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Long-term Performance of HDPE Geomembranes Exposed to a High Temperature Brine Solution

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ABSTRACT

Geomembrane application temperatures continue to climb as their use is expanded into more challenging environments. The common factor in these new applications is higher temperature. Examples such as flowback liquid storage in hydraulic fracturing applications can reach 90C or more while long term brine storage and evaporation ponds are reaching even hotter temperatures. 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 geomembrane material exposed to a brine solution was evaluated over a year-long period and compared to other geomembrane materials. The geomembrane samples were exposed to three different service temperatures and then periodically evaluated for antioxidant retention. The newly developed geomembrane presented in this study showed better resistance to hot brine than regular HDPE geomembrane materials.

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 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 goals of this research was to find a suitable PE-RT resin that was available in North America and could be used for geomembrane. The 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 4-year program of selection and evaluation testing. The selection of the resin and heat aging testing was presented at Geotechnical Frontiers 2017 in Orlando (Mills, Beaumier, 2017). Tensile testing of the geomembrane at elevated temperatures was presented at GeoVancouver (Beaumier, et al, 2016). The resistance to chlorine was presented at Geosynthetics 2017 in Santiago Chile (Rangel, et al, 2017). This paper focuses on the elevated temperature brine solution testing that was part of the material 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 Ewais et al (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 (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 is to determine what improvements in longevity will be realized by using PE-RT resins for geomembranes.

There are a number of longevity studies that have been completed 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.

This is the fourth technical paper on the PE-RT geomembrane that is being studied. Previous papers on long term oven aging, chlorine resistance, and tensile resistance at elevated temperatures have already been presented. This study on brine resistance completes the publication of the studies into this new geomembrane material.

METHODOLOGY

The methodology consists of a protocol that was developed to evaluate geomembrane resistance to different chemical solutions including chlorine, brine, and other chemicals. The methodology consists of an immersion protocol and then evaluation of the specimens after immersion.

Immersion Testing Protocol. This immersion testing protocol was first outlined in the paper by Mills (2011). Materials are prepared in accordance with condition A of test method ASTM

D1693 Standard Test Method for Environmental Stress-Cracking of Ethylene Plastics. The test was then modified to replace the liquid of immersion with another solution under study such as a brine solution or other liquid formulations.

All plastic samples are first melted and blended in a two-roll mill and then immediately molded to the correct specimen thickness in a compression molding machine to the requirements of condition A which is 3.0 to 3.3mm thick. This blending step makes sure that the ingredients are fully blended in the small specimens. The compression molding makes sure that all materials end up at the same test thickness regardless of their initial form.

There are three evaluation methods after immersion in the test liquid. The first evaluation is the visual evaluation outlined in ASTM D1693. The visual evaluation for cracking assumes that the specimen will crack completely; however, a more common result was that the surface would oxidize with varying degrees of cracking forming on the surface.

The second and third evaluation methods use tests designed to measure residual antioxidant in the polymer. Two tests were used. ASTM D 3895 Standard Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry (OIT) and ASTM D5885 Standard Test Method for Oxidative Induction Time of Polyolefin Geosynthetics by High-Pressure DSC (HPOIT). The OIT method uses a test temperature of 200C and air at ambient pressure. OIT testing typically reveals the residual level of anti-oxidant (AO) in a specimen. The HPOIT test uses a test temperature of 150C but with a higher pressure of pure oxygen at 3.4 mPa. HPOIT testing typically reveals the residual level of UV stabilizers which can also contribute to long term stability.

Oxidation of Polyolefins first shows as an attack to the surface of the polymer. As part of the development of this test protocol we found that sampling the full thickness of the immersed specimen did not show significant degradation. The sampling method used for our evaluation testing was to slice a sliver of the immersed specimen along the peak of the surface with a microtome cutter. This sliver would then represent the surface that was exposed to the chemical at the location of highest stress in the specimen. Since OIT and HPOIT test pieces are only 5.0 mg the sliver of polymer taken was usually around 0.12 mm thick.

Long-term Brine Immersion Test. The long-term brine immersion test was part of a larger study to investigate the performance of a number of new resins. A previous paper explored the initial selection of materials and outlined the long-term temperature properties (Mills and Beaumier, 2017). This paper gives details of the brine testing which was part of that larger study. Only a few of the materials tested in the larger study are reported here as the other materials were eliminated by previous tests in the study.

The brine solution used is a formulation that was originally developed by the authors for compatibility testing. The formulation was developed from water test reports from flowback brine water in Australia. The use of this brine formulation was first reported at Geosynthetics 2015 (Mills, 2015). The solutions in the immersion test tubes were changed every week from a prepared batch of solution. The solution has the following formulation:

- 100 g/L NaCl
- 62 g/L NaHCO3
- 50 g/L Na2CO3
- in de-ionized water
- pH = 9.3+/- 0.4

Three test temperatures were chosen for these immersions. The test tubes were placed in an oven to maintain temperatures. The three test temperatures used were 70C, 90C, and 100C. Maintaining the 100C solution was challenging (see figure 1).

This was a long-term test with long term periods between sample evaluations. A separate ASTM D1693 test tube was prepared for each temperature and each testing period. Ten different materials were loaded into each test tube so that when a test tube was removed at the planned interval a complete set of specimens were available for testing. The planned exposure intervals were 1200 hours, 2400 hours, 4800 hours, 8800 hours (1 year), plus a spare. Only one specimen was prepared per data point as this test program had 900 specimens overall. After immersion the specimens were removed and rinsed with de-ionized water. They were then identified and bagged while they waited for evaluation. All specimens of all formulations were immersed; however, only a few were evaluated fully as materials that performed poorly in earlier tests were eliminated.

MATERIALS

The materials from the long-term brine immersion study that will be reported here are Sample 2 which is a standard HDPE geomembrane; sample 4 which is a standard HDPE geomembrane with added UV and antioxidant; sample 5 which is the new HDPE resin which is the subject of our developments, and sample 15 which is a geomembrane from another supplier which is said to have long term high temperature resistance.

- Sample 2 – standard HDPE geomembrane (GRI-GM13)
- Sample 4 – HDPE geomembrane with added UV and AO
- Sample 5 – new high temp geomembrane (HEATGARD HDPE)
- Sample 15 – a high temp HDPE from another supplier

Figure 1. Brine solution test tubes in oven

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 geomembranes. 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 2 from Hsuan and Koerner (1999). The first stage 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 as the ultimate limit of the geomembrane's service life. In the absence of antioxidant protection damage to the polymer will start to occur and will eventually be seen as measurable changes to physical properties.

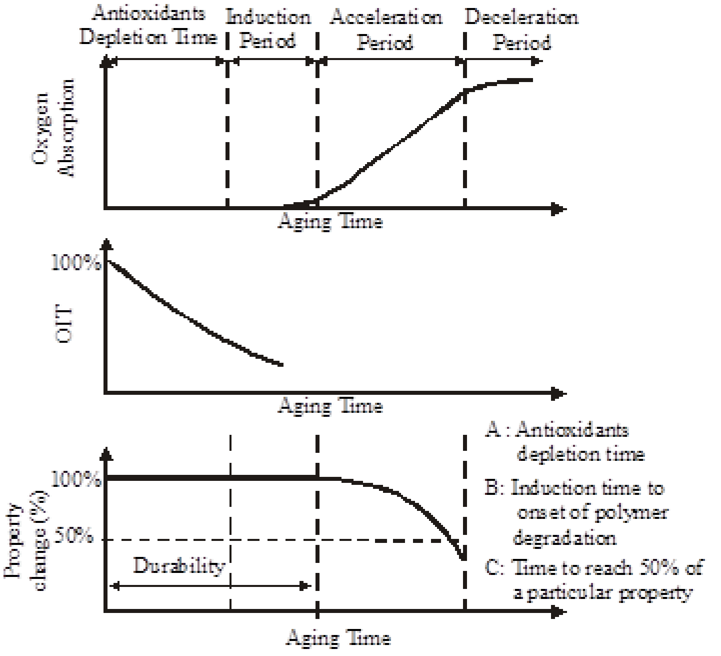

Figure 2. Degradation mechanisms of polyethylene, Hsuan et al. (1998).

RESULTS AND DISCUSSION

Looking at the OIT measurements there is a drop in antioxidant levels until a residual level is reached (Figures 3, 4, and 5). Initial depletion starts rapidly and then starts to level off as the antioxidant is reduced in the surface of the geomembrane. The higher temperatures accelerate this depletion; however, there does not appear to be much of a difference between the 90C and 100C immersion results. The results between the 70C and the 90C/100C immersions are much more distinct. Notice that at all temperatures the slope of the depletion line for sample #5 is less than the other formulations and on most of the graphs ends up as one of the higher values after 8800 hours.

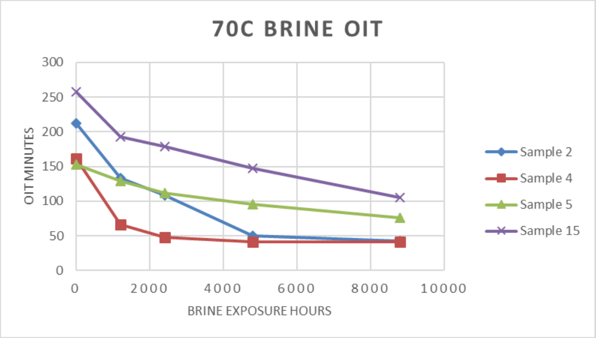

Figure 3. OIT results at 70C

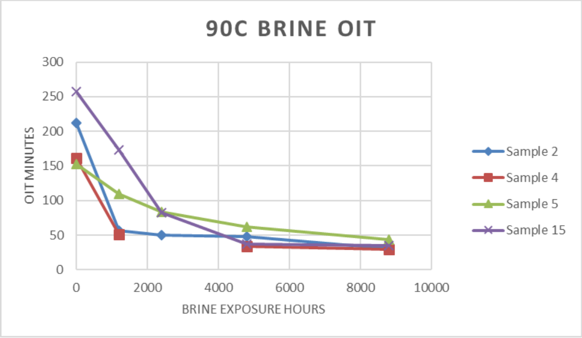

Figure 4. OIT results at 90C

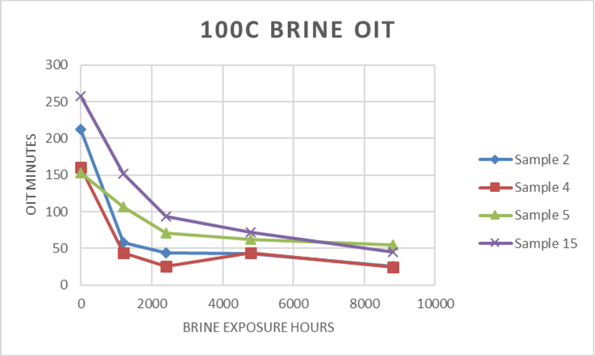

Figure 5. OIT results at 100C

The second set of results at the HPOIT measurements. HPOIT results do not appear to be affected as much as the OIT results. In Figures 6, 7, and 8 the HPOIT results remain fairly consistent over the entire 1-year immersion period. Sample 4 which has an additional loading of UV stabilizer shows some effect but the other samples show little change over the same period.

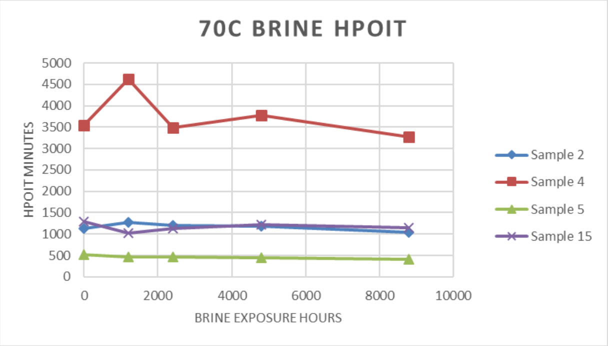

Figure 6. HPOIT results at 70C

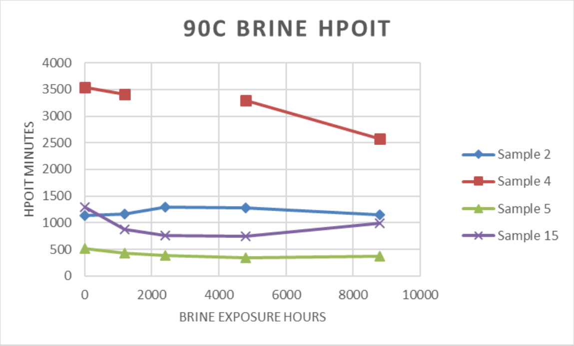

Figure 7. HPOIT results at 90C

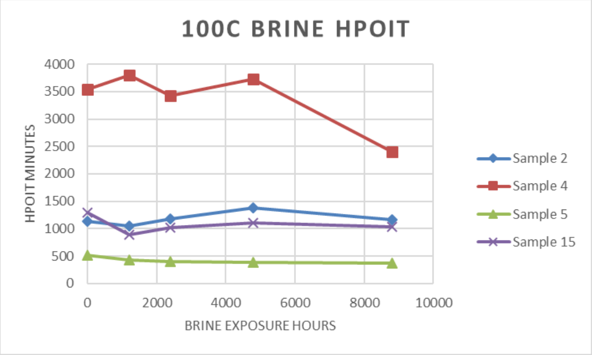

Figure 8. HPOIT results at 100C

Let's focus our attention on the OIT results then and look at three of the materials from the study. Sample 2 is first. This standard HDPE material is normally only rated for 60C service. In Figure 9 the results show that the 70C immersion declines to a residual OIT in 4800 hours but that at 90C and 100C the OITs decline to a residual in only 1200 hours.

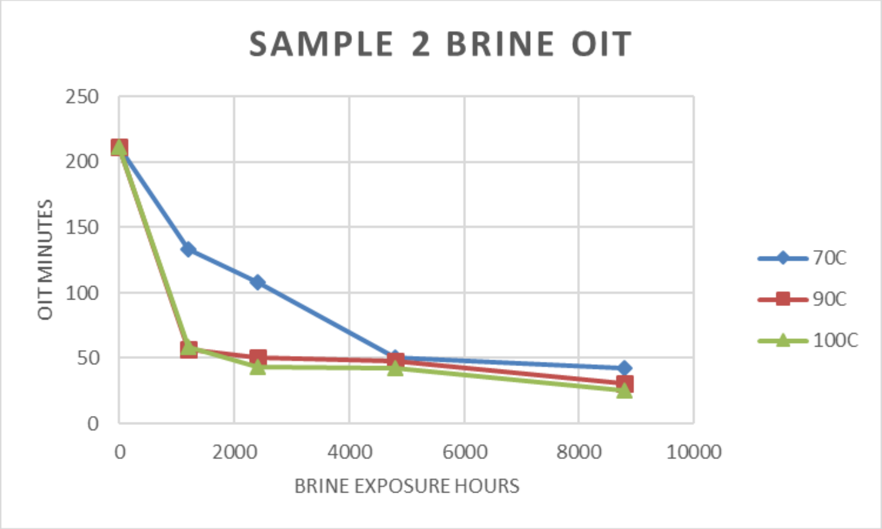

Figure 9. Sample 2 OIT results

Sample 15 shows better resistance to brine (figure 10). This sample has a fairly linear depletion of AO at 70C. At 90C and 100C the sample shows a decrease to 4800 hours and then appears to reach a residual OIT. The 90C and 100C lines appear to cross at 2400 hours however this appears to reinforce the earlier observation that the 90C and 100C results are very similar.

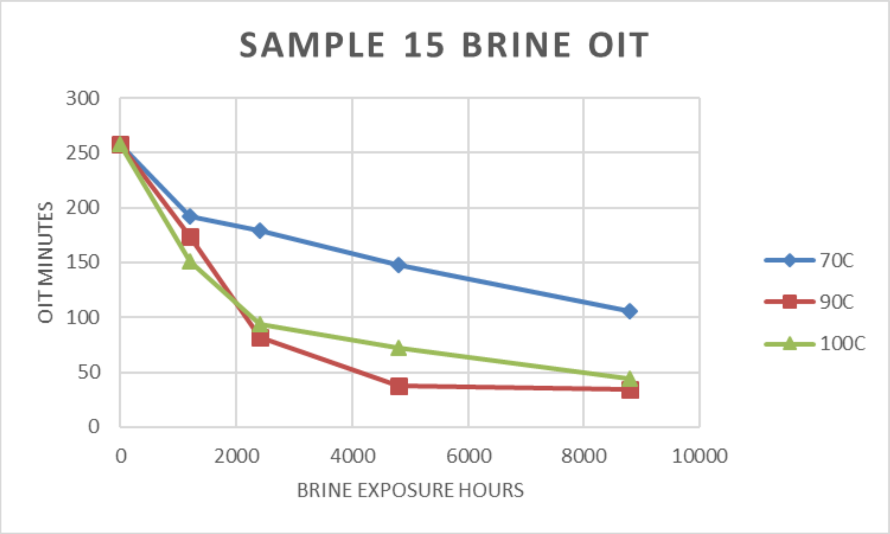

Figure 10. Sample 15 HPOIT results

Sample 5 is the material that was chosen for our new high temp geomembrane development and has been commercialized as the HEATGARD HDPE geomembrane. In figure 11 the 70C curve is smooth and at a lower slope than all other samples. The 90C and 100C curves are also at lower slopes than all the other samples implying a slower overall loss of AO. The 90C and 100C curves cross over after 4800 hours but once again this is likely because the two temperatures are showing very similar results.

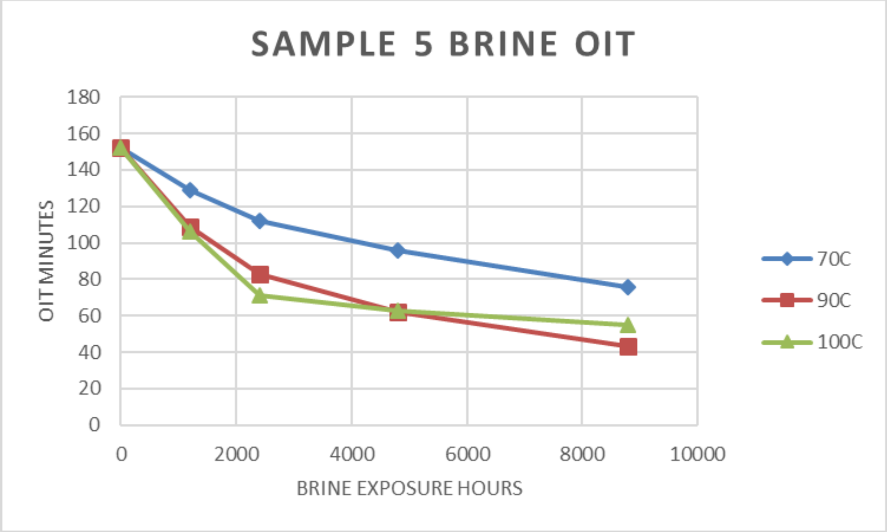

Figure 11. Sample 5 HPOIT results

In previous studies of these materials; Mills, Beaumier (2017); and Rangel et al (2017) an Arrhenius model was prepared that let us extrapolate the time to AO depletion from temperature. In this study on brine it does not appear that an effective Arrhenius model can be plotted from the data. In sample 2 (figure 9) there is not enough differentiation between the 90C and 100C curves. In sample 15 and 5 (figures 10 and 11) the 90C and 100C curves cross over themselves.

CONCLUSION

The exposure of HDPE geomembranes to high temperature brine depletes the antioxidant levels as measured by the OIT test. Testing with the HPOIT test does not show changes significant to be able to predict service life. This testing exposed HDPE materials for a year to determine the antioxidant depletion rate at elevated temperatures.

Special grades of HDPE from the pipe industry designed for higher temperatures showed better performance in brine immersions and better retention of antioxidants at elevated temperatures. The newly developed geomembrane represented by sample 5 in this study has better resistance to hot brine than regular HDPE geomembrane materials.

REFERENCES

Mills A., (2015) *Geomembrane Resistance to Hot Brine in Produced Water and Flowback Applications,* Geosynthetics 2015, Portland Oregon (2015)

Rangel E., Mills A., Beaumier D., Fraser B., (2017) *A new geomembrane for chlorinated water containment*, Geosynthetics 2017, Santiago Chile (2017)

Mills A., Beaumier D., (2017) *Long-term Performance of HDPE Geomembranes Exposed to High Service Temperature*, Geotechnical Frontiers 2017, Orlando Florida (2017)

Beaumier D., Mills A., Dolez P., Blond E., (2016) *Tensile resistance of geomembranes for high temperature applications*, GEOVANCOUVER, Canadian Geotechnical Conference, Vancouver B.C. (2016)

American Standard for Testing Materials (2015), *Standard Test Method for Oxidative Induction Time of Polyolefin Geosynthetics by High-Pressure Differential Scanning Calorimetry*, D5885/D5885M-15.

Abdelaal F. B., Rowe K. R. (2014), *Effect of High Temperatures on antioxidant depletion from different HDPE geomembranes,* Geotextiles and Geomembranes, 42 (2014), 284-301.

American Standard for Testing Materials (2014), *Standard Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry*, D3895-14.

Rowe K. R., Ewais A. M. R. (2014), *Antioxidant depletion from five geomembranes of same resin but different thicknesses immersed in leachate*, Geotextiles and Geomembranes, 42 (2014), 540-554.

American Standard for Testing Materials (2013), *Standard Practice for Air-Oven Aging of Polyolefins Geomembranes*, D5721-08 (2013).

Plastic Pipe Institute (2013), *TR-4 HDB/HDS/SBD/PBD/MRS Listed Materials*.

Mills A. (2011) *The Effects of Chlorine on Very Low Density Thermoplastic Olefins Geomembranes Exposed to High Service Temperature*, Geo-Frontiers 2011, Dallas TX (2011)

Rowe K. R., Islam M. Z., Brachmann R. W. I., Arnepalli D. N. and Ewais A. R. (2010), *Antioxidant Depletion from a High Density Polyethylene Geomembrane under Simulated Landfill Conditions*, Journal of Geotechnical and Geo-environmental Engineering, ASCE, V. 136, No. 7.

American Standard for Testing Materials (2010), *Standard Practice for Molding Thermoplastic Materials into Test Specimens, Plaques, or Sheets*, D4703-10a.

Koerner R. M., Hsuan Y. G. (2002), *Antioxidant Depletion Time in High Density Polyethylene Geomembranes*, United States Environmental Protection Agency, EPA/600/R-02/099 Appendix B.

Hsuan Y. G., Koerner R. M. (1999), *Antioxidant Depletion Lifetime in High Density Polyethylene Geomembranes, Journal of Geotechnical and Geo-environmental Engineering*, ASCE, V. 124, No. 6.