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RADIATION DOSE AND ANTIOXIDANT DEPLETION IN A HDPE GEOMEMBRANE

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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.

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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 et al. 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 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.

BACKGROUND

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 1998, Peacock 2000):

$$RH + \alpha,\beta,\gamma \rightarrow R\bullet + H\bullet \quad (1)$$

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•:

$$R\bullet + O_2 \rightarrow ROO\bullet \quad (2)$$

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

$$ROO\bullet + RH \rightarrow ROOH + R\bullet \quad (3)$$

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.

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:

$$ROO\bullet + AO \rightarrow \text{Stable Products} \quad (4)$$

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

$$\frac{d[AO]}{dt} = -CD_R \quad (5)$$

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

MATERIALS AND METHODS

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 subsequently.

Exposure Experiments

The GMs were exposed to α particles from a sealed source of ^{241}Am and β particles from a sealed source of ^{99}Tc (Eckert and Ziegler, Valencia, California) (Fig. 1a, b). ^{241}Am was used as a surrogate for U because of the similarity in their energy spectra. The sealed ^{241}Am source had a nominal activity of 1.85 MBq with an active diameter of 9.5 mm and a peak energy of 4.7 MeV. The radiation foil consisted of ^{241}Am in a gold matrix with aluminum backing. The sealed ^{99}Tc source had a nominal activity of 32.3 kBq with an active diameter of 16 mm. The ^{99}Tc in the source was deposited onto a plastic film covered with a 5-μm titanium foil.

Square GM specimens with dimensions of 21 mm x 21 mm were placed directly beneath a sealed source (Fig. 1b) and exposed for 1, 5, 10, 20, or 50 hr at room temperature of 22 ºC. After exposure, a sample was cut from the center of the exposure area for measurement of OIT. GM specimens of different thickness (0.04, 0.1, 0.2, and 2-mm-thick) were exposed to evaluate depth of penetration relative to thickness of the GM.

Oxidative Induction Time (OIT)

Antioxidant depletion in the HDPE GM was characterized by OIT tests conducted in accordance with ASTM D3895 using a Q100 differential scanning calorimeter (DSC) (TA Instruments, Wood Dale, IL). OIT is proportional to the amount of antioxidant remaining in the HDPE GM; i.e., higher OIT indicates that the GM has a greater concentration of antioxidants. OIT was measured on specimens of HDPE GM before and after irradiation.

The initial OIT was 197 $\pm$ 5 min for the 2-mm-thick HDPE GM. For the thinner specimens, the initial OIT was 185 $\pm$ 1.2 min (0.04 mm), 189 $\pm$ 1.6 min (0.1 mm), and 194 $\pm$ 0.8 min (0.2 mm). The similarity of the OIT data for conditions prior to radiation suggest that the grinding, heating, and extrusion process had minor effect on antioxidant concentration, but the effect was greater for thinner GM specimens due to their larger ratio of surface area to thickness.

Crystallinity

Crystallinity of the HDPE GM was measured using the DSC following the procedure in ASTM E794. HDPE GM specimens with mass between 10 and 15 mg were sealed in an aluminum pan, placed in the DSC, and then heated to 200 °C at a rate of 10 °C/min under a nitrogen atmosphere. The heat of fusion was calculated by the area above the melting endotherm. Crystallinity was computed as the ratio between the measured heat of fusion and the heat of fusion of 100% crystalline HDPE (i.e., 290 J/g) as defined in Flory and Vrij (1963).

The initial crystallinity was 43.4 ± 0.6% for the 2-mm-thick HDPE GM. For the thinner specimens manufactured for the study, the crystallinity was 40.5 ± 1.1 % for 0.04-mm-thick specimen, 42.1 ± 0.2 % for 0.1-mm-thick specimen, and 43.0 ± 0.1 % for 0.2-mm-thick specimen. Thus, the grinding, heating, and extrusion process had a minor effect on crystallinity.

Dose Deposition and Penetration Depth

Dose deposition and penetration depth of α and β particles in the GM specimens during the sealed source experiments were estimated with the GEANT4 software program (Agnostinelli et al. 2003). GEANT4 solves the linearized Boltzmann transport equation for particles passing though user-specified geometries, and is widely used in nuclear, high-energy, and medical physics (Agnostinelli et al. 2003). Energetic particles are transported according to physical interactions stochastically sampled from probability distributions, with the resulting energy deposition recorded in a voxelized grid. Particles are tracked until all of their kinetic energy is deposited or they leave the geometry of interest (e.g., leave a GM specimen). The standard physics package in GEANT4 supports simulation of radioactive isotopes, with full transport and decay of all subsequent daughter products (Agnostinelli et al. 2003).

The sealed sources were simulated to be in direct contact with the GM specimens and surrounded on all other sides by air (Fig. 1). The GM was simulated as CH_2 with a uniform density of 0.942 Mg/m^3. The change of density between amorphous and crystallinity region of GM was assumed to be negligible and not included in the model. The GM was represented with a 41 x 41 x 1000 voxel grid corresponding to a voxel size of 0.5 mm × 0.5 mm × 0.002 mm. The geometry and activity provided by the manufacturer of each sealed source was used as input to GEANT4. Peak energies predicted by GEANT4 for α and β particles were identical to those published by manufacturer of the sealed sources, indicating that the GEANT4 simulations represented the transport of α and β particles from the sealed sources reliably. Each GEANT4 model simulated

10,000,000 single decay events and integrated the total energy deposition. Dose per decay was computed by normalizing total energy deposition profile.

RESULTS AND DISCUSSION

Antioxidant Depletion for Sealed Source Experiments

OIT as a function of exposure time for the HDPE GM is shown in Fig. 2. OIT decreased faster for the thinner specimens. For example, OIT of the 0.1-mm-thick GM decreased from 189 min to 177 min after exposure to ^{241}Am for 50 h (Fig. 2a), whereas OIT of the 0.2-mm-thick specimen decreased from 194 min to 189 min with the same exposure. Exposure to β radiation had a similar effect (Fig. 2b), except the depletion rate was greater for α exposure (^{241}Am) relative to β exposure (^{99}Tc) due to the lower activity of the ^{99}Tc sealed source. For example, OIT of the 0.04-mm-thick GM decreased from 185 to 174 min after exposure to ^{99}Tc for 50 h (Fig. 2b), whereas exposure to ^{241}Am for 50 h resulted in OIT decreasing from 185 to 158 min for 0.04-mm-thick GM (Fig. 2a).

Depletion of antioxidants occurs when α and β particles break C-C or C-H bonds (Phillips 1988, Whyatt and Farnsworth 1990, Mason et al. 1993, Costa et al. 2008). The antioxidants protect the HDPE GM from degradation by reacting with free radicals that form when the C-C or C-H bonds are broken (Hsuan and Koerner 1998, Gulec et al. 2004). Depletion of OIT diminishes as the thickness of the HDPE GM increases (e.g., 0.2-mm-thick and 2-mm-thick), indicating that the α and β particles have less impact as the depth of penetration diminishes relative to the thickness of the GM. Areas close to the source are expected to have greater antioxidant depletion, and those farther away less depletion.

GEANT4 was used to simulate dose deposition and particle penetration for the sealed source experiments as a function of depth in the GM. Predictions of dose deposition per decay from the GEANT4 simulation at the center of exposed area of the HDPE GM are shown in Fig. 3

for ^{241}Am (α, Fig. 3a) and ^{99}Tc (β, Fig. 3b). The peak dose at the surface of the GM was predicted as 2.2 x 10^{-7} Gy per decay from ^{241}Am and 5.2 x 10^{-10} Gy per decay from ^{99}Tc. For both sources, the dose decreases with depth and becomes negligible at 28 μm (α, Fig. 3a) or 0.48 mm (β, Fig. 3b). Exposure time does not affect the maximum penetration depth, which is controlled by the peak energy of the particle (approximately 4.7 MeV for α particle, 294 keV for β particle) provided that the density and composition of the exposed material does not change significantly.

These findings suggest that the HDPE GM is not affected by α particles from the ^{241}Am at distances greater than 28 μm from the sealed source. For β particles from the ^{99}Tc, the distance is 0.48 mm. Consequently, the impact of radiation on the overall GM diminishes as the GM becomes thicker. Radiation from α particles affects approximately 70% of the 0.04-mm-thick HDPE GM specimen, 28% of the 0.1-mm-thick specimen, 14% of the 0.2-mm-thick specimen, and only 1.4% of the 2-mm-thick specimen. Similarly, β radiation affects 100% of the 0.04-mm-, 0.1-mm-, and 0.2-mm-thick HDPE GMs, and only 24% of the 2-mm-thick specimen.

Predicting Antioxidant Depletion

The OIT measurement reflects the aggregate impact of antioxidants in all areas of the GM, and therefore represents an average reduction in antioxidant concentration. In reality, antioxidant depletion is depth dependent, with decreasing depletion as the distance from the radiation source increases. Measuring the variation in OIT within the thin specimens was not possible with the resources available. Thus, to estimate the depth dependence, a multilayer model was created where the HDPE GM is divided into a series of layers of equal thickness, with a uniform dose applied to each layer (Fig. 4). Those layers within the depth of penetration of α or β particles have non-zero dose and are defined as comprising the “impacted zone” (Fig. 4). Layers outside the depth of penetration have zero dose and comprise the “unimpacted zone.” The impacted zone is thicker for β radiation (Fig. 3b) than α radiation (Fig. 3a) because β particles penetrate deeper in the GM (Fig. 3b) than α particles.

Antioxidant concentration in the i^{th} layer with dose deposition ($D_{i(z,t)}$) is assumed to follow the relationship in Mason et al. (1993):

$$[AO]_i = [AO]_0 - kD_{i(z,t)} \quad (6)$$

where $[AO]_0$ is the initial antioxidant concentration (before irradiation), $[AO]_i$ is the antioxidant concentration after receiving $D_{i(z,t)}$, and k is a depletion coefficient that depends on the antioxidant package and type of radiation. The dose $D_{i(z,t)}$ is a function of depth from the surface (z) and exposure time (t). By mass conservation, the average antioxidant concentration in the GM after exposure, $[AO]_{ave}$, is the arithmetic mean of $[AO]_i$ in each layer:

$$[AO]_{ave} = \frac{\sum_{i}^{n}([AO]_0 - kD_{i(z,t)})}{n} \quad (7)$$

where n represents the number of layers in the HDPE specimen. Mason et al. (1993) indicate that OIT is related exponentially to antioxidant concentration:

$$OIT_{[AO]} = \delta e^{\theta[AO]} \quad (8)$$

where $OIT_{[AO]}$ is the OIT with [AO] in the specimen, δ is a material-dependent constant, and θ is an antioxidant concentration constant that is unique to each antioxidant package. Combining Eqs. 7 and 8 yields the average OIT $\{OIT_{[AO]ave}\}$ of the GM as a function of the initial OIT $\{OIT_{[AO]o}\}$ corresponding to the initial AO concentration $\{[AO]_0\}$ and the depth dependent distribution of dose $[D_{i(z,t)}]$:

$$OIT_{[AO]_{ave}} = OIT_{[AO]_0} e^{-k^*\sum_{i}^{n}\frac{D_{i(z,t)}}{n}} \quad (9)$$

where k* (=θk) is the effective radiation depletion coefficient and represents the original antioxidant concentration and the antioxidant package [units for k* are in ln(min)/Gy]. The parameter δ in Eq. 8 is implicit in $OIT_{[AO]o}$ in Eq. 9. Linearization of Eq. 9 yields:

271 $$\ln(OIT_{[AO]_{ave}}) = \ln(OIT_{[AO]_0}) - k^*(\sum_{i}^{n} \frac{D_{i(z,t)}}{n}) \quad (10)$$

272 Eq. 10 was fit to the OIT data from the sealed source experiments using simultaneous
273 linear least-squares regression with n = 1000. The doses [$D_{i(z,t)}$] in Eq. 10 used in each fit were
274 computed as the product of the normalized dose-per-decay (Fig. 3) and the exposure time-
275 integrated activity of each sealed source. These fits are shown in Fig. 5. A step-by-step example
276 of the calculation procedure is in the Appendix. The fit of Eq. 10 is better for thicker specimens (>
277 0.1 mm), which may be due to uncertainty in the thickness of the thinner GMs. The caliper used
278 to measure GM thickness had a precision of 0.02 mm, leading to the greater uncertainty in
279 thickness for the specimen as the thickness decreased.

280 Eq. 10 was checked by estimating OIT of the 0.1, 0.2, and 2.0-mm-thick HDPE specimens
281 for 50 hr of exposure to ^{241}Am using k* obtained by fitting Eq. 10 only to the OIT data for the 0.04-
282 mm-thick specimen. The dose deposition profile from GEANT4 for a 0.04-mm-thick specimen was
283 used as $D_{i(z,t)}$ when fitting Eq. 10 to the OIT data. For the estimates of OIT, the dose deposition
284 from GEANT4 used in Eq. 10 corresponded to 0.1, 0.2, and 2.0-mm-thick HDPE specimens. As
285 shown in Fig. 6, good agreement exists between the estimated and measured OIT after 50 hr of
286 exposure, regardless of thickness, when parameterized using only the data from tests conducted
287 on 0.04-mm-thick specimens.

288 OIT estimated with the multilayer model as a function of depth is shown in Fig. 7 for 0.2-
289 mm-thick HDPE specimens exposed to α (Fig. 7a) and β (Fig. 7b) radiation for up to 50 h. For α
290 radiation, OIT depletion is largest at the surface of HDPE GM due to the high radiation dose at
291 the surface, and diminishes rapidly with depth until the maximum depth of penetration is reached
292 at 28 μm (depth of impacted zone, Figs. 3 and 4). Beyond this depth, no change in OIT is
293 estimated due to radiation, although other mechanisms could contribute to antioxidant depletion
294 in an actual application. For β radiation, the dose is greatest at the surface but spans the entire

thickness (Fig. 3). Consequently, antioxidant depletion is greatest at the surface, but extends throughout the entire thickness because of the greater penetration of β particles (Fig. 7b). As the exposure time increases, greater OIT depletion occurs in the impact zone for both α and β particles. The depth of the impact zone, however, remains constant at the maximum depth of penetration.

PRACTICAL IMPLICATIONS

Dose Expected in LLW Liner Application

GEANT4 was used to estimate doses that would be realized in the field for a composite liner overlain by LLW leachate. The conceptual model was similar to that used for interpreting the sealed-source experiments, and included three layers: a thin (10 mm) layer of leachate, a 2-mm-thick HDPE geomembrane, and a 100-mm-thick soil layer representing a geosynthetic clay liner over an attenuation layer (Fig. 8). The leachate was assumed to be water (density = 1.0 Mg/m^3), the GM was assumed to be CH_2 with a density of 0.942 Mg/m^3, and the soil layer was approximated as SiO_2 with a density of 1.8 Mg/m^3. Thickness of the leachate layer was chosen as 10 mm due to limited depth of penetration of α and β particles in water. The GM layer was represented to a 21 $\times$ 21 $\times$ 1000 voxel grid, with a voxel size of 10 mm $\times$ 10 mm $\times$ 0.002 mm.

Radioactive source particles were simulated with a uniform distribution within the leachate. The U concentration was assumed to be 1500 μg/L as reported in Tian et al. (2017b), with ^{234}U, ^{235}U, and ^{238}U in their natural abundance. The ^{99}Tc concentration was simulated to be 29.6 Bq/L as reported in Tian et al. (2017b). Total dose was computed as the product of the normalized dose-per-decay and the 1000 yr time-integrated activity of each isotope.

Dose profiles in the GM for ^{234}U, ^{235}U, ^{238}U, and ^{99}Tc as well as their combined dose for the 1000-yr service life are shown in Fig. 9. The peak dose is 2.42 Gy at the surface, with α-particles from U comprising the majority of the dose. ^{234}U contributes 1.21 Gy and ^{238}U contributes 1.15 Gy. ^{235}U and ^{99}Tc contribute the remaining 0.06 Gy. The rapid decrease in dose between 0.0

and 0.07 mm corresponds to the maximum penetration of α particles emitted from U (4.27–4.86 MeV) and its daughter products (e.g., 4.68 MeV for ^{230}Th, 4.60 for ^{226}Ra, and 7.68 MeV for ^{214}Po) in the full decay chain. The dose from β radiation emitted from ^{99}Tc reaches approximately 0.5 mm, but is much smaller due to the lower activity and peak energy of ^{99}Tc. The profiles of U also exhibit a small dose throughout the entire thickness due to β or γ radiation emitted from daughter isotopes. Some of daughter isotopes have a very long half-life (e.g., 75,380 yr for ^{230}Th).

Doses in an actual HDPE GM in a LLW containment system may be lower due to simplifying assumptions in the GEANT4 model. For example, nonwoven geotextiles are normally deployed on top of HDPE GMs as a protective layer, and leachate will be in the pores of a granular leachate collection system (LCS) on top of the GM. The geotextile and the LCS will shield the radiation, resulting in a lower dose to the GM. Consequently, the dose deposition predicted by the GEANT4 model probably is an overestimate for an actual liner configuration.

Antioxidant Depletion

OIT in the GM at 1000-yr was estimated as a function of depth using the multilayer model and the α and β dose profiles in Fig. 9. At 1000 yr, OIT at the surface of GM would decrease less than 0.01 min due to α radiation emitted from U (Fig. 10a) and less than 0.2 min due to β radiation emitted from ^{99}Tc (Fig. 10b). Given that the initial OIT of the HDPE GM is 197 min, the depletion of antioxidants due to α and β radiation from LLW leachate would be negligible over the 1000-yr service life, and is likely much smaller than depletion from other mechanisms (antioxidant leaching, conventional oxidation, oxidation catalyzed by metals) (Tian et al. 2014, 2017a). The actual OIT depletion due to radiation may be even lower due to the aforementioned simplifying assumptions in the model.

These computations were based on radionuclide concentrations in leachate in existing DOE on-site disposal facilities that employ waste acceptance criteria (WAC) to ensure adequately low doses to receptors. If these WAC were less stringent, however, the activity in the leachate

could increase, resulting in a higher dose and potentially greater antioxidant depletion. To evaluate this scenario, the dose was assumed to be 10x or 100x higher than the current equivalent dose over 1000 yr. The estimated impact of these higher doses on antioxidant depletion in the HDPE GM is also shown in Fig. 10.

The increase in α radiation results in a decrease in OIT < 0.5 min for a 100x higher dose, which is much smaller than the OIT depletion likely to occur due to other mechanisms (Tian et al. 2017a) over 1000 yr. Increasing the β dose by 100x higher leads to a larger (20 min) decrease of OIT at the surface of HDPE GM, which is approximately 10% of the initial OIT, but is still considerably smaller than the depletion of OIT expected by other mechanisms. Thus, less stringent WAC are unlikely to have a significant impact on antioxidant depletion of HDPE GMs in LLW disposal facilities. However, the combined impact of radiation and other degradation mechanisms (e.g., oxidation degradation, thermal degradation) will accelerate the rate of decomposition of HDPE GM beyond that shown in Fig. 10. The overall degradation cannot be predicted based on the impacts of radiation alone.

SUMMARY AND CONCLUSIONS

The effect of α and β radiation on antioxidant depletion was investigated for a high-density polyethylene (HDPE) geomembrane (GM) used for liners in low-level radioactive waste (LLW) disposal facilities. Specimens of HDPE GMs were exposed to sealed sources of ^{241}Am and ^{99}Tc for 1−50 h to simulate α and β radiation from LLW. OIT tests were conducted on the specimens after irradiation to examine antioxidant depletion. Dose deposition and depth of penetration of α and β particles in HDPE GMs were predicted using the GEANT4 software program, which is used to predict particle migration through matter in nuclear and medical physics. A multilayer analytical model was created to estimate antioxidant depletion in HDPE GMs as a function of dose deposition, and to estimate antioxidant depletion in a field scenario where a GM is used in a composite liner in a LLW disposal facility.

The following conclusions are drawn from this study:

- Antioxidant depletion in HDPE GMs increases with increasing exposure to α and β radiation, but is highly sensitive to the thickness of the GM. Larger increases in antioxidant depletion occur in thinner GMs. Radiation by α and β particles had negligible impact on antioxidant depletion in the 2-mm-thick HDPE GM used in this study.
- Estimates obtained with the GEANT4 program illustrate that α particles from a sealed source of ^{241}Am carrying 4.7 MeV penetrate approximately 28 μm into a 2-mm-thick HDPE GM, and β particles from ^{99}Tc carrying 294 keV penetrate approximately 0.48 mm. The shallow penetration estimated with GEANT4 is consistent with the sensitivity of antioxidant depletion to GM thickness measured in this study. The GEANT4 simulations showed that dose deposition of α and β radiation is highest at the surface, and drops rapidly with increasing depth into the GM (more rapidly for α relative to β).
- Estimates obtained with the GEANT4 program illustrate that α particles from U (e.g., penetration depth < 0.7 μm) and β particles from ^{99}Tc (e.g., penetration depth < 0.5 mm) in LLW leachate will predominantly affect only the surface of a typical 2-mm-thick HDPE GM. The total dose at the surface is on the order of 2.4 Gy over a 1000-yr period for typical LLW leachate, and diminishes more than an order of magnitude within 0.1 mm from the surface of the GM. Estimates of antioxidant depletion for these doses made using the multilayer analytical model indicate that OIT depletion due to α radiation from LLW leachate is likely to be less than 0.1 min (initial OIT = 197 min) over 1000 yr, and less than 1 min from β radiation. This suggests that radiation from LLW is unlikely to have a significant effect on the service life of GMs relative to other physical and chemical mechanisms.
- The multilayer model was used to evaluate how increasing doses due to less restrictive waste acceptance criteria might affect antioxidant depletion. Increasing the dose by 100x caused a

decrease in OIT from 197 min to 177 min over 1000 yr. While not insignificant, this loss of antioxidants is much less than anticipated due to other mechanisms over 1000 yr.

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APPENDIX

The following illustrates how the multilayer model is used to predict the impact of radiation on antioxidant depletion in an HDPE GM. The analysis consists of three steps.

Step 1: Obtain dose per decay in each sublayer of HDPE GM

For the multilayer model, a HDPE GM is discretized into n sublayers of equal thickness. For the estimates made in this study, n = 1000 and the total thickness of the GM is 2 mm corresponding to a sublayer thickness = 2 μm. The dose in each sublayer is assigned from the dose deposition curves predicted by GEANT4 for α or β radiation. The average dose per decay ($D_{i\text{-per decay}}$) in each sublayer is obtained from the dose deposition profile as shown in Fig. A1:

$$D_{i-\text{per decay}} = \frac{D_{i-\text{top}} + D_{i-\text{bot}}}{2} \quad \text{(A1)}$$

where $D_{i\text{-top}}$ is dose per decay at the top of the i^{th} layer, $D_{i\text{-bot}}$ is dose per decay at the bottom of the i^{th} layer, and $D_{i\text{-per decay}}$ is the dose per decay assigned to the i^{th} layer. For example, for the 6^{th} layer (depth = 0.010 to 0.012 mm), the dose in the HDPE GM at depth of 0.010 mm is 1.3×10^{-7} Gy and at 0.012 mm the dose is 9.4×10^{-8} Gy. Thus, the average dose deposition per decay in the 6^{th} layer is 1.12×10^{-7} Gy.

421

422 **Step 2: Calculate dose deposition in HDPE GM after exposure**

423 Step 1 yields the dose deposited per decay of the radiation source. Total dose deposition
424 in layer i of an HDPE GM [$D_{i(z,t)}$] over a period of time is the summation of these doses over time.
425 The total dose is computed as the product of the dose per decay at a given depth (z) (Fig. A1),
426 the source activity, and the exposure time (t).

427 $$D_{i(z,t)} = D_{i\text{-per decay}} \times \text{activity} \times \text{time} \quad \text{(A2)}$$

428 For example, the total dose deposited in the 6th layer after 1 hr of exposure can be calculated as:

429 $$D_{6(0.11mm,1hr)} = 1.12\times10^{-7}\,\frac{Gy}{decay}\times1.85\times10^{6}\,\frac{decay}{s}\times3600s = 746Gy$$

430

431 **Step 3: Determine radiation depletion coefficient**

432 The effective radiation depletion coefficient k* is obtained regressing Eq. 10 on OIT data from
433 sealed source experiments using the doses computed in Step 2 as follows:

434 $$\ln(OIT_t) = \ln(OIT_0) - \frac{k^*}{n}\sum_{i=1}^{n} D_{i(z,t)} \quad \text{(A3)}$$

435 In Eq. A3, OIT_t is the OIT measured on a specimen exposed for exposure time t in a sealed source
436 experiment, OIT_o is the initial OIT of the GM prior to irradiation, and $D_{i(z,t)}$ corresponds to the doses
437 in the sublayers of the specimen computed using the procedure in Step 2. An example is shown
438 in Fig. A2 for data from sealed source experiments conducted with ^{241}Am for 1, 5, 10, 20, and 50
439 hr on 0.2 mm-thick specimens with the OIT determined by DSC. Eq. A3 is regressed
440 simultaneously on data from sealed source experiments on specimens of various thickness (0.04,
441 0.1, 0.2, and 2 mm in this study) to obtain a single k* for the source, GM polymer, and antioxidant

442 package. From the regression shown in Fig. A2, $k^* = 7.12 \times 10^{-6}$ [units = ln(min)/Gy] for α radiation
443 for the dose from ^{241}Am in Gy and OIT in minutes.

444

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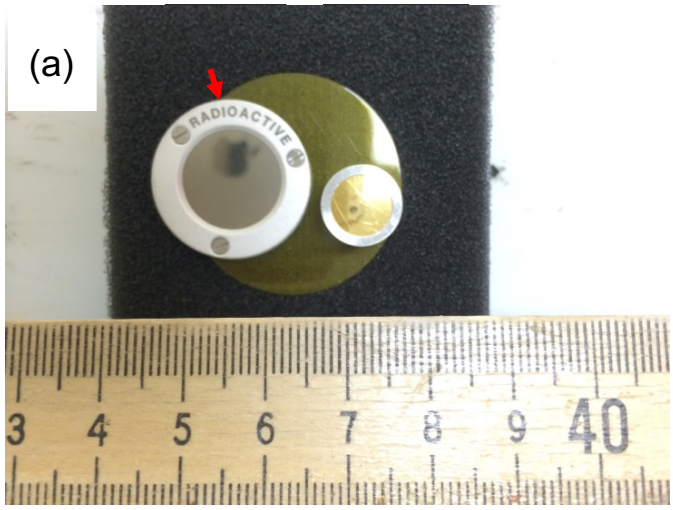
LIST OF TABLES AND FIGURES

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



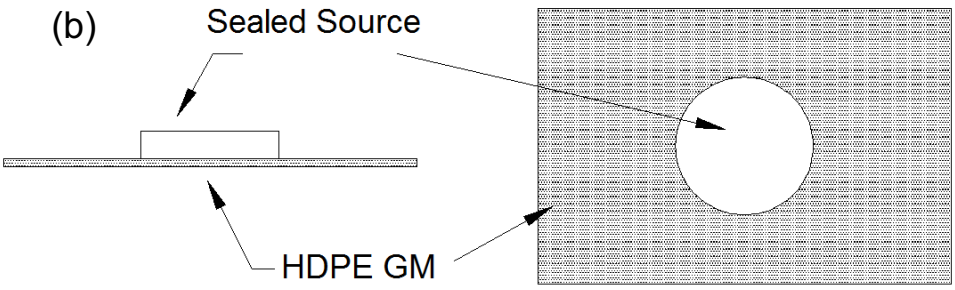


Fig. 1. Set up for sealed-source experiments: (a) sealed sources of ^{99}Tc (left) and ^{241}Am (right) and (b) GM installed under the sealed source for exposure. Divisions on scale in (a) are in mm.

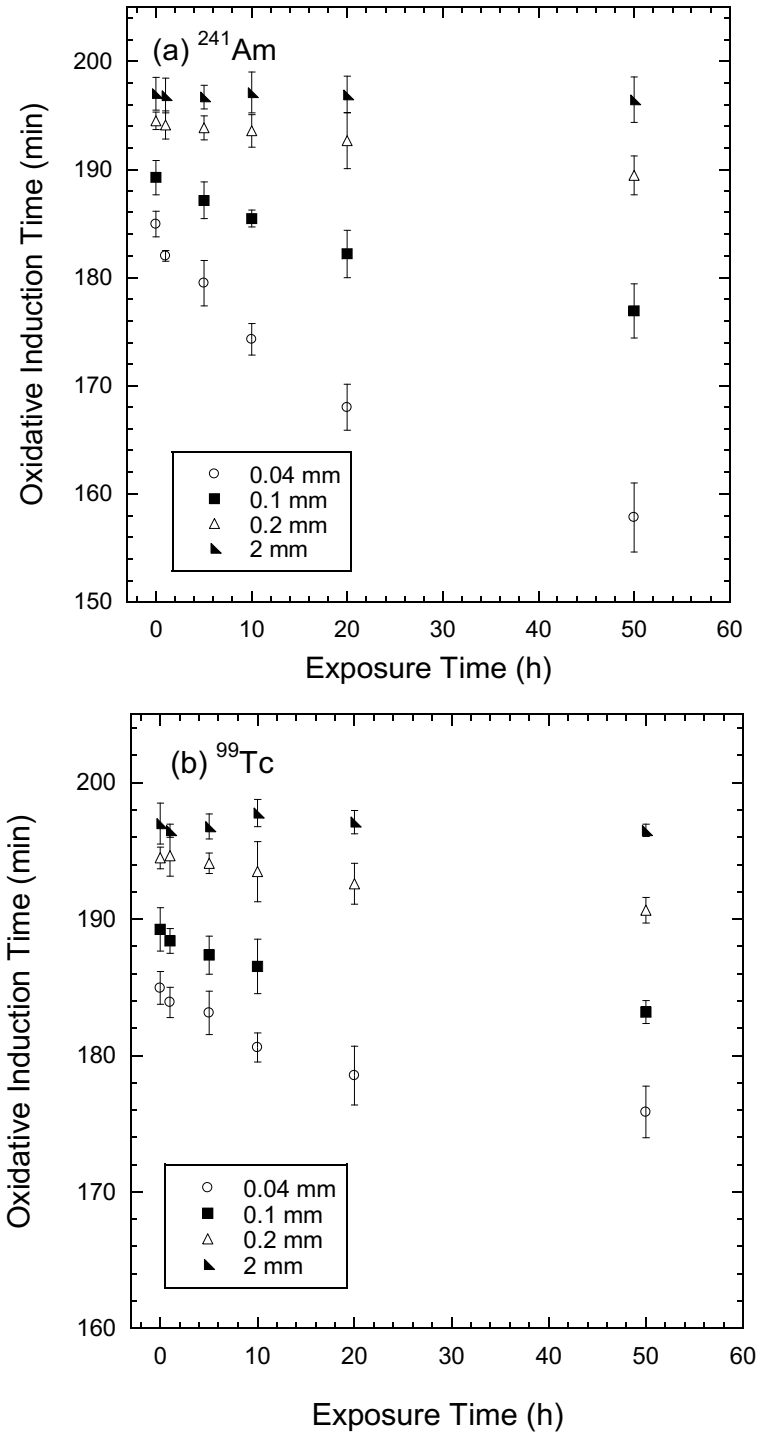


Fig. 2. OIT vs. exposure time for HDPE GM specimens exposed to sealed sources of ^{241}Am (a) and ^{99}Tc (b) for up to 50 h. Error bars represent standard deviation of three measurements.

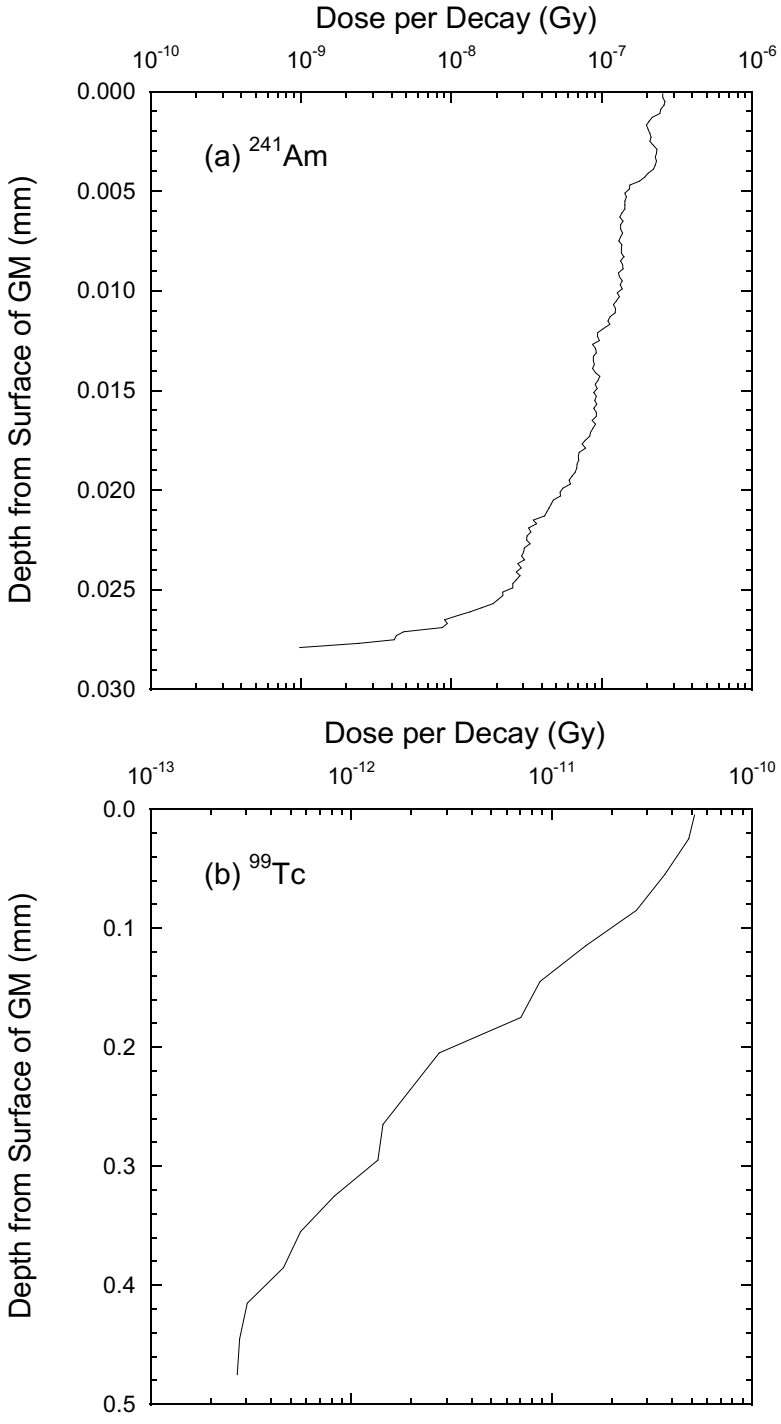


Fig. 3. Dose per decay as a function of depth from the surface of the GM predicted by GEANT4 for HDPE GM exposed to a sealed source of ^{241}Am (a) or ^{99}Tc (b).

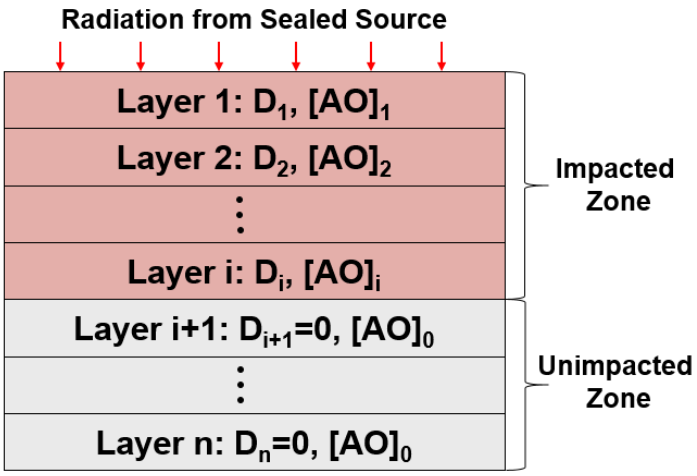


Fig. 4. Layering in multilayer model for antioxidant depletion in HDPE GM exposed to radiation with antioxidant concentration $[AO]_l$ after exposure to radiation dosage D_i. Each layer in un-impacted zone (no dose) has the initial antioxidant concentration $[AO]_0$.

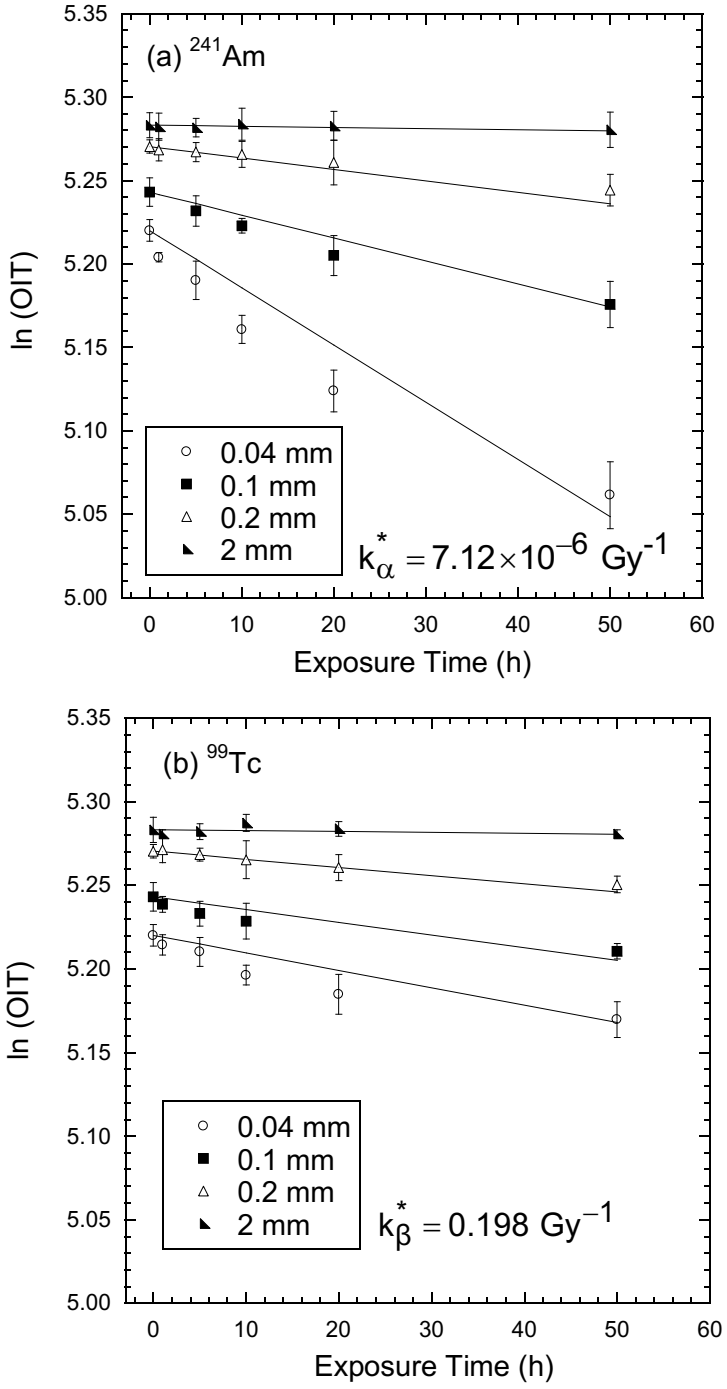


Fig. 5. Fit of Eq. 10 to obtain k* using OIT data for 0.04, 0.1, 0.2, and 2-mm-thick HDPE GM specimens after exposure to sealed sources of ^{241}Am (a) and ^{99}Tc (b) for up to 50 h. Fit made using simultaneous regression on data from all specimens.

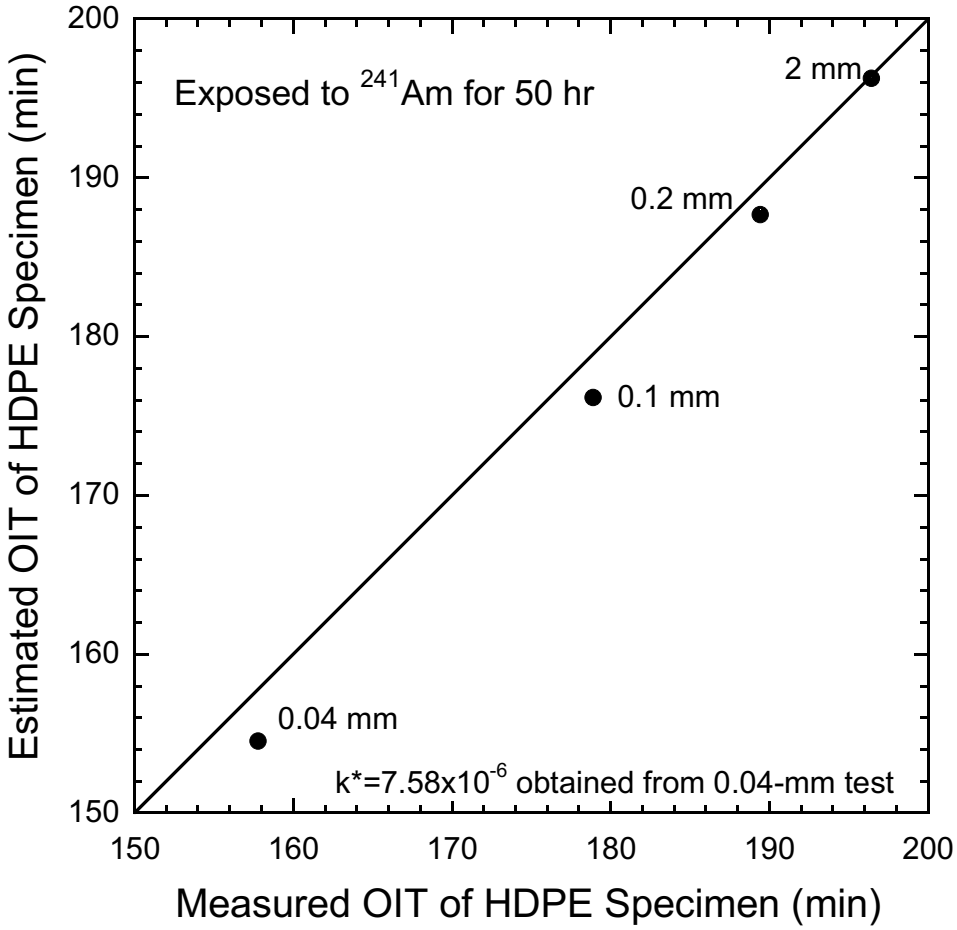


Fig. 6. Measured OIT vs. Estimated OIT of HDPE specimens exposed to sealed source of ^{241}Am for 50 hr [units for k* in ln(min)/Gy].

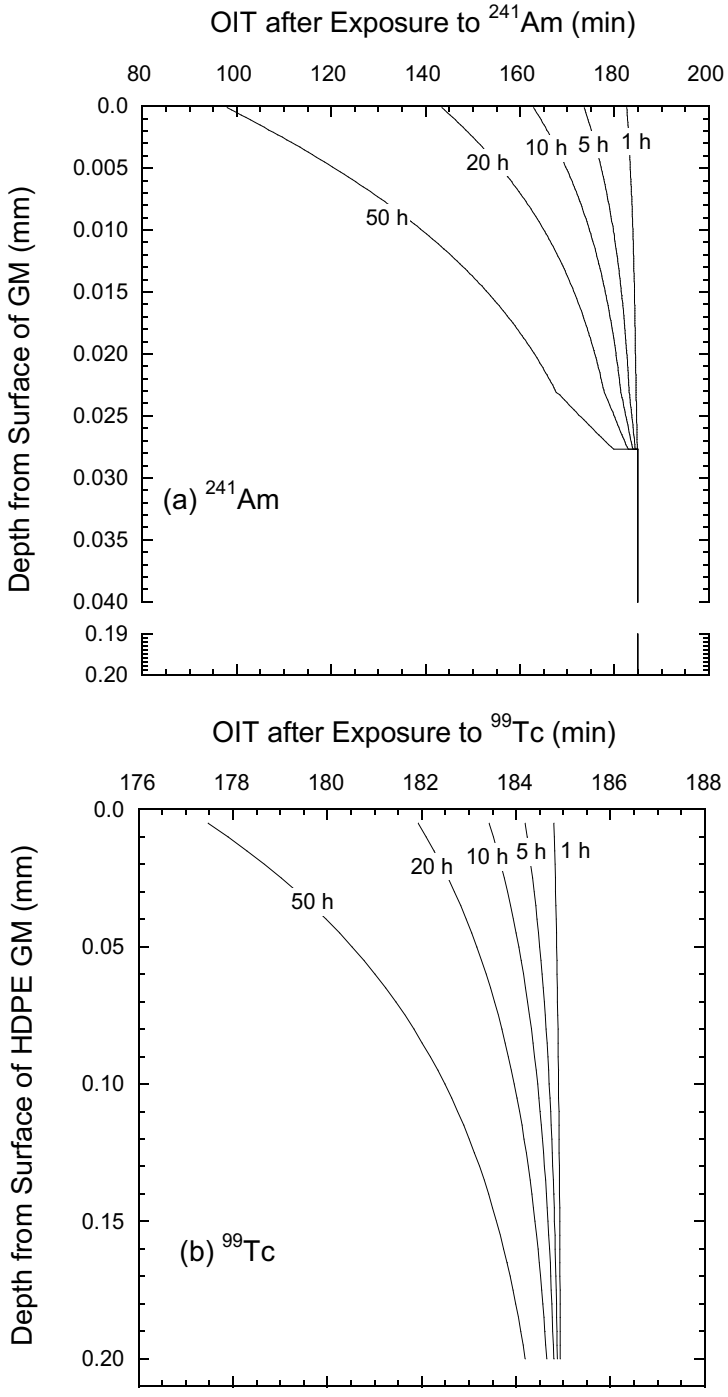


Fig. 7. OIT as a function of depth from surface of GM computed using multilayer model for 0.2-mm-thick HDPE GM exposed to sealed source of ^{241}Am (a) or sealed source of ^{99}Tc (b).

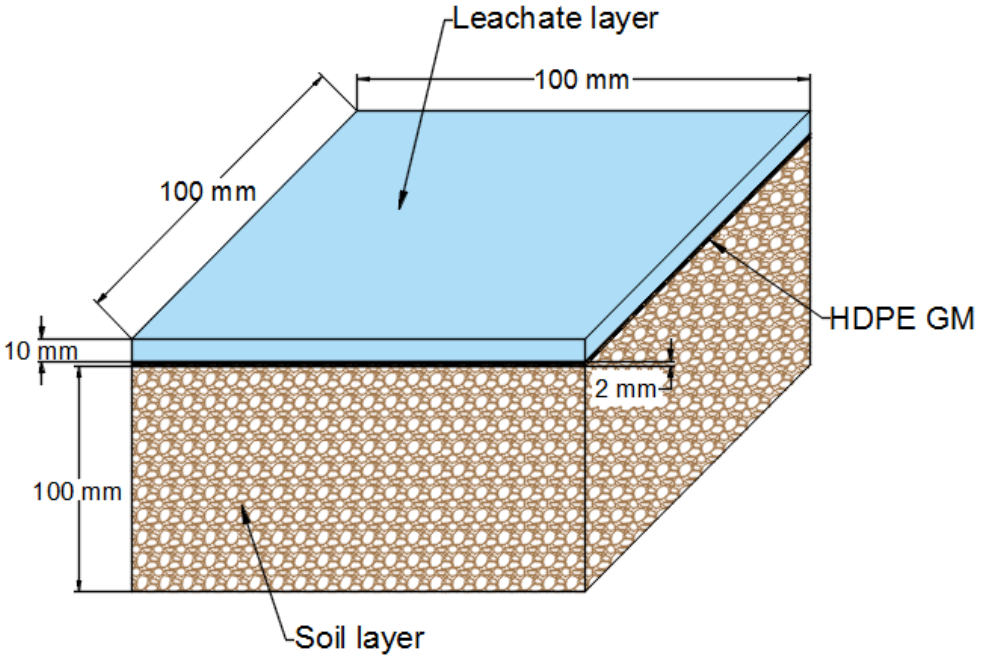


Fig. 8. Domain simulated with GEANT4 representing composite liner with HDPE GM on compacted clay liner with thin layer of LLE leachate pooled above. LLW leachate assumed to contain radionuclides and major cations and anions in Table 2 based on the leachate characterization reported in Tian et al. (2016, 2017a).

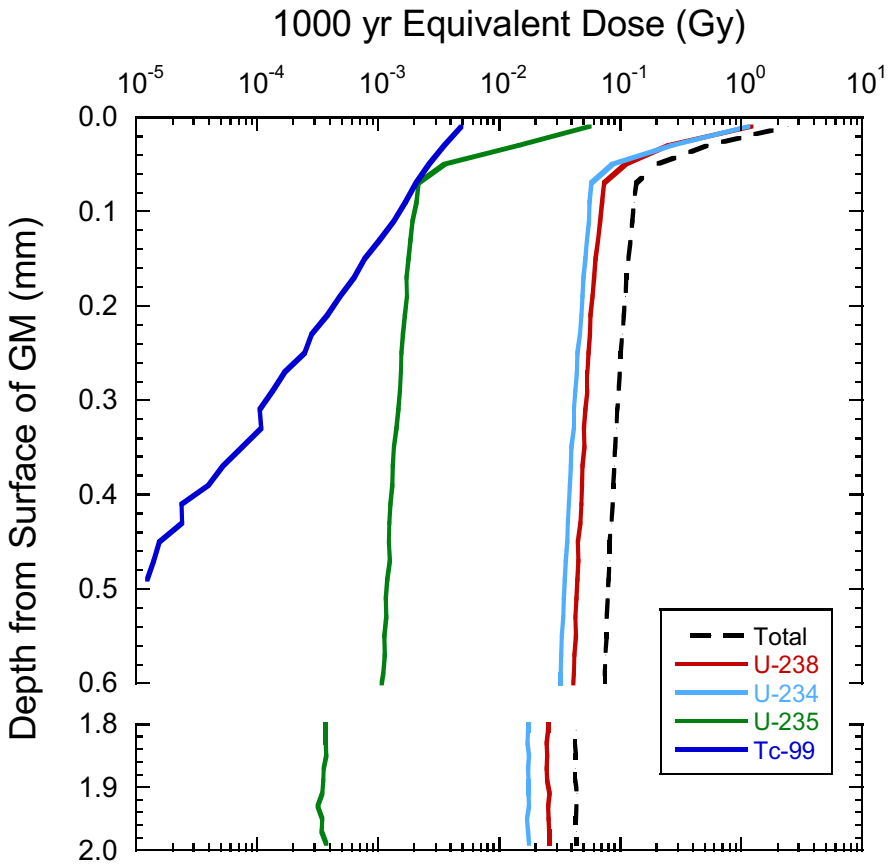


Fig. 9. Dose as function of depth in HDPE GM in a composite liner overlain with LLW leachate after 1000 yr of exposure as predicted with GEANT4.

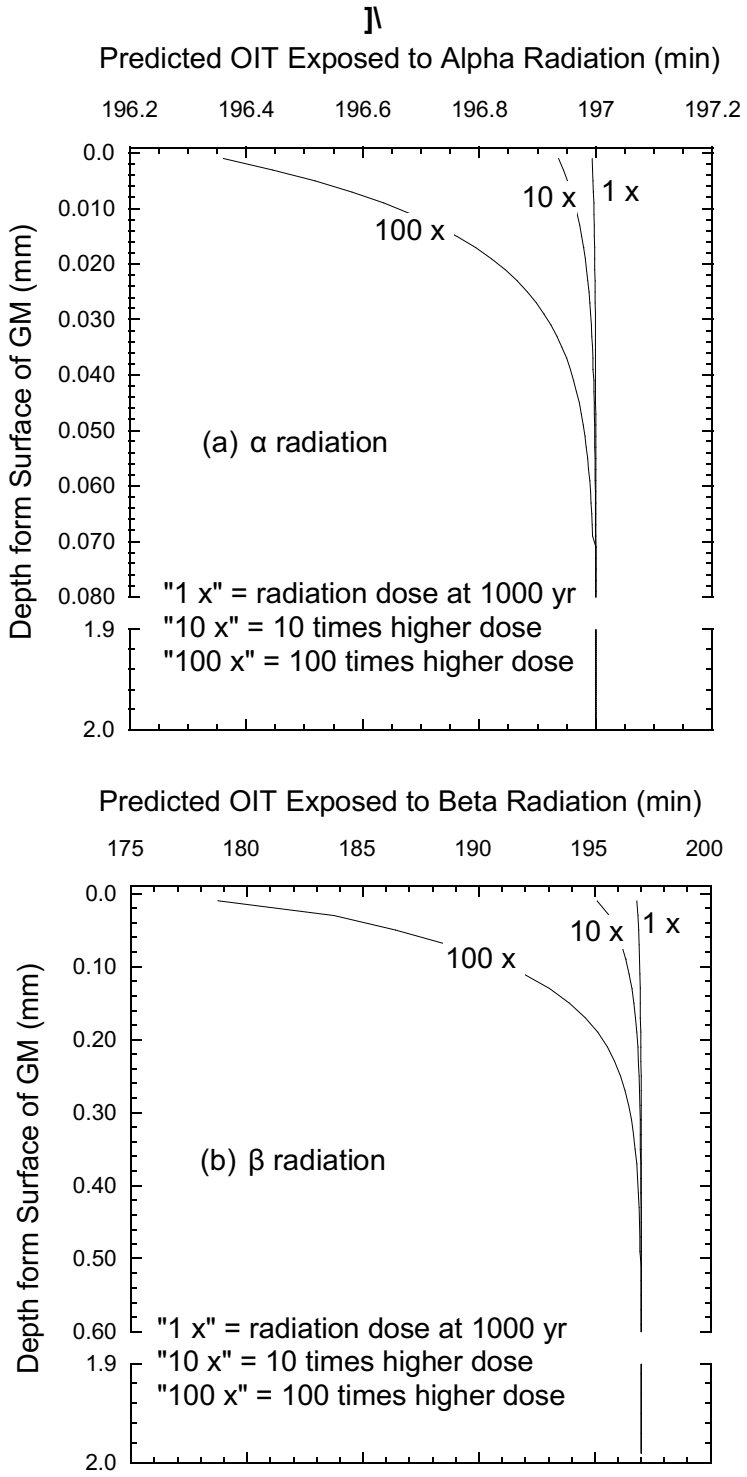


Fig. 10. OIT as a function of depth in HDPE GM exposed to α (a) and β (b) radiation for 1000 yr for base case and doses 10x and 100x higher than dose for base case.

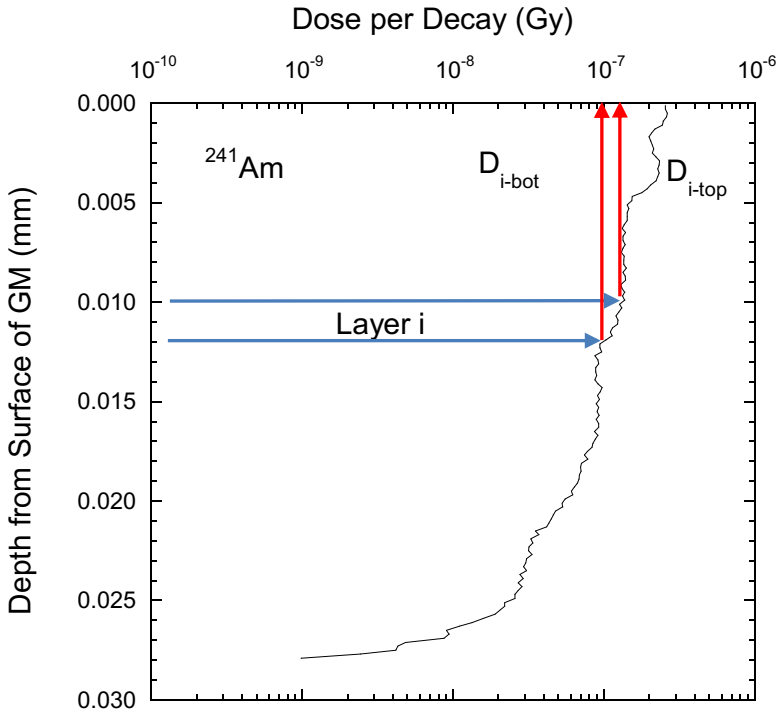


Fig. A1. Dose per decay as a function of depth from the surface of the GM predicted by GEANT4 for HDPE GM exposed to a sealed source of ^{241}Am.

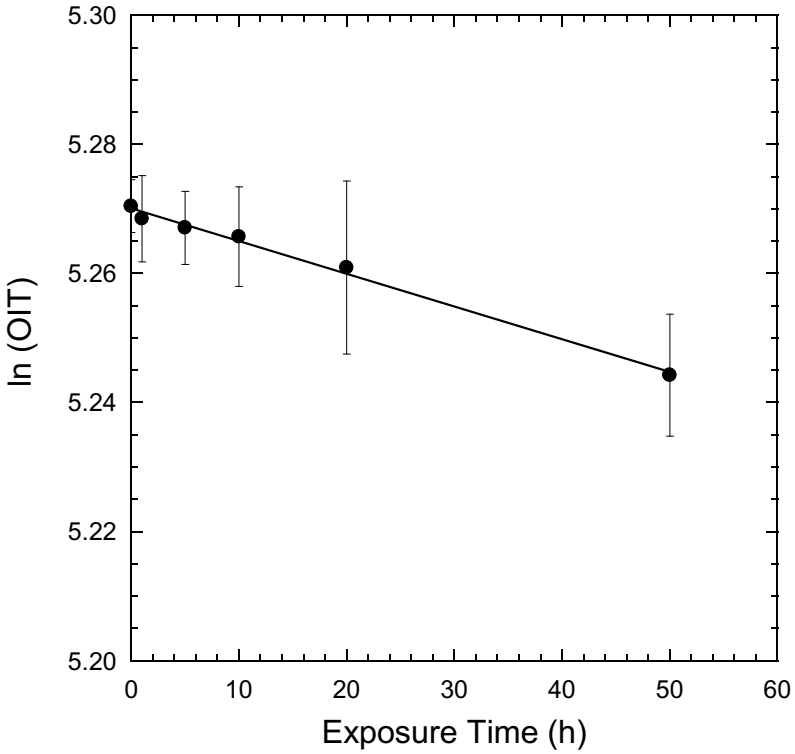


Fig. A2. Fit of multilayer model Eq. A3 (solid line) to OIT data for 0.2-mm-thick HDPE GM specimens after exposure to sealed sources of ^{241}Am for up to 50 h.