

Geomembrane Resistance to Hot Brine in Produced Water and Flowback Applications

Andrew Mills, C.E.T., Layfield Canada Ltd, Canada, amills@layfieldgroup.com

ABSTRACT

There are a number of developing geomembrane applications where hot salt water needs to be contained over the long term. One application is in hydraulic fracturing operations (fracing), where salt water comes up from underground as a by-product of drilling. The two types of returned water include produced water (which originates in the formation) and flowback water (which is water returned from fracturing). A second application is the bypass water from Reverse Osmosis (RO) water treatment systems which is sometimes used as a water treatment method for recycling water for oilfield use. Both of these applications create high salt content water, which needs to be stored. Salt water storage applications become more critical when the salt water needs to be stored for an extended period of time. This paper describes the development of a testing protocol to accelerate testing with hot brine solutions and the results of that testing.

1. INTRODUCTION

1.1 Background

In Australia, hydraulic fracturing and reverse osmosis operations produce a lot of hot salt water. This water is left to evaporate in lined ponds or stored until an alternate disposal method is available. In evaporation ponds, the salt becomes increasingly concentrated, while in long term salt storage ponds, the liquid starts at high salt concentrations. Since both the evaporation ponds and the salt storage ponds are in very warm areas, the ponds' temperatures can be significant. Storage temperatures of up to 60C are common in Australia.

Hot salt water is also generated by oil field operations in the form of produced water. This water is released from the geologic formation and comes to the surface as hot salty water. This water often needs to be stored for short periods; however, the temperature of this water when it surfaces can be 80C or more (depending on the depth of origin). As more produced water is brought to the surface, additional storage and disposal methods are needed, and evaporation and storage ponds look like good options. We were challenged to find a way of verifying that geomembranes could provide long term service for salt water storage, produced water, and salt water evaporation ponds.

1.2 Produced Water

"During hydrocarbon exploration and extraction, water is typically co-produced from the same subsurface geologic formations" (USGS Produced Waters website). Produced water is a growing concern in a number of areas as several contaminants can come out of the ground with this water. The most common contaminants are salts, and in some regions, the produced water is saltier than seawater. Locations in North America with high salt content produced water include large areas of New Mexico; however, individual highly saline wells can be located in many drilling areas.

Disposal of produced water in many areas is a difficult problem, and accidental release can contaminate surface water and subsurface aquifers. Current research is investigating an underground plume of brine from reserve pits (a type of pond) in the Williston Basin area of the US (Gleason et al, 2014). Concerns for the containment of produced water could lead to restrictions on

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oil and gas recovery in the future. Confirming the effectiveness of geomembranes for produced water containment is important to help sustain the safe operations of this industry.

1.3 Reverse Osmosis

In Australia, the lack of water in many areas has led to the widespread adoption of Reverse Osmosis (RO) water treatment systems. These systems are used in municipal, industrial, mining, and oil and gas water treatment systems. Each RO treatment system produces a stream of bypass water that contains all the ions that are removed from the water. This bypass water can have a very high salt content. RO is sometimes used to treat recovered water from oil and gas operations. This results in a stream of reusable water along with a smaller quantity of highly saline bypass brine. Many of the locations where this treatment method is used are remote sites, and disposal options are few. In Australia, the remote locations also have some of the hottest temperatures, so brine storage temperatures are high. Permanent brine storage in lined geomembrane containment is an important option for facility operators.

2. TESTING PROTOCOLS

2.1 Selecting the Methods

To help answer this salt water problem, we used two testing protocols. The first protocol was proposed by the researcher, John Scheirs, of the testing lab Excelplas in Australia. That first protocol used unstressed samples suspended in brine at a number of temperatures. The second test protocol (the stressed testing) was one that we first used in 2007 for monitoring the chemical interaction of antioxidants in PP geomembranes (Mills 2011). We've since learned that John Scheirs had also been using a similar method to investigate chemical interactions; however, at the time of this investigation, we did not know he was also using the stressed method. Both the stressed and unstressed methods were used in this evaluation.

2.2 Materials and Sample Preparation

The main material investigated in this evaluation was a proprietary polyolefin material with an exceptionally high loading of antioxidants. The trade name of this material is Enviro Liner® 6000HD, and will be identified throughout this paper as Polyolefin A. In 2014 we added a second material which is sold into the North American oil and gas market, which is identified by the trade name Enviro Liner® 1000. This material will be identified throughout this paper as Polyolefin B. Polyolefin A is a flexible geomembrane material with very high loadings of UV and antioxidants.

Polyolefin B has more modest antioxidant loadings reflective of other geomembranes in common use. In the unstressed testing protocol, individual test specimens were cut from sheet material that was 1.0 mm thick. The test specimens were cut to conform to the after-immersion tests, such as tensile testing, as illustrated in Figure 2. In the stressed testing protocol, the sheet material was blended for 3 minutes on a two-roll mill and then compression molded to a 3 mm thick plate. Specimens of the materials were die-cut from these plates and then scored with a razor knife. These specimens were then bent into the appropriate holder for the test, as shown in Figure 3.

2.3 Immersion Test Liquid

The selection of the salt solution started with a project inquiry from Australia. An oilfield client had several brine containment ponds to build and was looking for assistance in evaluating geomembranes. The selection of the three salts shown in Table 1 was based on discussions with that Australian client. These three salts are common in the concentrated brine solutions in the region of Australia where our client was operating. Note that a solution of this composition is fairly basic and has a pH of around 11. All the testing reported in this paper used this particular brine solution for the test liquid.

Table 1. Salt Solution

Ingredient	g/L
Sodium Chloride	100
Sodium Bicarbonate	62
Sodium Carbonate	50

2.4 Antioxidant Testing

Once the samples completed their immersion testing, one of the key evaluations was to measure residual antioxidant levels. ASTM D5885 High Pressure Oxidative Induction Time (HP OIT) was used for this evaluation. The HP OIT test applies heat in the presence of 3500kPa (500 psi) of oxygen to accelerate the consumption of antioxidants. When the antioxidant is consumed, the heat flow of the sample rapidly accelerates until the sample is consumed. Essentially the antioxidant prevents the specimen from burning until the antioxidant is consumed, at which point the sample is burned rapidly. Figure 1 shows the rapid spike in heat flow, which indicates when the antioxidant is depleted. Figure 1 shows the plot of heat flow for one of the stressed samples exposed for 300 hours.

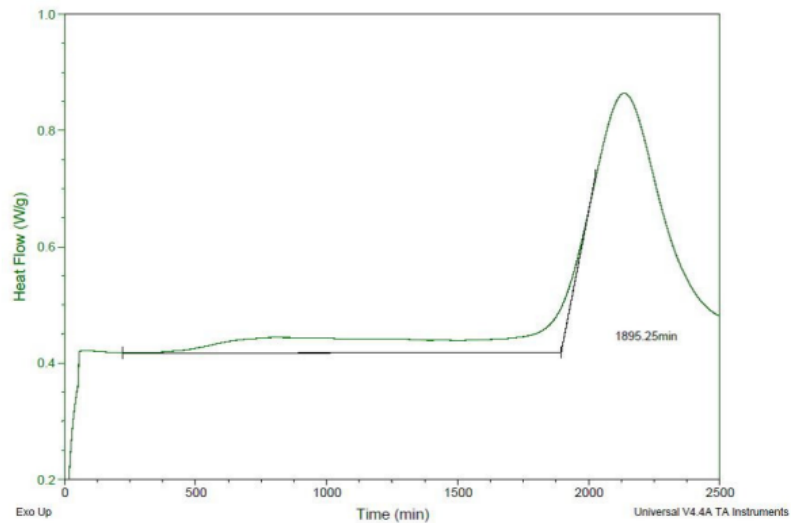


Figure 1. HP OIT plot showing 1,895 minutes.

The HP OIT test is a measure of the performance of the antioxidant and does not actually measure the presence of the antioxidant chemical. Tests that measure the actual chemical levels of antioxidants may be in error, as chemical reactions may deactivate antioxidants while they are still physically present. The HP OIT test measures the effective levels of antioxidants that remain when the sample is tested and is a more accurate measurement.

2.5 Unstressed Immersion Testing

The unstressed immersion test protocol suspended pre-cut specimens of 1 mm Polyolefin A in the brine solution according to ASTM D5747. Four test temperatures were used; Room temperature, 85C, 95C, and 105C. Special frames were built to suspend the specimens as there were issues with keeping the specimens upright in the solution due to the high density of the liquid. Specimens were immersed for 6 weeks (1000 hours) before evaluation. Each covered test vessel was heated and maintained at the appropriate temperature for the duration of the test. The liquid in each pot was stirred every two days and topped up as needed with fresh solution. Images of the test set up are in Figure 2. Testing after immersion included physical changes such as weight, thickness, and volume changes. The samples were also tested for tensile, elongation, and antioxidant retention (HPOIT).



Figure 2. Pre-cut specimens in special sample holders and immersed in the brine solution.

2.6 Stressed Immersion Testing

The stressed immersion testing protocol used a stressed specimen of the geomembrane in a heated, concentrated brine solution to accelerate antioxidant depletion. This testing protocol had worked well in previous testing by this author in evaluating antioxidant depletion in PP geomembranes in chlorine solutions (Mills 2011). The brine testing used the same testing protocol but with a concentrated salt solution. The stressed immersion testing protocol follows the changes in antioxidant levels to see if, at some point, the antioxidant levels stabilize. There are two parts to this protocol; the immersion testing and the antioxidant evaluation.

Chemically challenging a polymer involves chemical concentration, heat, and stress. The stressed test protocol used ASTM D1693 for the chemical immersion. In the ASTM D1693 test, the polymer is moulded into a specimen that is 3 mm thick. The specimen was cut into a strip and scored with a razor blade to make a stress concentration point. The strip was then bent 180 degrees and

held in a test frame, illustrated in Figure 3. The test frame is placed in a test tube full of the immersion liquid and then heated to a test temperature.

For the salt solution testing, the test liquid and temperature were changed from that specified in ASTM D1693. This model accelerated degradation using a hot salt water solution. This test used a 90C test temperature and a salt solution with the ingredients listed in Table 1.

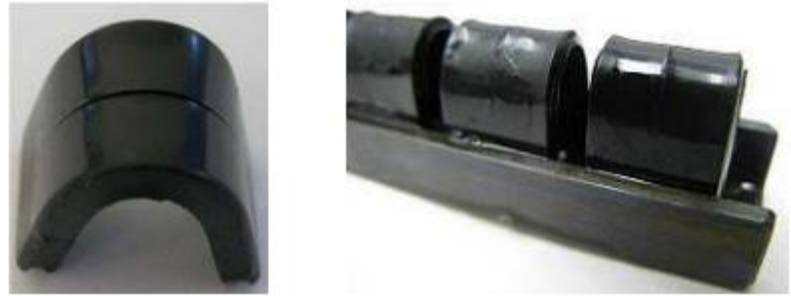


Figure 3. Bent strip specimen and position in holder.

In order to maintain the chemistry of the solution, a large volume of the solution was made up in advance. The test tubes containing the specimens had the liquid changed each week with a fresh charge of the prepared solution. This ensured that the chemical properties of the salt solution remained constant over the test period.

Polyolefin A was immersed for 2,400 hours (100 days) in 2011 in the first round of testing. The 2,400 hour immersion did not appear to show an endpoint to the testing, so it was repeated in 2013/14. This second round extended the immersion period to 4,800 hours (200 days). The 2013/2014 test included samples of both Polyolefin A and Polyolefin B.

The materials were evaluated with HP OIT after 150 hours, 300 hours, 600 hours, 1200 hours, 2400 hours, and 4800 hours of immersion time (the actual time may vary, but these were the targeted immersion times). At the end of each of these immersion periods, the samples were visually inspected to see if any cracking had occurred. Then the samples were sent for antioxidant testing.

3.RESULTS

The first results available were the tensile tests from the unstressed immersion. Evaluation of changes in weight, volume, and thickness did not show significant changes. Tensile testing results are shown in Figure 4. Although there appears to be a slight downward trend with increasing temperature the results were not considered conclusive. The final evaluation of the unstressed immersion specimens used the HP OIT test. In this case only the 105C immersion specimens were tested. The HP OIT results for the unstressed immersion specimens are included in Figure 5.

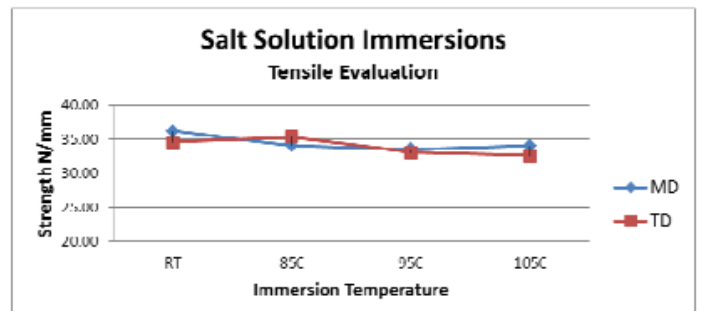


Figure 4. Tensile evaluation of the unstressed immersion samples.

The evaluation of the stressed immersion specimens was done exclusively by HP OIT testing. The results of the HP OIT testing are shown in the graph in Figure 5. The graph shows the two tests run in the stressed condition on Polyolefin A in 2011 and 2014 as well as the data from the unstressed immersion test on Polyolefin A run in 2011. The specimens tested from the unstressed test were the 105C immersion specimens. The immersion test results for Polyolefin B in 2014 are also shown.

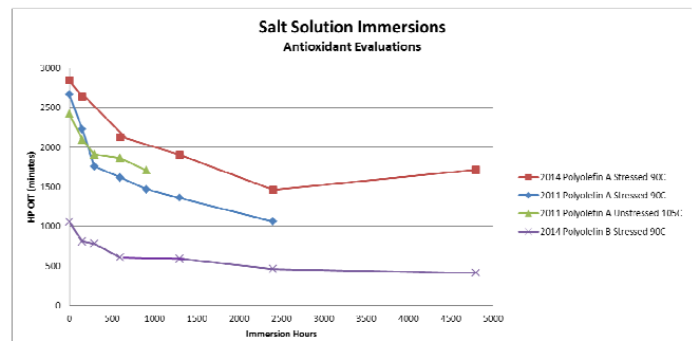


Figure 5. HPOIT results for salt solution testing.

4. DISCUSSION

Initial exposure to a strong brine solution using an unstressed immersion method had minimal effect on the physical properties of the materials tested. While there appeared to be a slight downward trend in the tensile values in Figure 4 the amount was not sufficient to form clear conclusions. The HP OIT testing of the antioxidant levels showed that the brine was having an effect. In

the initial testing in 2011 the HP OIT tests did not reach a steady state. The first round of tests stopped at 1,000 and 2,400 hours of immersion which did not appear to be sufficient time to allow these materials to stabilize.

When the stressed immersion testing was repeated in 2013/2014 the immersions were carried out to 4,800 hours. Both Polyolefin A and Polyolefin B appeared to stabilize after 2,400 hours and achieved a fairly steady state.

Polyolefin A is a heavily stabilized material which is identified by the manufacturer as a fortified geomembrane. The additional stabilizers in that formulation gave it a higher initial starting point which appeared to help it maintain stabilization after long term immersion. Standard geomembranes have a specification for HP OIT of 400 minutes (GRIGM17). In this testing both samples of Polyolefin A started well above 2,500 minutes of HP OIT and maintained a level above 1,000 minutes after 2,400 hours of immersion. Polyolefin B started with an HP OIT above 1,000 minutes and maintained a level above 400 minutes after 4,800 hours of testing. This near steady state after 2,400 hours of immersion at 90C is a positive indicator that these materials would last many years as brine containment geomembranes at lower temperatures.

5. CONCLUSION

Over the past 3 years immersion testing in concentrated brine was carried out on two polyolefin geomembrane materials. Initial testing of samples that were immersed in an unstressed immersion did not show significant physical property changes. The first study of antioxidant loss after a stressed immersion of 2,400 hours did not reach a steady state. The second round of stressed immersion tests on two polyolefin materials showed that antioxidant depletion stabilized after 2,400 hours and that the materials appeared to achieve a steady state. Fortified geomembranes with a higher starting level of HP OIT retained a higher level HP OIT after immersion testing. The steady state level of antioxidants in the geomembrane materials appeared to be suitable for long term exposure to brine.

The materials tested appeared to reach a near steady state of antioxidant depletion after 2,400 hours of stressed immersion at 90C. With its higher initial level of antioxidants and higher retained level after immersions the Polyolefin A would be a good candidate for the long term containment of brine solutions. Polyolefin B is also suitable for brine containment but does not have the additional cushion of antioxidant of the fortified Polyolefin A material and would therefore be suitable for shorter periods.

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