Long-term Performance of HDPE Geomembranes Exposed to High Service Temperature

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ABSTRACT

Polyethylene geomembranes typically have poor behaviour when exposed to high temperature. Polyethylene materials soften as the temperature increases and lose their strength completely near 120C. Other research with landfill liners has shown that increasing the service temperature of a polyethylene geomembrane to 85C can reduce the service life of the liner to as little as 3 years through the rapid depletion of antioxidants.

In this paper, the performance of a high temperature resistant geomembrane material was evaluated over a year-long period and compared to other geomembrane materials. The samples were exposed to three different service temperatures and then periodically evaluated for antioxidant retention. An Arrhenius-model was used to project antioxidant depletion. The projected service life of HDPE geomembranes exposed to high temperatures in these conditions was estimated considering antioxidant depletion as the end-of-life criteria.

BACKGROUND

In late 2013 a new type of polyethylene resin started showing up in geomembranes in Europe. These resins were grades of High Density Polyethylene (HDPE) and were intended for use at higher temperatures than regular geomembrane resins.

The new higher-temp HDPE resins were identified by the term PE-RT which stood for Polyethylene – Raised Temperature. PE-RT resins are now well-established in the domestic hot water piping industry and their physical properties are outlined in ASTM F2769. This ASTM specification covers PE-RT pipe used for temperatures up to 82C (180F) and 6.9 bar (100 psig).

Historically geomembrane resins have a lot in common with the piping industry. The current geomembrane resins known as HDPE (technically Medium Density Polyethylene or MDPE; in this paper geomembrane will be referred to as HDPE but the resin will be referred to as MDPE) are variations on pipe grade resins used for large diameter polyethylene pipe. Geomembrane and polyethylene pipe both share requirements for chemical resistance, durability, and resistance against stress cracking. The first PE-RT geomembrane was made by a European manufacturer who makes both pipe and geomembrane.

One of the main goals of this research was to find a suitable PE-RT resin that could be used for geomembrane. Much of the initial research was focused on the selection of a suitable material and then determining whether that resin was suitable for use as a geomembrane material. This paper outlines a portion of the selection and evaluation testing.

The investigation of the PE-RT resins for use in geomembrane began with a review of possible sources. Investigation found one PE-RT resin available from Germany, two from France, one from Korea, and three from the US. Samples of all seven resins were brought in for evaluation.

The next thing to be checked was whether any of these resins would run on the available geomembrane production equipment. The resin would have to run on blown film geomembrane equipment which requires resin with a significant melt strength. To check melt strength the resins were sent for rheology testing. The first screening test was done using a capilliary rheometer (ASTM D3835). This initial screening eliminated the German resin, one of the French resins, and one of the US resins. Extrusion testing of the samples followed on a small blown film line and the Korean resin was eliminated. The eliminated resins did not have sufficient melt strength to be made into blown film at geomembrane thicknesses. Others were eliminated due to economics or supply difficulties. In the end 3 PE-RT materials were chosen for further evaluation.

Current testing of PE-RT resins is entirely based on pipe testing. The Plastics Pipe Institute has established standards for pipe used in hot water containment and provides a listing of the resins and manufacturers that meet their requirements in document called PPI-TR4 (PPI 2013). The fundamental test of longevity for plastic pipe is defined in ASTM D2837. This test takes sections of pipe and pressurizes them at various pressures and measures the time to failure. Based on the progression of failures at different pressures and temperatures an estimate of the 50-year design pressure is predicted. In the specification for PE-RT pipe ASTM F2769 calls up a required Hydrostatic Design stress of 2.76 mPa (400 psi) at 82C (180 F) and 6.9 bar (100 psig) pressure.

Making the connection between the service conditions of hot water piping and geomembrane use is not a straightforward comparison. Research done by the Geo Engineering Centre in Kingston, Canada has shown problems with regular HDPE geomembranes at elevated temperatures under stresses at the bottom of landfills. In papers by Rowe et al (2010) and Rowe and Ewais (2014) the longevity of a typical HDPE geomembrane could be as little as 3 years at 85C. Research on PE-RT resins used in geomembranes was similarly sparse with only the paper by Ramsey and Wu (2013) showing some initial test results. In the Ramsey paper there are results from a 6 month oven aging test at a single temperature; however, the longevity of these new geomembrane materials at elevated temperatures was not clearly established.

The goal of this research project was to determine what improvements in longevity would be realized by using PE-RT resins for geomembranes.

There are a number of longevity studies under way as part of this research. The first studies began in 2014 and included oven aging, hot brine solution testing, and chlorine resistance testing. Two additional studies were added in 2015. One was to study the resistance of a PE-RT material to specific variations of potable water. The other study was of the tensile strength of high temperature materials at various temperatures. The tensile strength study has been published by Beaumier et al (2016).

This paper concentrates on the oven aging testing that began in 2014. The oven aging tests were set up to generally follow ASTM D5721. Test modifications include testing at three different temperatures and a significant extension of the testing period. ASTM D5721 uses a temperature of 85C for a period of 90 days. In the 2014 oven aging test three equally spaced temperatures were used; 70C, 90C, and 110C. The choice of these temperatures was made because ovens at these three temperatures are in continuous operation in the lab where the research was completed. The evaluation periods chosen were 1,200 hours, 2,400 hours, 4800 hours, and 8,800 hours (1 year). These evaluation periods follow a progression established in other tests conducted by the authors in previous work. The evaluation of the specimens in the oven aging test was done by Oxidative Induction Time (OIT; ASTM D3895) and High Pressure Oxidative Induction Time (HPOIT; ASTM D5885). This paper discusses the results up to the 8,800 hour mark (1 year) however two additional specimens are still being exposed for future testing if needed.

THEORY

Geomembranes will observe two main types of aging: from physical change or chemical degradation. During physical aging, the material will reach thermodynamic equilibrium by molecular re-organization, aging may be observed by a change in crystallinity. During chemical aging, thermo-oxidation (from heat) or radioactive-degradation (from UV radiation) will lead to a reduction of engineering properties of the geomembrane. When looking at long-term applications of geomembranes, chemical aging is, by far, the most important aging process to consider.

Chemical aging of HDPE geomembrane is often detailed by four stages, as shown in figure 1 (Hsuan and Koerner (1999)). The first one is the antioxidant depletion time where antioxidants act like a sacrificial barrier to oxidation. This stage can be longer or shorter depending on the type and the quantity of antioxidants. The second stage is the induction period, characterized by the time between the end of the antioxidant depletion and the beginning of the degradation. The two last stages are the accelerating and the decelerating period where engineering properties are dramatically affected.

From an engineering standpoint, the end of antioxidant depletion may be considered the limit of the geomembrane’s service life. Degradation of the polyethylene will occur once the antioxidant is depleted which will eventually be observed as mechanical property changes.

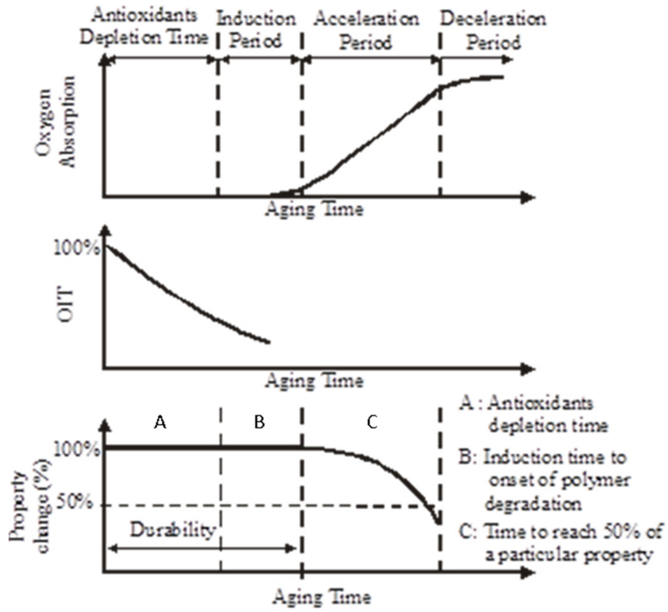

Figure 1. Degradation mechanisms of polyethylene, Hsuan and Koerner (1999).

The antioxidant (AO) depletion of HDPE geomembranes is commonly monitored by the oxidative induction time test (OIT; ASTM D3895) or the high-pressure oxidative induction time test (HP-OIT; ASTM D5885), measured by differential scanning calorimetry (DSC). In this study, the antioxidant depletion was modeled by a first-order differential equation. The AO depletion was thus evaluated by the following equation, from Koerner and Hsuan (2002):

$$\ln(OIT) = -S_{OIT} \cdot t + \ln(OIT_{initial}) \tag{1}$$

Where

OIT: Oxidative Induction Time at a duration time of t.

$OIT_{initial}$: Oxidative Induction Time before aging.

S_{OIT}: Depletion rate (ln min/day), calculated by the slope of OIT vs time.

t: Duration of the exposure (days).

The depletion rate is evaluated at each temperature, from regression of ln(OIT) with time. Note that OIT is replaced by HPOIT for the estimation of AO depletion by HP-OIT.

The relation of depletion rate with temperature is modeled by Arrhenius relation:

$$S_{OIT} = A \cdot \exp\left({}^{-E_a}\!/_{RT} \right) \tag{2}$$

Where

A: Constant (ln min/day).

E_a: Activation Energy (J/mol)

R: Gas Constant (8.315 J/mol K)

T: Temperature (K)

The slope from the relation of $\ln(S_{OIT})$ vs 1/T is used to calculate the activation energy to gas constant ratio, calculated as $-E_a/R$. Whilst the ordinate is used to calculate the constant A, the ordinate being ln(A).

Once the kinetic parameters are computed, the depletion rate can be extrapolated according to the equation (2). The exposure time to deplete all the antioxidants can be calculated as a function of the temperature by solving " t " in the equation (1).

MATERIALS

The samples selected for testing included 3 PE-RT resins. A sample of a PE-RT geomembrane sourced from a manufacturer in Europe was added for comparison and control samples of HDPE geomembranes were added. Initially there were a number of different blends that were prepared; however, many of these blends were dropped as the test progressed until only the most promising remained. The samples are identified as follows:

Sample 1. PE-RT resin from a source in France
Sample 2. HDPE control sample
Sample 4. HDPE control sample with a different blend of additives
Sample 5. PE-RT resin from a source in the US
Sample 12. PE-RT resin for a source in the US
Sample 15. PE-RT geomembrane from a European manufacturer

Since one of the main goals of this testing was the selection of a suitable resin for future study a review was completed after the first 2,400 hours of testing. Sample 12 was the least effective in the oven aging test and was dropped. Both sample 1 and sample 5 showed very good and nearly identical results. Sample 5 was ultimately selected for further study as the more economical of samples 1 and 5. Both of the HDPE control samples, sample 2 and sample 4, showed similar depletion rates to 2,400 hours, but sample 2 was kept as the control sample as this material met the requirements of a GRI-GM13 HDPE geomembrane (Geosynthetic Institute 2012). Once this initial selection was made the balance of the testing concentrated on the long-term stability of samples 5 and 15 with sample 2, being the control material.

METHOD

Samples were prepared from extruded geomembranes, including different formulations but also different thickness. In order to obtain similar diffusion of oxygen through the material, test samples were compression molded from the geomembrane materials to a controlled thickness of 1.5 mm. Heat aging was done in forced-air convection ovens at three temperatures: 70, 90, 110°C, in accordance with ASTM D5721. Antioxidant depletion was measured periodically with exposure periods of 1200 hours, 2400 hours, 4800 hours, and 8800 hours. After exposure, materials were tested for OIT using ASTM D3895 and HP-OIT using ASTM D5885 methods.

Samples were blended and moulded before testing according to ASTM D4703-10a. Samples were initially blended at 177 °C for 4 to 5 minutes using a two-roll mill and then, sheets were molded using a compression molding press, and controlled at a thickness of 1.5 mm using a flash picture-frame mold. The hot molding was done at 177 °C for ten minutes, including five minutes under a pressure of 5 MPa. Cooling rate was controlled at 15 °C/minutes, as the cooling rate will influence the crystallinity of polyethylene.

The oven aging was performed at the temperatures of 70 °C, 90 °C and 110 °C. The specimens were hung vertically in air convection ovens that were controlled within 1 °C.

After the planned exposure times of 1200, 2400, 4800 and 8800 hours, two specimens of each type of material and aging temperature were taken for oxidative induction time (OIT) and high pressure oxidative induction time (HP-OIT) testing.

RESULTS AND DISCUSSION

Determination of depletion rates. First look at the depletion rates showed that HPOIT values did not change sufficiently to allow analysis. Figure 2a shows the change in OIT values at 70C and Figure 2b shows the HP-OIT values of the same test specimens. This paper continues with the analysis of antioxidant depletion rates by looking at the OIT test results. Future work will analyze the HP-OIT results.

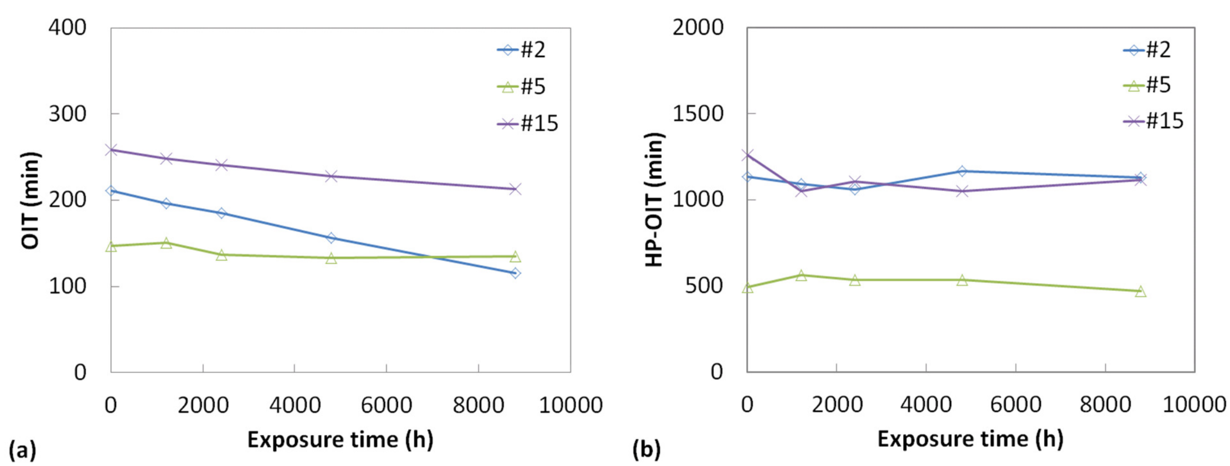

Figure 2. OIT (a) and HPOIT (b), monitored after oven aging at 70°C.

Data were plotted using a first-order reaction of depletion rate with time. At temperatures of 90 and 110°C, the OIT values decrease rapidly and then taper off to an almost constant OIT. The decreasing slope of the logarithm of OIT vs time was included in the depletion rate calculation but OIT data after reaching a constant OIT was not. The analysis has thus excluded the circled points marked on Figures 3a and 3c.

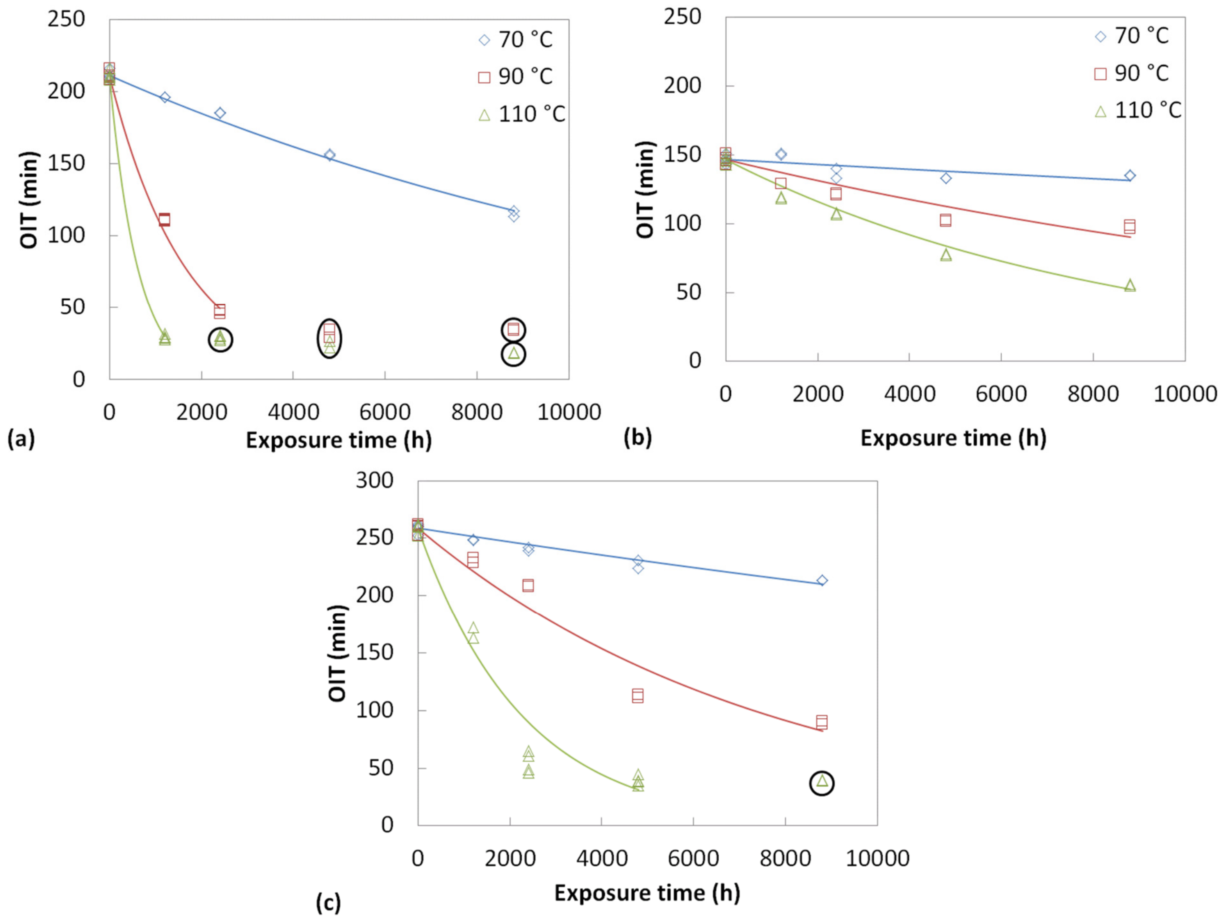

Figure 3. Residual OIT by comparing samples: a) sample 2, b) sample 5, c) sample 15.

Determination of kinetic parameters. Figure 4 shows the Arrhenius plot of the natural logarithm of the depletion rate versus the inverse of the temperature for the three different aging methods. The activation energy was calculated from the slope of the linear regression and the pre-exponential factor was calculated from the ordinate.

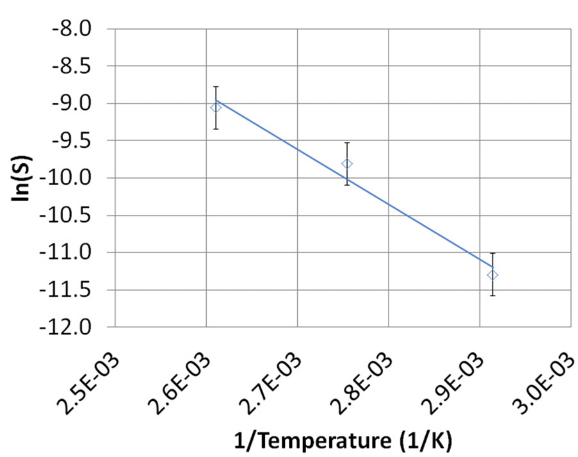

Figure 2. Arrhenius plot from OIT testing on sample 5.

The kinetic parameters are shown in the table 1 for each aging method. The activation energy of sample 5 is about 25% lower than the other three formulations, which lead to a slower depletion rate, detailed on Table 1.

Table 1. Kinetic parameters from OIT testing after different aging method

Sample #	Activation energy E_a (kJ/mol)	Pre-exponential factor A (ln min/h)
2	87.8	1.8e+9
5	61.4	3.0e+5
15	80.0	3.7e+7

Depletion time of antioxidants. The time to deplete all the antioxidants can be calculated by a rearrangement of the equation (1) introducing the kinetic parameters. The time to reach antioxidant depletion is calculated as the time when a residual OIT of 0.5 min is attained, which represents a pure HDPE geomembrane without antioxidant. At the end of this time, the mechanical properties of the geomembrane begin to degrade until they reach 50 % of their initial values and a failure is declared. As expected by the kinetic parameters, the projections of time to deplete all of the antioxidants at lower temperatures are less important. As temperature rises, the AO depletion time of the PE-RT resins (samples 5 and 15) increases when compared to the common HDPE grade (sample 2).

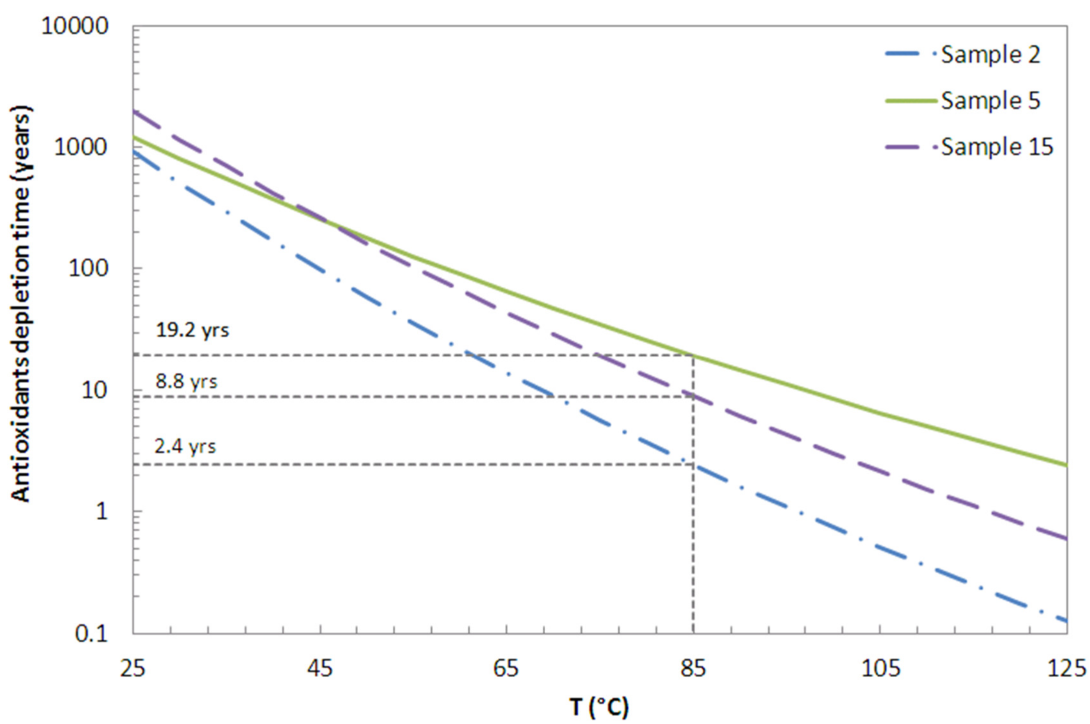

Figure 3. Antioxidant lifetime for different temperatures

High temperature lifetime prediction. Figure 5 shows the estimated lifetimes of the geomembrane materials tested. These lifetimes are the point at which the antioxidants are expected to be depleted at the temperatures shown.

The control HDPE sample showed a time to antioxidant depletion of 2.4 years at 85C. This estimation correlates with other author's lifetime projections (Abdelaal and Rowe (2014), Rowe et al. (2010)) of about 3 years. Looking a bit more closely shows that this type of regular HDPE would have a 20-year life expectancy if the temperature were kept below 60C.

Sample 5 showed a time to antioxidant depletion of 19.2 years at 85C. This is significantly better than the performance of the regular HDPE geomembrane tested. Sample 5 showed the best performance in this testing.

Although sample 15 is an existing geomembrane that uses PE-RT resins it did not show up quite as well in this testing. The time to antioxidant depletion for Sample 15 at 85C was estimated at 8.8 years. For Sample 15 to be used in a 20-year application, it would need to be limited to 75C according to this data (specifically 19.1 yrs at 75C).

Comparison between industries. This testing shows that carefully selected PE-RT resins can be expected to perform as geomembranes in higher temperature applications. This testing also shows that it is not always practical to take test data from other industries and apply that data without verification. The test data from the pipe industry bases its longevity predictions on pipe burst strengths and not antioxidant depletion. ASTM F2769 lists a 50-year design life for PE-RT resins at 82C and both of the PE-RT resins used in the geomembranes in this test have passed that requirement for pipe. In geomembrane oven aging testing Sample 5 would see antioxidant depletion in 22.9 years and Sample 15 in 11.1 years when extrapolated to 82C.

CONCLUSION

The exposure of HDPE geomembranes to high temperatures in an air environment shortens their lifetimes significantly. This testing exposed HDPE materials for a year to determine the antioxidant depletion rate at three elevated temperatures. This testing appeared to correlate with previous studies on regular HDPE that showed antioxidant depletion predictions of only a few years at 85C.

Special grades of HDPE from the pipe industry designed for higher temperatures showed better performance in oven aging testing and better retention of antioxidants at elevated temperatures. Of the two PE-RT geomembranes tested one showed a 19.2 year lifetime to antioxidant depletion at 85C while the other showed an 8.8 year lifetime to anti-oxidant depletion.

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