

Geomembrane Performance Testing - Impacts of a Negative Langelier Saturation Index on Geomembranes

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ABSTRACT

In 2013, we were informed of a possible failure of a linear low density (LLDPE) liner used in a reverse osmosis potable water treatment application in Australia. Further testing confirmed the material had a premature loss of antioxidants resulting in surface cracking and welding problems. Additional analysis confirmed the fluid had an unusually negative Langelier Saturation Index (LSI) of -3.5. It was determined that a negative 3.5 LSI indicated the water was extremely under saturated with calcium carbonate resulting in a highly corrosive environment to the liner and distribution system. This paper explains the research undertaken to investigate the impacts of a negative LSI and the performance testing completed to determine a suitable replacement geomembrane.

1. INTRODUCTION

In 2013, we were informed of some welding problems as part of a repair being performed on a 1.00 mm (40 mil) Linear Low Density Polyethylene (LLDPE) liner in Australia. The project included a geomembrane liner and floating cover system for a 60 million litre (15.8 million gallon) potable water storage facility in a rural region of Australia. The water treatment system feeding this pond used a reverse osmosis (RO) system exclusively. This paper describes the problems that were encountered, the investigations into the theory of the Langelier Saturation Index that appeared to be a contributing factor, and the testing conducted to verify a suitable replacement liner and cover.

Reverse Osmosis is used extensively in Australia to prepare potable water from brackish surface or ground water. Water is forced through a semi-permeable membrane at high pressures to remove salts and other impurities. Reverse Osmosis is used for the desalination of seawater and brackish water. The RO process removes many types of molecules and ions from solutions and is used in both industrial processes and for the production of potable water.

2. BACKGROUND

The initial geomembrane liner and floating cover materials were supplied and installed late in 2010. In 2012, structural modifications to the pond required repairs to the liner. These repairs included replacing an older plastic inlet pipe which had shown major deterioration. The repair consisted of pulling back the floating cover, removing a concrete structure in the pond and then repairing the geomembrane and the cover. The first indications of a problem showed up during the liner repair with the installer having difficulty making extrusion welds. The installer made what adjustments they could at the time, the repair was completed, and the pond put back into service.

3. INSPECTION

The following year there appeared to be leakage in the leak detection system and the owner hired a third party QC firm to perform an inspection. The inspector quickly found that there were problems with the repair welds and a number of the extrusion beads had come loose with resulting seam failures. Analysis of the welds showed an unusual lack of antioxidants and some cracking and crazing around the inlet pipe. The liner appeared to have been oxidized on the surface which made welding difficult. This led to a more detailed inspection where the floating cover was inflated. Inspection of the liner surface under the cover showed cracking and crazing on the bottom of the pond and in some limited areas on the slopes. The liner was cracking where it had been folded due to water pressure.



Figure 1. Damage at the top of a fold in the liner

The second issue was completely unexpected. Once the inspectors looked at the cover they were surprised to see blisters covering most of the bottom of the cover. Most of the blisters were small and tightly spaced but a few larger ones were present. When cut the blisters appeared to be filled with water. The cover material had been made on 3-layer coextrusion equipment with 15%/70%/15% layer ratio. When the blisters were measured they were consistently half-way through the bottom skin layer. The bottom skin layer and the core layer were of identical formulations.

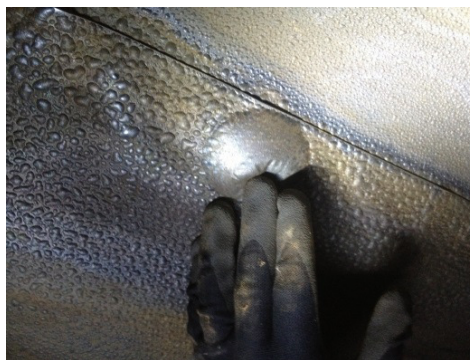


Figure 2. Blistering in the underside of the floating cover.

4. INITIAL TESTS

At this point we started our investigation. We tested residual antioxidants with HPOIT testing; we performed FTIR scans, and did SEM microscopic investigation of the surface and the cross section of the material. This analysis showed that the material had failed due to oxidative cracking brought on by the presence of chlorine. "Oxidative degradation embrittles the geomembrane making it more susceptible to stress cracking and lowering the material tensile strengths" (Schiers 2009).

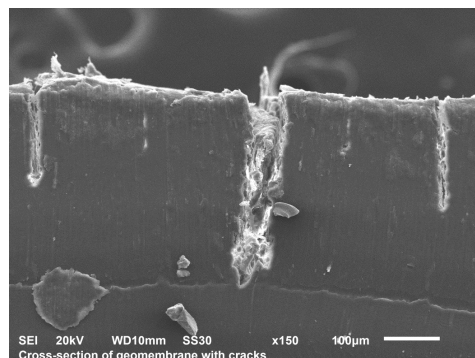


Figure 3. SEM view of cross section showing cracking.

5. INVESTIGATION

We initially had no immediate answers as to what appeared to be causing the premature material failure. At that point we started research into the RO process and RO geomembrane applications used in both Australia and North America. We were familiar with reports of prior geomembrane failures in Australia linked to RO water containment but not in LLDPE materials.

This led us to take a closer look at the water in the ponds. This is a remote site and water is scarce. The water at this particular site is pumped from a brackish aquifer to the water treatment plant where it is processed. The first problem is temperature. The water is quite hot when it arrives at over 50C. The first treatment step is to cool the water to 30C in cooling towers. Then there are two filtration steps; a multimedia filter and a cartridge filter. After this the water is sent to the Reverse Osmosis trains. The output water is adjusted for pH by adding caustic and then sodium hypochlorite is added to protect the water in storage. This is the water that is sent to the storage pond.

The resulting water is exceptionally clean with very few remaining minerals or salts. This water is intended for use in a nearby processing plant and the water quality is controlled for that process. Use of this water as potable drinking water is a secondary use; the treatment plant is primarily designed to make process water. This leads to water being stored with an unusually low Langelier Saturation Index. The owner was able to share water quality data with us; however no reported data appeared to be at concerning levels. TDS levels were consistently below 200 and water temperatures ranged from 35 to 45C.

In a report to the project owner on Oct 31st, 2013 we outlined the problem.

We've had a number of conversations with a few people regarding this liner problem. Of course one of the complicating issues is the heat of the water and the climate at this location. We are not aware of any other examples where large ponds of potable water are stored at the same temperatures as are present on this site. We have followed the problems of liner oxidation in Polypropylene liners in Australia and have done tests using chlorine solutions to try and model that problem. In this case the water temperature of 35-45C is close to our accelerated test temperature of 50C. Chlorine by itself could be a significant factor here however we have had this LLDPE material in chlorinated water at higher concentrations (cool water of course) and have not seen this type of degradation previously.

In talking with John Schiers of Excelplas testing labs he shared with us his theory that water with a negative Langelier Saturation Index (-LSI water) could be a significant cause of liner failures in Australia. Although he was not able to share the private research that he has completed he was clear that the -LSI water that is typical of RO water treatment systems could be a major part of the issue. Additional discussion with Greg Moore of Moore Materials Technology led to his comment that;

"Another aspect is the effects of the mobility of any disinfectants such as chlorine. It is the free chlorine which is the most aggressive part of the chlorine and in municipal supplies with well stabilized water not all of the added chlorine is converted to free chlorine but in a water with a very negative LSI, just about all would be converted to free chlorine which might make it more corrosive. "

We also called David Heumann of the Los Angeles Department of Water and Power. He is the internal corrosion specialist with LADWP. His experience was that he had never heard of an LSI lower than -1.5 in municipal water applications. In the LADWP system they take action when the LSI reaches -0.3 by adding calcium carbonate to bring the water back to a mineral balance. Below -1.5 there is a risk of damage to concrete water piping which they have in widespread use in their system.

Our conclusion was that there appears to be credible evidence that a -LSI could be part of the issues we are facing. In our previous testing on chlorine our LLDPE held up quite well. Something else appears to have accelerated oxidation here and the best theory we have come up with is the -LSI water.

6. LANGELIER SATURATION INDEX

"The Langelier Saturation Index (LSI) is a measure of a solution's ability to dissolve or deposit calcium carbonate and is often used as an indicator of the corrosiveness of the water. It is calculated using the pH, alkalinity, calcium concentration, total dissolved solids, and water temperature of a water sample collected at the water source. The index is not related directly to corrosion, but is related to the deposition of a calcium carbonate film or scale. When no protective scale is formed, water is considered to be aggressive and corrosion can occur. Highly corrosive water can

cause system failures or result in health problems because of dissolved lead and other heavy metals. An excess of scale can also damage water distribution systems, necessitating repair or replacement.” (Hach 2014).

LSI	Indication
LSI <0	Water is undersaturated with respect to calcium carbonate. Undersaturated water can remove existing calcium carbonate protective coatings in pipelines and equipment.
LSI =0	Water is considered to be neutral. Neither scale forming nor scale removing.
LSI >0	Water is supersaturated with respect to calcium carbonate and scale forming may occur.

LSI	Indication
-2.0 < -0.5	Serious corrosion
-0.5 < 0.0	Slightly corrosive but not scale forming
LSI = 0	Balanced
0.0 < 0.5	Slightly scale forming but non corrosive
0.5 < 2.0	Scale forming but non corrosive

Figure 4. Langelier Index Rating Indicators

As shown in Figure 4, water with an LSI below -0.5 indicates that the water is under saturated with calcium carbonate resulting in a corrosive environment in the water distribution system. On our project we were investigating LSI levels of the water that were LSI -2.4 to LSI -3.0 with reported historical spikes as high as LSI -4.5. These values appeared to be well outside of normal; most LSI charts do not show values smaller than -2.0 and many LSI calculators do not report values in these lower ranges. It appears that the lowest possible LSI value would be an LSI -6.0 which would be associated with liquids such as distilled water.

The owner had a history of the geomembranes used on site which had shown a number of failures over the years. PVC, Reinforced Polypropylene, and Chlorosulfonated Polyethylene materials had all shown problems on this site. We also found out that an LLDPE floating cover in another pond had also blistered and that the entire bottom surface of the cover had fallen away in places. One positive note was that an HDPE liner installed in mid 1990's, while showing reported lower antioxidant levels, appeared to be performing well in another pond.

In order to determine whether LSI was having an effect on the liner materials we would need to do some testing; however, the immediate requirement was to return the pond to service for the upcoming season of high water demand. The short term solution was to sink the floating cover and use it as a liner for one season. Although the cover had blistering on the bottom surface the top of the cover was still intact. The floats and weights were removed from the cover, the inlets and outlets connected, and the cover was pressed into service as the liner.

7. LSI IMMERSION TESTING

New liner and cover materials would need to be on site in 6 months which gave us about 4 months to perform testing. Based on our previous experience conducting immersion testing for chlorine (Mills 2011) we decided to follow a similar testing protocol. The test uses stressed material samples immersed at higher fluid temperatures and then measure antioxidant retention. This testing can help us find a point where materials will stabilize to an equilibrium point or encounter further antioxidant depletion often to the point of stress cracking. The stressed test protocol uses ASTM D1693 for the fluid immersion and ASTM D5885 for the analysis of residual anti-oxidant.



Figure 5. Example of a Bent strip samples prepared for ASTM D1693 immersion testing

The biggest issue was to create water for testing with a strongly negative LSI. There were two problems. The first was to find a source of water that had a low starting LSI, and the second was to be able to periodically test the water to ensure that it maintained its properties.

Fortunately the lab that we chose to perform this work had its own RO treatment system which was used to produce water for High Performance Liquid Chromatography (HPLC) testing. The second problem was to measure the water properties. Most available test methods were not accurate enough to measure a strongly negative LSI. We had to try a number of tests for calcium hardness before we found one that was reliable. We also needed to complete a series of tests to see if we could maintain the LSI values of the solution over time. A large volume of the test solution was made in advance and the solution in the test tubes was changed every week to maintain liquid properties.

The immersion testing included testing materials to two different LSI fluid conditions. One set of material samples were immersed in a conditioned fluid with a LSI -4 solution at 70°C (158°F) with 5 ppm chlorine solution from HPCL water at a pH of 7. A control immersion was also run with a second set of material samples at a targeted LSI = 0 using the same water as in the first immersion but with added calcium carbonate for a balanced hardness. This immersion was also run at 70°C (158°F) with 5 ppm chlorine and a pH of 7. Both sets of materials were tested for HP OIT prior to immersion, and periodically through the testing.

The materials tested included and LLDPE, and HDPE, and a Coextruded material. The LLDPE sample was made from the same lot number of resin as had been used in the liner and cover on the pond that failed. The HDPE material was from stock. The Coextruded material (Coex) was made with HDPE skins on an LLDPE core. This Coex material was heavily fortified with antioxidants.

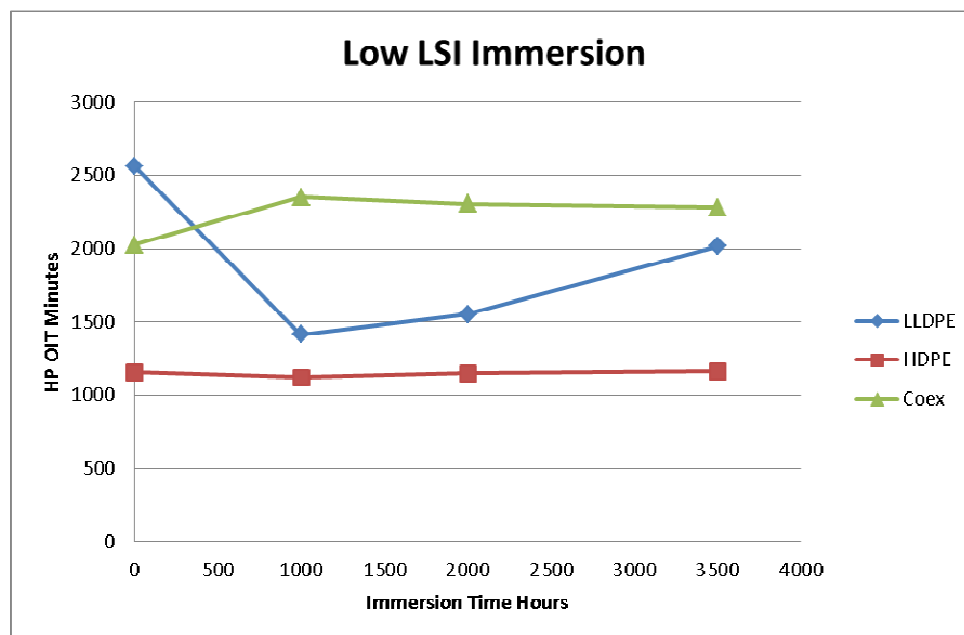


Figure 6. Results of low LSI immersion testing.

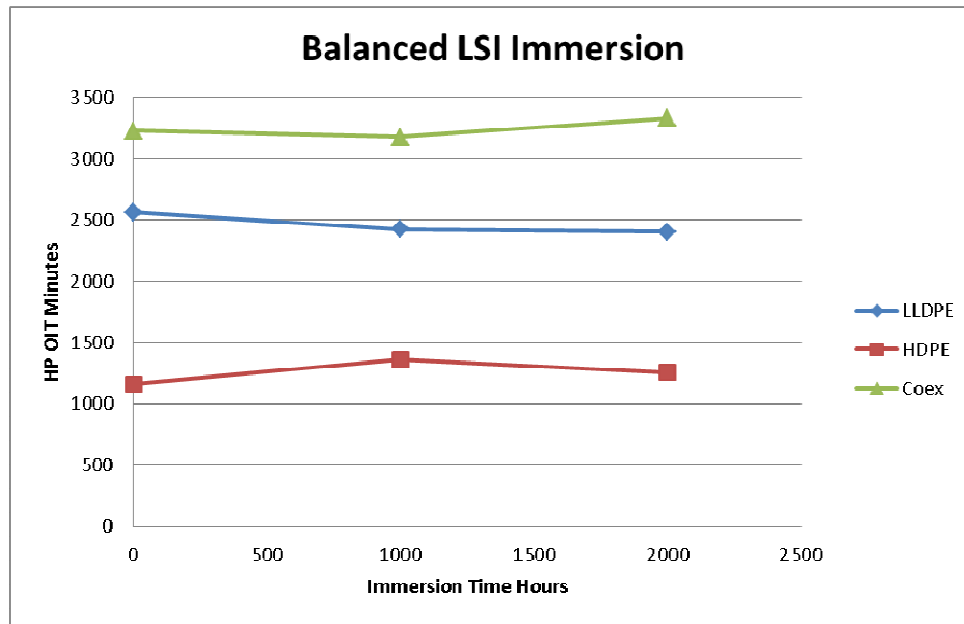


Figure 7. Control testing with balanced LSI immersion.

8. RESULTS

The initial results show that the LLDPE suffered an initial loss of HPOIT of a little less than half of its initial value. Continued testing after that shows an increase in HPOIT values which is unexpected. It is important to note that it proved to be quite difficult to consistently replicate the negative LSI fluid conditions from site with laboratory test conditions. Changing the fluid every week appeared to keep the conditions consistent however we are not clear on what would have caused the HPOIT values to go back up. In the control testing the LLDPE reacts as expected with no significant changes. The results for the Coex with HDPE skins and the HDPE both show good results in both immersions.

9. LINER RECOMMENDATIONS

From this testing and other information obtained from our research we proposed a fortified grade of HDPE as the replacement material for the liner and floating cover. A fortified geomembrane is defined as a product heavily treated with stabilizers providing enhanced heat, UV stability and chemical resistance (Schiers 2009). In order to provide flexibility in the defined sump sections of the floating cover we proposed that strips of the Coex material be placed in the sump areas. The HDPE and the surface layers of the Coex material were both made with the same fortified formulation with an initial HPOIT value of over 3,000 minutes. With most standard HDPE geomembrane materials today being produced from Medium Density Polyethylene (MDPE) resins with a relatively low HP OIT starting level, we concluded that the fortified formulation of HDPE was a better recommendation for the owner.

The owner sent some of our samples to an independent lab which verified some of our findings. The owner accepted our recommendation and proposal and the materials were manufactured and shipped to site in June of 2014. Installation is under way as this paper is being written.

10. CONCLUSIONS

Based on our research and performance testing, we were able to provide some answers and solutions to an owner who was having difficulty with water that had been produced by the RO water process and had an exceptionally low LSI. Although we do not expect to see water containment with such low LSI levels in the future we are expecting to encounter more RO water treatment facilities as water demand increases in dry climates. This project shows us that even well-formulated geomembranes can run into unexpected service conditions which can cause problems. This paper shows the importance of conducting site specific performance testing for unknown and difficult containment applications and how higher performance, fortified geomembranes can assist in overcoming these problems.

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