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Radiation dose and antioxidant depletion in a HDPE geomembrane

Kuo Tian[a,*], Craig H. Benson[b], Youming Yang[c], James M. Tinjum[d]

[a] Sid and Reva Dewberry Department of Civil and Environmental Engineering, George Mason University, Fairfax, VA 22030, USA
[b] School of Engineering, University of Virginia, Charlottesville, VA 22904, USA
[c] Department of Radiation Oncology, University of California, Los Angeles, CA 90095, USA
[d] Department of Engineering Professional Development, University of Wisconsin-Madison, Madison, WI 53706, USA

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ABSTRACT

The impact of α and β radiation on antioxidant depletion in smooth high-density polyethylene (HDPE) geomembranes (GMs) is described. Smooth HDPE GMs having different thickness (0.04-mm, 0.1-mm, 0.2-mm) were created by mechanically pulverizing sections of 2-mm-thick smooth HDPE GM and extruding the polymer at different thicknesses using a film blowing machine. The 2-mm-thick smooth HDPE GM was also used in the experiments. HDPE GM specimens were exposed to sealed sources of ^{241}Am and ^{99}Tc for 1–50 h to simulate the impact of α and β radiation from U and ^{99}Tc in low-level radioactive waste (LLW) leachate. Standard oxidative induction time (OIT) tests were conducted to determine antioxidant depletion. No change in OIT occurred in the 2-mm-thick HDPE GM after exposure to sealed sources of ^{241}Am and ^{99}Tc for 50 h. In much thinner GMs (e.g., 0.04 mm), however, significant antioxidant depletion occurred after exposure most likely due to penetration of α and β particles. Penetration depth of α and β particles and dose deposition in HDPE GMs were estimated with the GEometry ANd Tracking (GEANT4) program. Predictions from GEANT4 show that maximum dose deposition occurs at the surface of the HDPE GM and decreases with depth. A multilayer model is used to estimate antioxidant depletion in HDPE GMs for depth-dependent doses. These estimates suggest that radiation from LLW leachate has an insignificant effect on antioxidant depletion in HDPE GMs due to the low dose deposition (e.g., 2.42 Gy) expected over a 1000-yr service life, even if the level of activity in LLW leachate increases 10x to 100x the level typical of today.

1. Introduction

Composite liners consisting of a geomembrane (GM) overlying a geosynthetic clay liner or a compacted clay liner are used in low-level radioactive waste (LLW) and mixed waste (MW) disposal facilities to limit release of contaminants (Powell et al., 2011; Tian et al. 2016; 2017a). High-density polyethylene (HDPE) GMs are most common in LLW and MW facilities, consisting of polymer resin (> 95%), carbon black (2–3%), and antioxidant (0.5–1%) (Hsuan and Koerner, 1998). The longevity of HDPE GMs installed in LLW disposal facilities has particular importance in the US because LLW and MW disposal facilities are required to have a service life in excess of 1000 yr (DOE, 2001). Conducting a performance assessment (PA) requires a method to estimate the rate of degradation of HDPE GMs and their service life in LLW and MW facilities. Without a method to estimate life expectancy, most PAs for LLW and MW facilities in the US ignore the contribution of GMs to control flux from a disposal facility (Tian et al., 2017a).

Estimating life expectancy requires understanding the non-physical degradation of HDPE GMs in their environment. HDPE GMs undergo non-physical degradation in three stages: antioxidant depletion (Stage I), induction time to the onset of polymer degradation (Stage II), and polymer property degradation (Stage III) (Grassie and Scott, 1985; Hsuan and Koerner, 1998; Rowe and Sangam, 2002; Gulec et al., 2004; Rowe et al., 2009, 2013, Tian et al., 2014, 2015, 2017a). The duration of Stage I (antioxidant depletion) is controlled by the rate of depletion of antioxidants (Hsuan and Koerner, 1998; Sangam and Rowe, 2002; Rowe and Rimal, 2008; Rowe et al., 2008, 2009, 2010, 2013, Tian et al., 2014, 2017a).

Previous studies have demonstrated that leachate composition affects the rate of antioxidant depletion in HDPE GMs (Osawa and Ishizuka, 1973; Rowe and Sangam, 2002; Gulec et al., 2004; Rowe et al., 2009, 2013, Tian et al., 2014, 2017a). Gulec et al. (2004) report that metals in acidic mine drainage (AMD) act as catalysts that accelerate decomposition of hydroperoxides, resulting in generation of free radicals that consume antioxidants. Rowe et al. (2008) indicate that surfactants in municipal solid waste (MSW) leachate accelerate the diffusive loss of antioxidants by increasing partitioning between the GM and surrounding leachate. Tian et al. (2017a) indicate that LLW

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[*] Corresponding author.
E-mail addresses: ktian@gmu.edu (K. Tian), chbenson@virginia.edu (C.H. Benson), youmingyang@mednet.ucla.edu (Y. Yang), jmtinjum@wisc.edu (J.M. Tinjum).

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leachates can promote radiative oxidation that consumes antioxidant if the dose is sufficient.

LLW leachate consists of inorganic macrocomponents (e.g. Ca, Mg, Cl, SO_4^{2-}), trace heavy metals (e.g., Fe, Cu), radionuclides (e.g., uranium, ^{226}Ra, and ^{99}Tc), and organic compounds (Tian, 2012; Tian et al., 2014, 2017a, b, Abdelaal and Rowe, 2015). Tian et al. (2017b) characterized the composition of LLW leachate based on field data collected from four LLW disposal facilities operated by the US Department of Energy for environmental restoration activities. U (6.4–3060 μg/L), ^{99}Tc (0.3–28 Bq/L), and ^{3}H (0.6–4629 Bq/L) were reported as the primary radionuclides in the leachates having concentration above the detection limit (Tian et al., 2017b). Abdelaal and Rowe (2015) report that leachates in six LLW disposal facilities in Canada contained ^{226}Ra (3.9–50 Bq/L) and ^{238}U (6–1500 μg/L). These radionuclides emit α (e.g., U and ^{226}Ra) and β (^{99}Tc and ^{3}H) particles, which can cause radiation-induced oxidation in HDPE GMs and accelerate degradation (Phillips, 1988; Costa et al., 2008; Tian et al., 2017a).

Tian et al. (2017a) conducted accelerated aging experiments to predict antioxidant depletion in a 2-mm-thick HDPE GM exposed to LLW leachate. A radioactive synthetic leachate (RSL) was created to represent leachates at disposal facilities operated by the US Department of Energy (Tian et al., 2017b). Comparative tests with non-radioactive synthetic leachate (NSL), which is chemically the same as RSL but devoid of radionuclides, showed only 7% difference in antioxidant depletion rates, suggesting that the effect of radiation from LLW leachate is limited.

The objective of this study was to estimate antioxidant depletion associated with the dose that would be deposited on a HDPE GM over a 1000 yr period in response to radiation emitted by radionuclides in typical LLW leachates, as well as leachates with higher radioactivity. Various total doses and dose rates were applied to HDPE GM specimens by irradiation with sealed sources of ^{99}Tc and ^{241}Am, which emit α and β particles that are present in LLW leachate and could penetrate a HDPE GM in a LLW facility. Antioxidant depletion after irradiation was evaluated by measuring the oxidation induction time (OIT) in HDPE specimens after exposure using differential scanning calorimetry (DSC). Radionuclide decay and dose deposition in the HDPE specimens were estimated using the GEometry ANd Tracking (GEANT4) program. Antioxidant depletion data and predictions from the GEANT4 simulation were used as inputs to a multilayer analytical model created to estimate antioxidant depletion as a function of dose deposition for different scenarios.

2. Background

2.1. Effect of radiation on degradation of HDPE GM

Polymer chains (RH) can dissociate into a free radical polymer chain (R•) and hydrogen (H•) when exposed to ionizing radiation having energy exceeding the energy associated with the covalent bond in the polymer chain (Phillips, 1988; Peacock, 2000):

$$\mathrm{RH} + \alpha, \beta, \gamma \rightarrow \mathrm{R}\bullet + \mathrm{H}\bullet \tag{1}$$

where α, β, and γ are sources of ionizing radiation. The R• generated by ionizing radiation can react with oxygen (O_2) to form ROO•:

$$\mathrm{R}\bullet + \mathrm{O_2} \rightarrow \mathrm{ROO}\bullet \tag{2}$$

and ROO• can react with RH to form ROOH and more R• (Eq. (3)):

$$\mathrm{ROO}\bullet + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}\bullet \tag{3}$$

This sequence of reactions is defined as radiation-induced oxidation (Mason et al., 1993; Peacock, 2000; Costa et al., 2008; Tian et al., 2017b).

Polymer degradation is affected by the type and energy of radiation (Phillips, 1988; Czvikovszky, 2004; Turner, 2007). Charged α particles penetrate polymers on the order of microns, charged β particles on the order of millimeters, and uncharged particles (e.g., neutrons and γ rays) can penetrate meters (Turner, 2007). Therefore, α and β particles typically affect the surface of a GM, whereas γ rays can affect the entire thickness of a GM (Tian et al., 2017a). A penetrating particle causes damage when the ionizing radiation associated with the particle has sufficient energy to exceed the carbon-carbon bond energy. The α particles emitted from U (e.g., peak energy from ^{238}U = 4.27 MeV) and ^{226}Ra (e.g., peak energy = 4.87 MeV) and β particles from ^{99}Tc (e.g., peak energy: 294 keV) are the predominant sources of radiation from LLW (Abdelaal and Rowe, 2015; Tian et al., 2017b). Ionizing radiation associated with α and β particles has sufficient energy to exceed the typical bond energy of carbon-carbon bonds in polymers (5–10 eV, Czvikovszky, 2004). Thus, α and β particles from LLW leachate can break bonds in HDPE GMs, and promote antioxidant depletion.

2.2. Effect of radiation on antioxidant depletion

Mason et al. (1993) examined the effect of γ radiation on antioxidant depletion in ethylene propylene rubber (EPR) and cross-linked polyethylene (XLPE) cable insulation used in nuclear power plants. The EPR and XLPE were prepared with different antioxidant packages and concentrations. Antioxidant depletion was monitored using standard oxidative induction time (OIT) tests according to ASTM D3895. Mason et al. (1993) report that OIT is exponentially related to antioxidant concentration initially added to the polymer and decreases exponentially as a function of exposure time at a constant irradiation dose. Mason et al. (1993) report that the concentrations of R• and ROO• are time varying and depend on the radiation dose rate (D_R). To interrupt oxidative reactions, antioxidants (AO) react with ROO• to form stable products:

$$\mathrm{ROO}\bullet + \mathrm{AO} \rightarrow \text{Stable Products} \tag{4}$$

Mason et al. (1993) indicate that consumption rate of antioxidant is related linearly to D_R:

$$\frac{d[\mathrm{AO}]}{dt} = -\mathrm{C}D_{\mathrm{R}} \tag{5}$$

where [AO] is the antioxidant concentration and C is a constant depending on properties of polymer.

3. Materials and methods

3.1. Geomembrane

A commercially available 2-mm-thick smooth HDPE GM representative of GMs used in LLW disposal facilities as well as thinner simulated GMs were used in this study. Properties of the 2-mm-thick smooth HDPE GM are in Table 1. The simulated GMs were created by mechanically pulverizing sections of 2-mm-thick smooth HDPE GM and extruding the polymer at different thicknesses (e.g., 0.04, 0.1, and 0.2 mm) using a film blowing machine (Dayton Model No. 6536, Dayton Manufacturing Company, Dayton, OH). Pulverizing and extruding the geomembrane had minor effect on the antioxidant concentration and the crystallinity of the polymer, as described

Table 1
Properties of HDPE GM used in Sealed Source Experiments.

Property	ASTM Method	Average
Density (kg/m^3)	D1505	946
Average Thickness (mm)	D5199	2.0
Carbon black content (%)	D4218	2.62
Standard Oxidation Induction Time (min)	D3895	197
High-Pressure Oxidation Induction Time (min)	D5885	831
Crystallinity (%)	E794	43.4
Melt Flow Index (g/10 min)	D1238	0.08