of antioxidants at the surface of the GM and loss of antioxidants by diffusion [2, 6]. Grassie and Scott [11] indicate that oxidation of polyethylene follows the free radicals mechanism, as shown in Fig. 1. Loop A consists of the formation of hydroperoxide (ROOH) and free radicals, and Loop B depicts the auto-accelerating process caused by decomposition of ROOH. Decomposition of ROOH increases the amount of free radicals, which attack the original polymer chain and accelerate chain reactions [6].

RH: Polyethylene polymer chain
R•: Reactive free radical
ROO•: Hydroperoxy radical
ROOH: Hydroperoxide
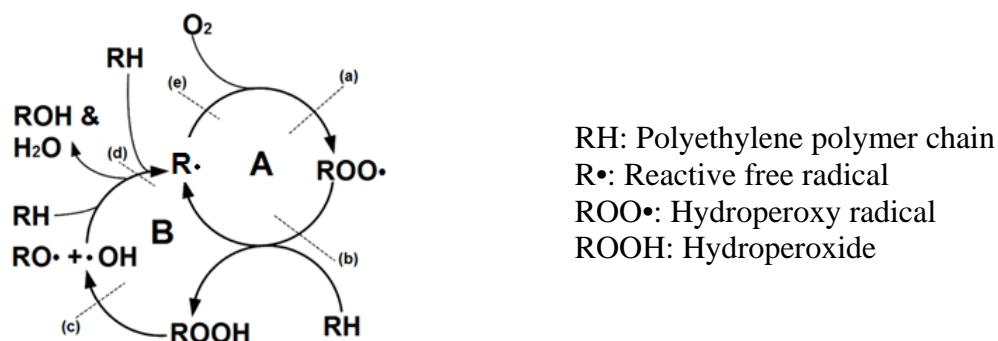
Fig. 1. Oxidation loops for polyethylene [adapted from Grassie and Scott (1985) and Rowe and Sangam (2002)].

The dashed lines in Fig. 1 represent locations where antioxidants used in a GM intercept the reaction and stabilize the polymer [2, 6]. The primary antioxidant acts by accepting or donating an electron. Antioxidants intercept the links (b) and (d) in Fig. 1 by donating an electron to react with the free radicals ROO·, RO·, and OH·, converting them to ROOH, ROH, and H_2O, respectively [6]. Another type of antioxidant performs as an electron acceptor. Electron acceptors break link (a) and (e) by converting alkyl free radicals (R·) to form a stable polymer chain. Secondary antioxidants are designed to intercept the link (c) to prevent hydroperoxides (ROOH) from becoming free radicals by changing the ROOH to a stable alcohol (ROH) [6].

Examination of antioxidant depletion in GMs installed in LLW composite liner system has been limited to date. The compatibility of GMs as a barrier material for radioactive waste have been explored [12, 13], but past studies have focused on degradation of physical properties (e.g., tensile properties) rather than antioxidant depletion of GMs. The objective of the study described in this paper was to estimate the rate of antioxidant depletion in 2-mm-thick HDPE GM within a LLW landfill system. This objective was met by conducting long-term immersion testing in leachate simulating conditions in LLW disposal facilities. Tests were conducted at four temperatures (25, 50, 70, and 90 °C), so that experiential data could be extrapolated to field conditions.

METHODS
Geomembrane and Exposure Liquid
A commercially available 2-mm-thick smooth HDPE GM was used in the experimental program. The initial standard oxidation induction time (Std-OIT) measured in accordance with ASTM D3895 was 197 min and the high-pressure oxidation induction time (HP-OIT) measured in accordance with ASTM D5885 was 831 min.

To simulate the field scenario of a LLW disposal facility, a radioactive synthetic leachate (RSL) was created that is representative of field leachate at LLW disposal facilities, as identified by analysis of data

from sites operated by the US Department of Energy [3]. Mean concentrations from Tian [3] were used for all chemical components, except for the radionuclides, which had concentrations near the upper bound reported by Tian [3] to represent a worst case. Composition of the synthetic leachate is summarized in Table 1.

Table 1. Composition of radioactive synthetic leachate (RSL).

Inorganic Components (mmol/L)			
Ca	4	As	0.001
Mg	6	Ba	0.002
Na	7	Cu	0.0002
K	0.7	Fe	0.04
Sulfate	7.5	Li	0.02
Cl	8	Mn	0.01
Nitrate/Nitrite	1.5	Ni	0.0003
Alkalinity	3.5	Sr	0.02
Al	0.03	Zn	0.0005
Radionuclides		Other Chemical Characteristics	
U-238 (µg/L)	1500	TOC	5 mg/L surfactant and 3 mg/L acetic acid
H-3 (Bq/L)	4440	ORP (mV)	120
Tc-99 (Bq/L)	29.6	pH	7.2

Note: H_2SO_4 used to adjust pH ≈ 7.2, Na_2S used to adjust oxidation reduction potential (ORP) to ≈ 120 mV, TOC = total organic carbon.

Immersion Test
Coupons of HDPE GM were immersed in three different liquids: RSL, non-radioactive synthetic leachate (NSL), and deionized water (DI) water. NSL had the same chemical composition as RSL, but without the radionuclides. DI water was used as a control. Insulated stainless steel tanks equipped with heaters and mixers were used for immersion [3]. Sealed plastic boxes (150 mm × 150 mm × 150 mm) filled with synthetic leachate were placed in stainless steel tanks (380 mm × 380 mm × 840 mm) filled with DI water. The plastic boxes were sealed with lids and a rubber gasket to prevent evaporation and to minimize the diffusion of oxygen into the liquid. Exposure temperatures were set at 25, 50, 70, and 90 °C.

Oxidation Induction Time (OIT)
Oxidation induction time (OIT) was measured by differential scanning calorimetry (DSC). Std-OIT testing was conducted in accordance with ASTM D3895 and HP-OIT testing was conducted in accordance with ASTM D5885. Std-OIT was measured at the Soft Material Laboratory at the University of Wisconsin-Madison using a TA Instruments Q100 DSC. HP-OIT testing was conducted by TRI Environmental (Austin, TX, USA). The HP-OIT test is similar to the Std-OIT test, except that higher gas pressure (3500 kPa) and lower temperature (150 °C) are applied during the test.

The HP-OIT increased during the first month of aging, and then decreased (Fig. 2). The mechanism behind the unexpected increase in HP-OIT is not clear. However, when this initial point (~ 200 min in Std-OIT) is ignored, a linear relationship exists between the Std-OIT and HP-OIT. Hsuan and Koerner [6], Sangam and Rowe [7], and Gulec at al. [10] report similar linear relationships, which indicate that the high temperature in the Std-OIT test does not destroy or mask the antioxidants. Therefore, hindered amines were likely not added to the HDPE GM that was tested, and the antioxidant package used in the GM likely was phosphite- and/or phenol-based.
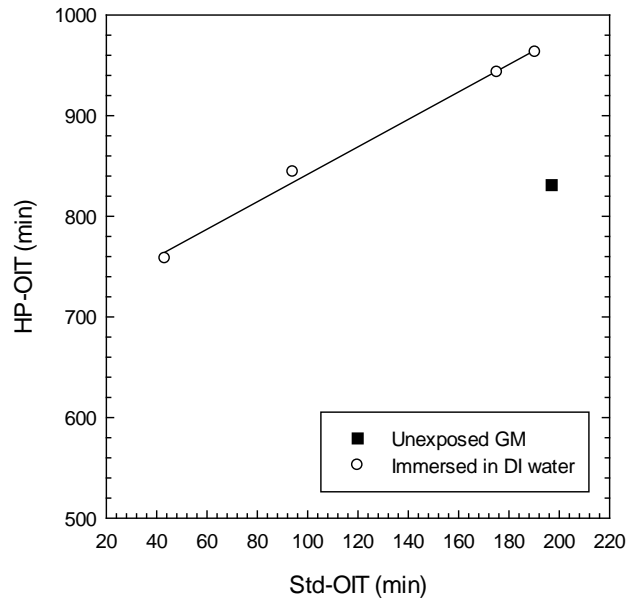
Fig. 2. Std-OIT vs. HP-OIT for HDPE GM specimens immersed in DI water. Specimen from right to left correspond to 1 mo at 50 °C, 1 mo at 70 °C, 2 mo at 90 °C, and 6 mo at 90 °C). Solid symbol is initial condition for unexposed GM.

RESULTS AND DISCUSSION

Antioxidant Depletion

The Std-OIT of the GM exposed to the RSL at 25, 50, 70, and 90 °C is shown in Fig. 3 (henceforth, "OIT" used in lieu of "Std-OIT" for conciseness). OIT decreases with immersion time and at a higher rate when exposed to high temperature. Similar results have been reported by others for other liquids [6, 7, 10, 14, 15]. The OIT decreased to approximately 10~13 min in RSL at 90 °C (Fig. 3a) and then leveled off. Similar behavior was observed for NSL and DI water at 90 °C (Fig. 4). Rowe at al. [15] define this leveling off as the residual OIT and indicate that the antioxidants remaining in the GM are no longer effective in preventing oxidation once the residual condition has been met.

Antioxidants depletion was assumed to follow a three-parameter first-order model [15]:

$$OIT_t = OIT_r + OIT_0 \exp(-st) \qquad (1)$$

where OIT_t = OIT at time t, OIT_0 = initial OIT, OIT_r = residual OIT, s = antioxidant depletion rate, and t = time.

Fits of Eq. 1 to the OIT data are shown in Fig. 3. The residual OIT (12 min) was determined by a simultaneous least-squares fit of all of the data for HDPE GM specimens exposed to RSL at 25, 50, 70, and 90 °C. The slope of linear regression in Fig. 3 represents the antioxidant depletion rate at each temperature, as shown in Fig. 3b. Antioxidant depletion rates for the three-parameter model for RSL, NSL, and DI water are in Table 2.

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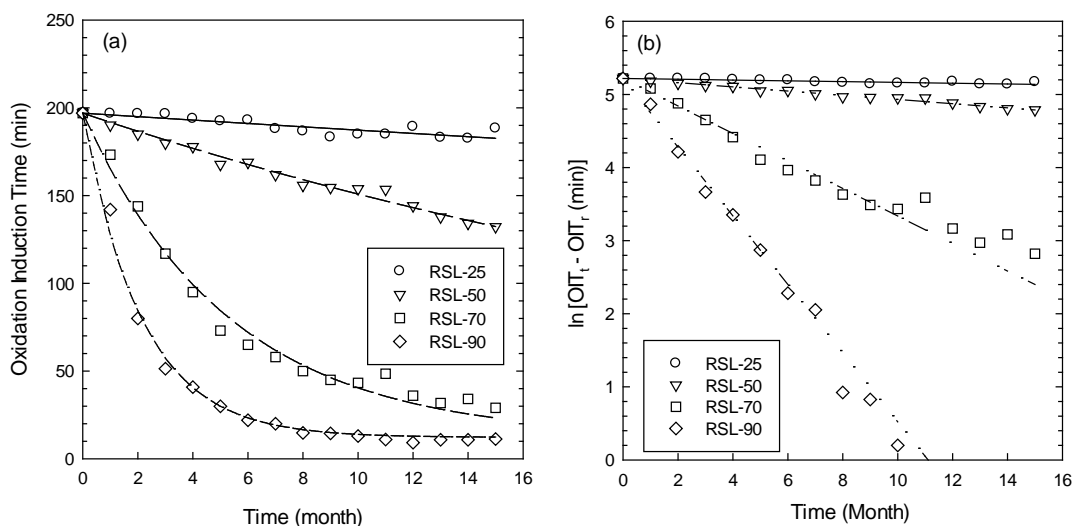
Fig. 3. OIT data for HDPE GM immersed in RSL as a function of aging time at 25, 50, 70, and 90 °C along with fits of Eq. 1.
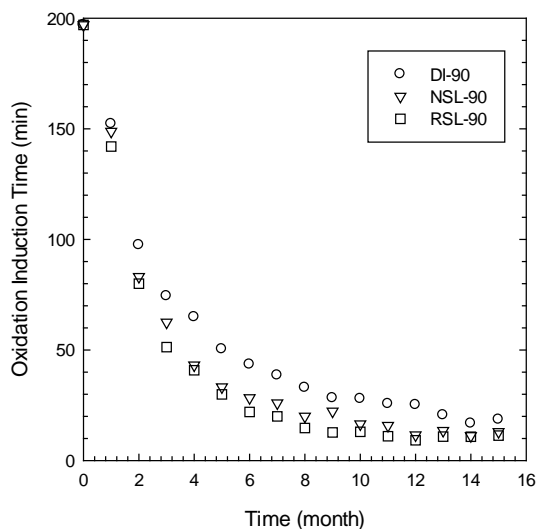
Fig. 4. Std-OIT depletion for GM exposed to DI water, NSL, and RSL.

The depletion rate for RSL at 90 °C is 0.46 month^{-1}, which is 2.5 times higher than that at 70 °C (0.18 month^{-1}), 16 times higher than that at 50 °C (0.028 month^{-1}), and 87 times higher than that at 25 °C (0.0053 month^{-1}). The fastest depletion occurs in RSL, followed by NSL and DI water (Table 2). At 90 °C, the antioxidant depletion rate in RSL (0.45 month^{-1}) is 1.04 times faster compared to the rate in NSL (0.44 month^{-1}), and 1.35 times faster compared to the depletion rate in DI water (0.33 month^{-1}).

The higher depletion rate for the GM immersed in NSL or RSL relative to the rate for DI water is attributed to the metals and surfactants in the leachate [10, 15]. Rowe and Rimal [8] indicate that surfactants can increase the wetting ability of the GM, resulting in more rapid loss of antioxidants via diffusion into the leachate. Moreover, Osawa and Ishizuka [4] indicate that the presence of transition

metals (e.g., Co, Mn, Cu, Al, Fe, and Mg) can break down hydroperoxides via redox reactions and create additional free radicals. The depletion rate increases because antioxidants are consumed by reaction with free radicals.

Table 2. Antioxidant depletion rates in DI water, NSL, and RSL.

Temperature (°C)	Antioxidant Depletion Rate [ln(min)/mon]		
	DI	NSL	RSL
25	0.0025	0.0049	0.0053
50	0.024	0.028	0.028
70	0.13	0.17	0.18
90	0.33	0.44	0.46

The modest difference between the depletion rate in RSL and NSL (Table 2) suggests that radiation in the RSL had limited or no effect on antioxidant depletion of HDPE GM. Two hypotheses can potentially explain the negligible radiation effect: (1) the concentration of radionuclides is so low that the radiation is negligible, or (2) the alpha and beta radiation emitted from U and ^{99}Tc in RSL does penetrate the overall thickness of GM, resulting in radiation effects limit to the surface. These hypotheses are being evaluated in a separate study.

Lifetime Prediction

An Arrhenius model was used to extrapolate the antioxidant depletion rates obtained at elevated temperatures to temperature expected *in situ*. The Arrhenius equation is:

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

where s is the depletion rate, A is a constant, E_a is the activation energy, R is the universal gas constant, and T is absolute temperature (°K).

Arrhenius graphs [ln(s) vs. 1/T] for the GM immersed in RSL, NSL, and DI water are shown in Fig. 5. The data in Fig. 5a for water immersion are consistent with the data from [9] and [10] after taking into account the difference in antioxidant packages and thickness of the HDPE GM. Activation energies calculated from the data in Fig. 5b using Eq. 2 and the depletion rates given in Table 2 are summarized in Table 3. The activation energy is deduced from the slopes of the Arrhenius graphs obtained by a least-squares fit to the data (shown in Fig. 5b).

The antioxidant depletion rate at different temperatures can be determined using the Arrhenius equation. The time to antioxidant depletion at site-specific temperatures is then computed using:

$$t = [\ln (OIT_0 - OIT_r)]/s \qquad (3)$$

Antioxidant depletion times computed with Eq. 3 are shown in Fig. 6 as a function of temperature for RSL, NSL and DI water. At a field temperature of 15 °C, which is typical of liner temperatures at LLW facilities operated by DOE [3], the antioxidant depletion time for 2-mm HDPE GM exposed to RSL is 217 yr. When the correction factor to represent one-sided depletion that occurs in a composite liner is applied (3.0) as suggested by [15], the field antioxidant depletion time for RSL is 650 yr (Fig. 6).
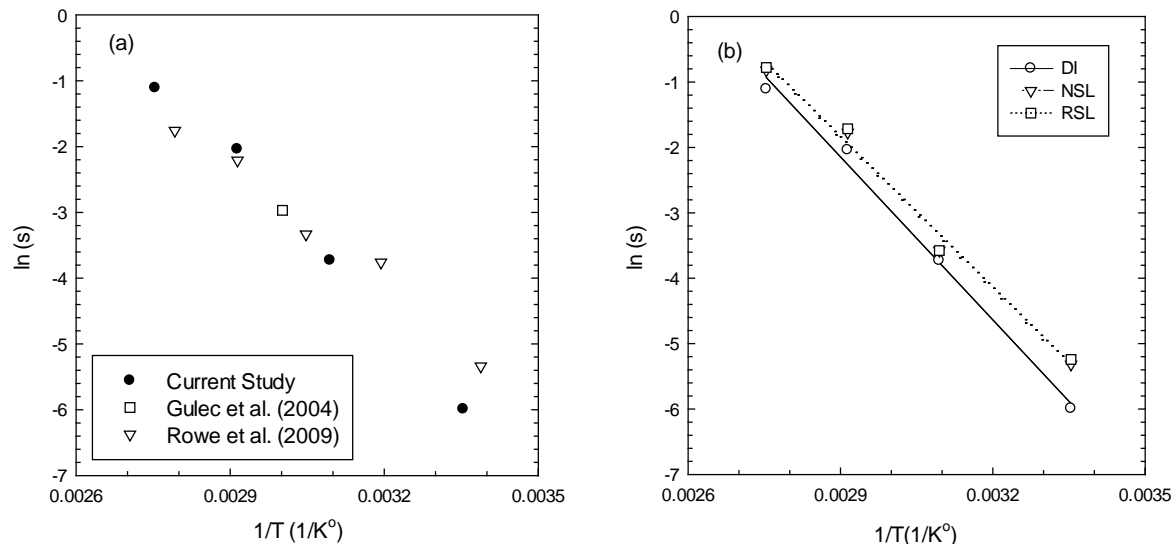
Fig. 5. Arrhenius plots for antioxidant depletion: (a) DI water (current and other studies), (b) DI water, NSL, and RSL.

Table 3. Arrhenius equation and activation energies from Fig. 5.

Group	Arrhenius Equation	R^2	Activation Energy (kJ/mol)
RSL	$\ln(s) = 20.40 - 7669 / K$	0.99	63.7
NSL	$\ln(s) = 20.46 - 7703 / K$	0.99	64.0
DI	$\ln(s) = 21.56 - 8299 / K$	0.99	68.9

SUMMARY AND CONCLUSIONS

This paper has described immersion tests conducted to evaluate antioxidant depletion in a high-density polyethylene (HDPE) geomembrane (GM) exposed to radioactive synthetic leachate (RSL), non-radioactive synthetic leachate (NSL), and DI water. NSL had the same chemical composition as RSL, but radionuclides were excluded.

Antioxidant depletion increased with immersion time and at a higher rate when exposed to higher temperature. Antioxidant depletion rates in radioactive synthetic leachate were 0.0053, 0.028, 0.18, and 0.46 month^{-1} at 25 50, 70, and 90°C.. Slightly lower rates were obtained with NSL and DI water. Additional study is being conducted to understand why the radionuclides in RSL did not have a significant effect on depletion rate and to investigate the effect of radiation on the antioxidant depletion of HDPE GMs in LLW disposal facilities.

Arrhenius modeling was used to extrapolate the laboratory immersion data at elevated temperatures to a 15 °C, which is a typical temperature for liner in a DOE low-level radioactive waste (LLW) disposal facility. The predicted time to antioxidant depletion based on the immersion test is 217 yr. When a correction factor of 3 is applied to account for one-side exposure in a composite liner, the predicted antioxidant depletion time is 650 yr. The actual service life will be longer than 650 yr because Stages II and III must occur after antioxidant depletion (Stage I) before the engineering properties of the geomembrane are affected adversely.
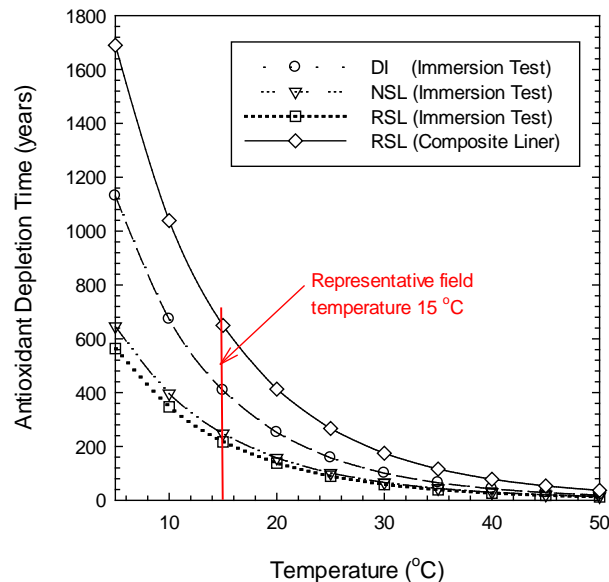
Fig. 6. Predicted antioxidant depletion time as a function of temperature and immersion liquid.

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