A new geomembrane for chlorinated water containment

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ABSTRACT

While it is common to think that drinking water is easy to contain in plastic containers the long-term containment of potable water is actually quite difficult. Chlorine is a strong oxidizer and can adversely affect the plastics used in water containment such as the piping, valves, seals, and geomembranes. Water that is purified by the reverse osmosis (RO) treatment method is even more aggressive. Reverse osmosis can create a shortage of calcium ions in the water which makes the water more corrosive. Calcium-deficient water will attack concrete, steel, and plastic pipe. Adding chlorine to reverse osmosis water accelerates the oxidation of plastic components in the containment area.

The authors will present their evaluation of a new geomembrane material that shows a significant improvement in chlorine resistance over previously available geomembranes. Chlorine immersion tests were conducted over a two year period at three different temperatures in a strong chlorine solution. The results of these chlorine immersions have been developed into an Arrhenius model that can predict the anti-oxidant retention time based on most containment operating temperatures. Additional tests were performed in calcium-deficient water to model the behaviour of the geomembrane in reverse osmosis water containment applications.

INTRODUCTION

This paper is the second in a series that outlines the results of a geomembrane study being done by Layfield. The 3-year study, funded in part by a government grant, is investigating a new class of high performance high-density polyethylene (HDPE) resins to see what new classes of geomembranes can be developed. This subject of this paper is chlorine resistance. One of the resins being investigated has shown significantly better resistance to oxidation in chlorinated water testing and those tests are detailed below. The chlorine tests culminate in an Arrhenius model of temperature versus time to depletion of antioxidant which is an important development that has not existed previously. As a result of these tests a new formulation of geomembrane is presented that has significantly improved chlorine resistance.

BACKGROUND

The use of polyolefins such as polyethylene, polypropylene, and polybutylene in potable water service has been challenging. Polyolefins appear to be more susceptible to oxidation caused by the disinfectants used in potable water such as chlorine, sodium hypochlorite, chlorine dioxide, and chloramines. The advantage of polyolefins is that they have an initial low cost so there continues to be development of polyolefins for potable water use.

Oxidation of polyolefins in potable water systems has led to a number of project problems. Polybutylene pipe was withdrawn from potable water service after a number of oxidative failures such as the examples outlined by Zhou et al (1996). Another example of oxidative failure of a thermoplastic polyolefin material used in geomembrane service is described in Mills (2011).

In recent years there have been additional failures in polyolefin pipe and geomembranes when exposed to Reverse Osmosis (RO) water. Reverse Osmosis is the process where water is forced at very high pressure through a membrane so that it disassociates into individual molecules. The water molecules are forced through the membrane and ions such as salt are prevented from passing. As fresh water sources become less available there are more RO treatment systems being installed, mostly in desalination plants. The use of desalinated seawater in mining has been growing in Chile in recent years and will soon provide more water that fresh water sources.

RO treatment removes salt and other ions from water and is one method for creating deionized water. Water has a natural affinity for calcium and deionized water is deficient in calcium. The level of dissolved calcium in water is measured using the Langelier Saturation Index (LSI). Water with an LSI of 0 is in balance and does not usually have adverse effects. Water with an LSI that is greater than 0 will have a tendency to deposit calcium. Water with an LSI of less than 0 creates a demand for calcium by the water. This can lead to corrosion in piping and tanks in a water system. The demand for calcium erodes concrete and can lead to premature pipe failure. Processing water with an RO system creates strongly negative LSI levels which can be highly corrosive. The effect of chlorine in very low LSI water appears to be more aggressive than chlorine in balanced LSI water. This leads to a stronger oxidative potential which can damage plastics such as geomembranes. A discussion of the effect of negative LSI water on polyolefins is outlined in Fraser and Mills (2015).

Finally, it is difficult to determine the long term suitability of a polyolefin for chlorinated water containment as the available testing methods are difficult to extrapolate into the future. In Mills, Beaumier (2017) we demonstrated that potable water pipe testing was not an accurate prediction of geomembrane service life (even for the same polyethylene material). In this series of tests we have attempted to extrapolate the resistance to chlorinated water (and low LSI water) to determine a suitable geomembrane lifetime.

METHODOLOGY

Our methodology consists of a protocol that was developed to evaluate geomembrane resistance to chlorine. The methodology consists of an immersion protocol and then evaluation of the specimens after immersion. Two tests are presented in this paper; a long term chlorine immersion test, and an LSI test.

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 chlorine solution and 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 (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 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 oxygen at ambient pressure. OIT testing typically reveals the residual level of anti-oxidant in a specimen. The HPOIT test uses a test temperature of 150C but with a higher oxygen pressure of 3.4 mPa. HPOIT testing typically reveals the residual level of UV stabilizers which can also contribute to long term stability. The results in this paper will focus on the OIT evaluation results.

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 chlorine immersion test

The long term chlorine 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 chlorine testing which was part of that larger study. Still to be published from that study are the results from long term brine immersions. Only a few of the materials tested in the larger study are reported here as the other materials were eliminated for early poor performance.

The materials from the long term chlorine immersion study that will be reported here are Sample 2 which is a standard HDPE geomembrane; 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 claimed to have long term chlorine resistance.

The basic test solution contained 5 ppm free chlorine in water. This chlorine solution was prepared from technical grade sodium hypochlorite. The water used for preparing the solutions was de-ionized water which has a negative LSI. The chlorine solutions were adjusted back to a 0 LSI level and a pH of 7.0 through the addition of sodium carbonate, calcium sulfate, magnesium sulfate, and potassium chloride. A large pre-mixed batch of this solution was prepared prior to the test.

The solutions in the immersion test tubes were changed every week from the pre-mixed batch to maintain the potency of the solution. The pre-mixed batch was tested periodically to ensure that the pH, LSI, and chlorine levels were constant.

Three test temperatures were chosen for these immersions. The test tubes were placed in either an oven or a liquid bath to maintain temperatures. The three test temperatures used were 50C, 70C, and 90C. In the test standard ASTM D1693 the instructions are to maintain the test temperature in a water bath.

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, and 8800 hours (1 year). 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.

LSI Testing

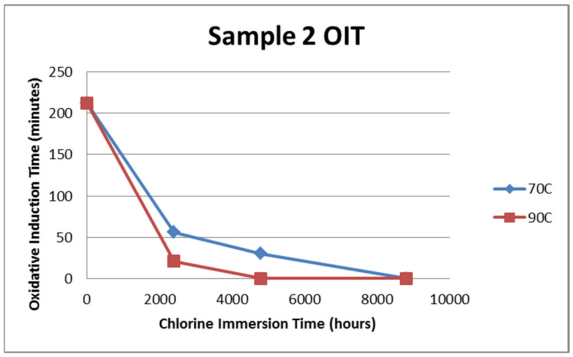
The second test was conducted to investigate the effects of water with a negative Langelier Saturation Index (LSI) on various polymers. This test also used our immersion testing protocol but used different liquids. In this LSI study solution A was a 5 ppm chlorine solution with an LSI of -4; solution B had no chlorine with an LSI of -4; and solution C had a 5 ppm chlorine solution with an LSI of 0.

Materials reported in this test are sample 2 and sample 5 from the long-term chlorine immersion test. Sample preparation, handling and evaluation were done in the same manner as the long-term chlorine immersion test.

RESULTS AND DISCUSSION

Long-term chlorine immersion results

OIT evaluation results are shown in Figure 1 for sample 2, Figure 2, for sample 15.



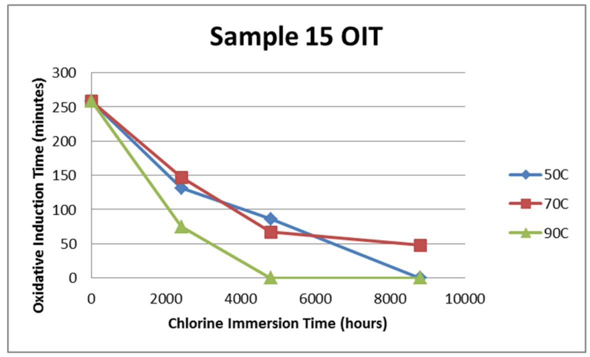


Figure 1 Sample 2 OIT results

Figure 2 Sample 15 OIT results

Sample 2 results fall rapidly in the first 4800 hours. The 50C results (not shown) are 0 at the 4800 hour mark. Sample 15 did better but still fell to 0 at the 50C and 90C test temperatures. Sample 15 results did not follow a predictable pattern with different temperatures behaving differently.

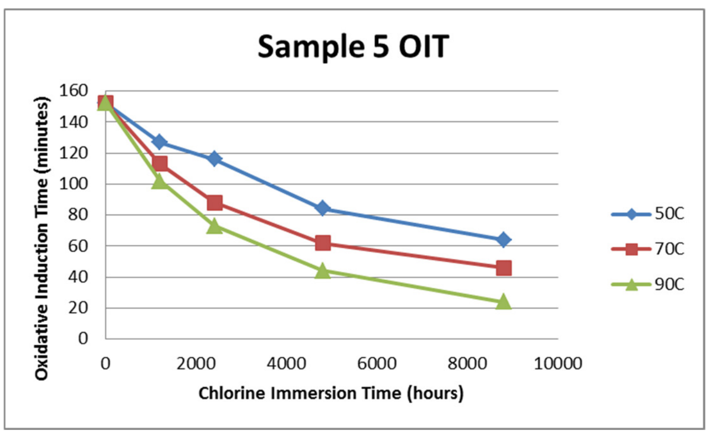
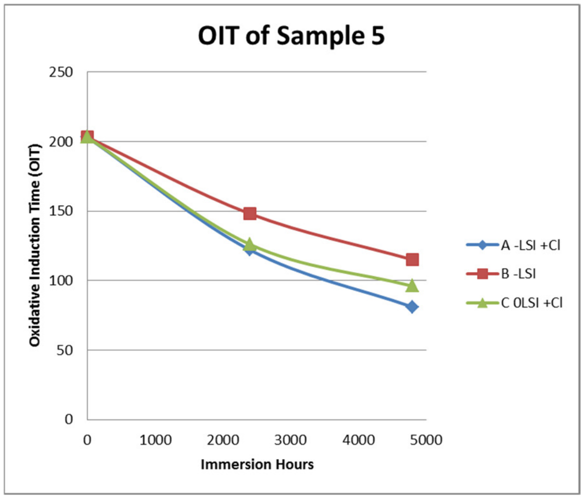


Figure 3 Sample 5 OIT results

Sample 5 OIT results are shown in Figure 3. The response of sample 5 to chlorine immersion appears to be regular and predictable. From these results we went on to prepare an Arrhenius model to predict longevity in a chlorinated water environment.

LSI Testing

The results of the LSI testing are shown in Figure 4 and 5.



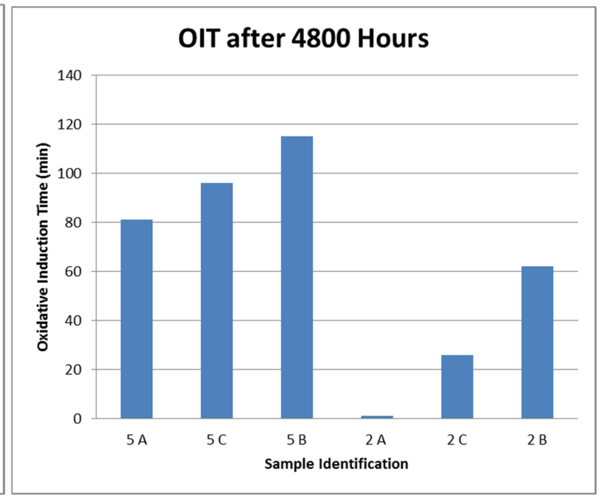


Figure 4 Sample 5 OIT in three solutions

Figure 5 OIT of sample 5 and 2 after 4800 hours

Solution A with chlorine and a low LSI level was the most aggressive showing that a negative LSI can accelerate the oxidative attack of chlorine. Solution C with chlorine and a balanced LSI was the next most aggressive, while solution B with a low LSI and no chlorine was the least aggressive.

Arrhenius model of the long-term chlorine immersion test

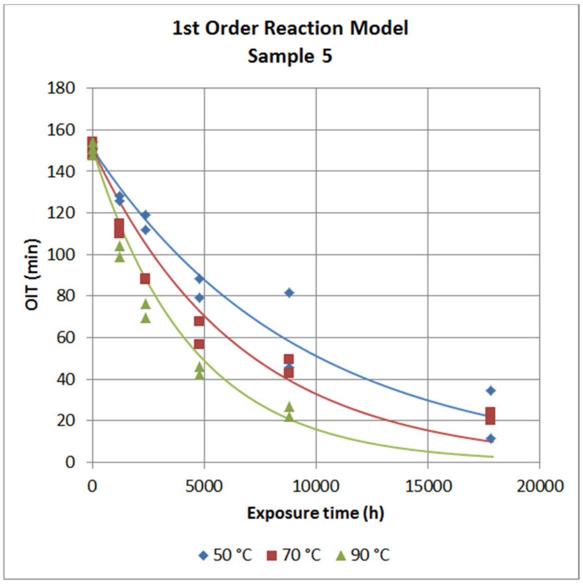
The Arrhenius model was used for the projection of antioxidant depletion after the long-term immersion to the 5-ppm chlorine solution. This approach was applied to geomembranes by Hsuan and Koerner (1998); modelling the antioxidant depletion as a first-order reaction with the rate of depletion (S) being related to the temperature (T) by the Arrhenius equation 1.

$$S = A \cdot e^{-(Ea / RT)} \tag{1}$$

In this testing the antioxidant depletion by OIT showed a better correlation using a second-order reaction than a first order reaction. Figure 6 and 7 show the first and second order curves, respectively. The second order reaction appears to show a better fit with the more rapid initial loss. Using the second-order reaction model, the antioxidant depletion follows equation 2.

$$OIT = (1/ OIT_i + k_2 * t)^{-1} \tag{2}$$

The depletion rate of antioxidants in chlorinated water is quite different than depletion in air only (such as an oven aging test). In chlorinated water, the depletion of antioxidants will be caused by both a reaction with chlorine and a reaction to oxygen (Singh, 2011). This accelerates the reaction rate. The second-order reaction rate was empirically determined by curve fitting in Figure 7. Second order reaction curves were also fit to the sample 2 and 15 OIT results.



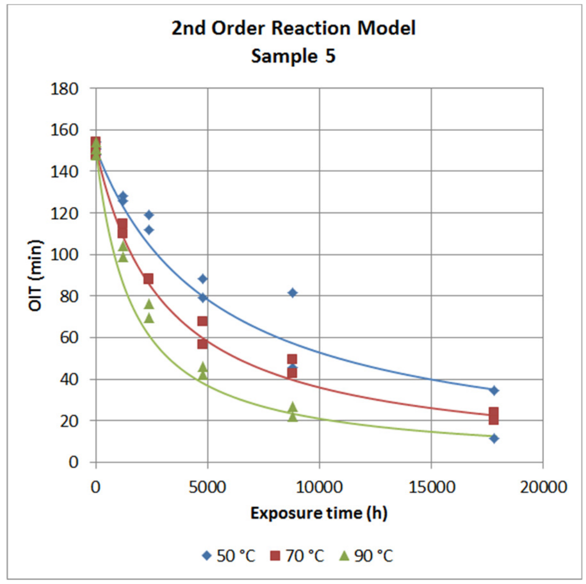


Figure 6 Sample 5 model by a 1st order reaction.

Figure 7 Sample 5 model by a 2nd order reaction.

From the Arrhenius projection and modelling with a second-order reaction, the long-term projection of samples 2, 5, and 15 are compared on Figure 8. Sample 5 shows significant improvement over 2 and 15. Sample 2, which is the regular HDPE geomembrane, shows only a 3 year time to depletion of antioxidant at 20C while sample 15 is marginally better at 5 years. Sample 5 shows a much better time to antioxidant depletion of 56 years at 20C and 26 years at 40C.

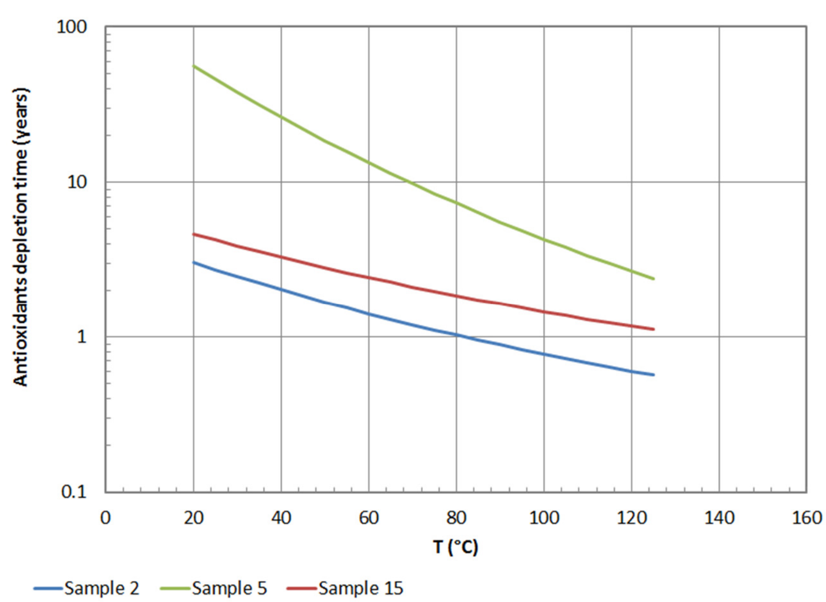


Figure 8 Antioxidant depletion using Arrhenius model, from exposure to chlorine water

A NEW POTABLE WATER GEOMEMBRANE

The resin formulation identified in this testing as sample 5 has been developed into a geomembrane and is commercially available. Key properties include potable water safety, predictable chlorine life expectancy, and excellent UV resistance in a black material. This material also has a long service life at elevated temperatures as presented in Mills and Beaumier (2017). This new geomembrane is installed using standard HDPE installation techniques.

CONCLUSION

Long term chlorine testing and testing in low LSI water solutions have identified a new formulation of HDPE that is better suited to chlorinated water storage than currently available materials. Using an Arrhenius projection the new formulation showed a predicted time to depletion of antioxidants of 56 years at 20C. Actual field service results may be different; however, the resistance to oxidation by chlorinated water in these lab tests showed that this new material is significantly better than current HDPE geomembranes.

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