Performance of Blended Polyolefin and LLDPE Geomembranes in Heap Leach Pads Based on OIT

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ABSTRACT

Geomembranes (GMB) are exposed to harsh conditions in heap leach pads including high stresses and exposure to extreme acidic/basic pregnant leach solutions (PLS). This study investigates the depletion of antioxidant at 85°C for a 2.0 mm blended polyolefin (BPO) and a 2.0 mm linear low density polyethylene (LLDPE) GMBs when exposed to PLS using immersion tests for 18 months. The two GMBs were immersed in highly acidic (pH=0.5) and basic (pH=13.3) PLS at 85°C. Standard oxidative induction time (Std-OIT) and high pressure oxidative induction time (HP-OIT) tests were performed to monitor the depletion of antioxidants. The results show that the Std-OIT depletion was faster in the basic PLS compared to the acidic PLS. However, the HP-OIT depletion rate in the basic PLS was faster than in the acidic PLS only for the BPO stabilized with hindered amine light stabilizer (HALS). In addition, the antioxidants depletion results showed that the relative performance of the antioxidants stabilizing the two GMBs was variable depending on the incubation fluid.

Keywords: Blended polyolefin; LLDPE; Geomembranes; Heap leach pads; Pregenant leach solutions.

INTRODUCTION

Ores are extracted from open pits or underground mining operations, then crushed to smaller particles that facilitate the extraction of minerals from ores in the next stage called ‘‘ore beneficiation’’. The three main beneficiation techniques in mining industry are: a) concentration, b) hydrometallurgy, and c) pyrometallurgy (Zanbak 2013). Leaching is a hydrometallurgy ore beneficiation method that involves various techniques such as, a) dump leaching, b) heap leaching, tank leaching, and d) pressure leaching (Zanbak 2013).

Selection of the most efficient ore beneficiation method depends on the ore type and grade. Heap leaching is considered an economic technique for low grade and large weight ores and has the advantage of consuming less water compared to other ore beneficiation methods (Smith 2008; Zanbak 2013). In heap leaching, crushed ores are stacked into a heap on a lined low permeability pad in relatively thin lifts (Thiel and Smith 2004). The heap is irrigated by a solvent for a certain
period using an irrigation drip emitter or sprinkler sprays (Lupo 2010). Percolating out from the base of the heap is a liquid called pregnant leach solution (PLS) that is collected using geopipes and discharged to a lined PLS pond. PLS is then processed to extract the desired metal and the spent solution is discharged to a barren lined pond that can be reused in irrigating a new lift of the heap (Thiel & Smith 2004; Breitenbach & Thiel 2005; Lupo 2010). Leaching cycles last for 30 to 120 days or longer, using a very strong acidic solution for extraction of copper and nickel and a basic solution for extraction of gold and silver (Breitenbach & Thiel 2005; Lupo 2010).

Geomembranes (GMBs) used as base liners in heap leach pads are subjected to high stresses and, in many cases, very acidic/basic leach solutions. In some cases, irrigation of the ore heaps with solvents induces exothermic reactions that increase the temperature at the surface of the GMB to 50-70°C leading to accelerated aging of the GMB (Thiel & Smith 2004; Renken et al. 2005; Breitenbach & Thiel 2006; Hornsey et al. 2010). Rowe et al. (2013) reviewed the type of GMBs used in 88 heap leach pad projects and reported that high density polyethylene (HDPE), linear low density polyethylene (LLDPE), and polyvinyl chloride (PVC) GMBs are used in 75%, 22%, and 3% of projects, respectively, however there is a growing interest in the use of LLDPE in heap leach pads.

Several researchers have investigated the effect of mining solutions on the longevity of GMBs. Thiel and Smith (2004) examined the behaviour of HDPE, LLDPE, and PVC GMBs immersed in concentrated sulfuric acid for 120 days at 50°C. The results showed that the HDPE and LLDPE GMBs lost 4% and about 10% of their initial tensile strength, respectively, after 120 days. PVC lost its flexibility due to losing plasticizers after about 30 days. The authors concluded that PVC is not suitable to be used in concentrated acid leaching operations. Gulec et al. (2004, 2005) performed immersion tests for a 1.5 mm thick HDPE in a synthetic acid mine drainage (AMD) solution (pH=2.1), acidic water (pH=2.1), and DI water in 20°C, 40°C, and 60°C for 22 months. Results showed that the antioxidant depletion rate was fastest in AMD, followed by acidic water, and DI water. No significant change in tensile strength was observed for the GMB in any of the incubation media at any test temperature in their two-year study. Jeon et al. (2008) indicated that the antioxidant depletion rate for a HDPE GMB immersed in a basic solution (pH=9) was 1.1-2 times faster than for an acidic solution (pH=5) at the same temperature. Abdelaal et al. (2011, 2012) and Abdelaal and Rowe (2013, 2014) investigated the antioxidant depletion from 1.5 mm LLDPE and HDPE GMBs in low and high pH solutions simulating heap leaching PLS (pH=0.5 and 13.5). In addition to the mining solutions, the depletion rates obtained from both GMBs were compared to immersion in municipal solid waste (MSW) leachate and de-ionized (DI) water. Results showed that antioxidant depletion from the HDPE was slightly faster than from the LLDPE GMB in all the examined solutions. Furthermore, the standard oxidative induction time (Std-OIT; ASTM D3895) depletion rate from both GMBs immersed in the low pH solution (pH =0.5) was slower than in MSW leachate with surfactant and DI water. While in the high pH solution (pH =13.5), the depletion was faster than the DI water but slower than the MSW leachate. Morsy and Rowe (2017) studied the performance of a 1.5 mm white blended polyolefin (BPO) GMB immersed in the same high pH PLS examined by Abdelaal et al. (2011) at temperatures of 65, 75, and 85°C. The observed Std-OIT depletion time for the GMB in the high pH solution was 8 and 11 months at 75°C and 65°C, respectively. None of these papers have examined the relative performance of blended polyolefin GMBs to polyethylene GMBs traditionally used in mining applications. Thus, the objective of this paper is to compare between the performance of a 2.0 mm BPO and LLDPE GMBs immersed in acidic and basic PLS at 85°C based on OIT depletion.
EXPERIMENTAL INVESTIGATION

Accelerating Aging and Incubation Media

Investigating the performance of the GMBs when exposed to heap leaching solutions was performed using accelerated aging immersion tests. Sixteen GMB coupons of dimensions 20×10 cm were immersed in 4-liter glass jars filled with low and high pH heap leaching solutions. The GMB coupons were separated by 5 mm glass rods to ensure exposure of the GMB to the incubation fluid on both surfaces. The glass jars were incubated in forced air ovens at a temperature of 85°C.

The low pH PLS (pH=0.5) was prepared by mixing inorganic salts containing heavy metal ions (e.g. Cu²⁺, Fe²⁺, Ni²⁺) with DI water. Sulfuric acid was used for titration to achieve a pH=0.5 (Abdelaal et al. 2012; Morsy & Rowe 2017). The high pH PLS (Abdelaal et al. 2011; Abdelaal & Rowe 2015; Morsy & Rowe 2017) was prepared by mixing inorganic salts (e.g. silver sulphate, copper sulphate, cobalt sulphate, aluminum sulphate) with DI water, and titration to a pH of 13.3 was achieved by adding a 15 molar sodium hydroxide solution.

Properties of the Tested Geomembranes

Two commercially available 2.0 mm smooth black GMBs were examined; LxD20 is LLDPE GMB that was manufactured in 2011 using Chevron K203 polymer resin, and BzS20 is BPO GMB that was manufactured in 2014. BzS20 had a proprietary blended polyolefin resin.

A series of index tests were performed to estimate the initial properties of the GMBs (Table 1) and to monitor the aging of the GMB with time. Both standard oxidative induction time (Std-OIT ASTM D3895; 35 kPa/200°C) and high pressure oxidative induction time (HP-OIT ASTM D5885; 3500 kPa/150°C) were used to assess the initial amount of antioxidants stabilizing the GMBs and their depletion with time. Std-OIT was used to detect the antioxidants that have an effective temperature greater than 200°C such as phenols and phosphites, while HP-OIT was used to detect antioxidants/stabilizers that volatilize at temperatures greater than 150°C such as hindered amine light stabilizers (HALS) and sulfur compounds.

<table>
<thead>
<tr>
<th>Property</th>
<th>Designator</th>
<th>Method</th>
<th>Unit</th>
<th>Mean ± SD²</th>
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<tr>
<td>Nominal thickness</td>
<td>LxD20</td>
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<td>2.0 ± 2.0</td>
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<tr>
<td></td>
<td>BzS20</td>
<td>ASTM D5199</td>
<td>mm</td>
<td>2.0 ± 2.0</td>
</tr>
<tr>
<td>GMB density b</td>
<td>BzS20</td>
<td>ASTM D1505</td>
<td>g/cm³</td>
<td>0.936 ± 0.936</td>
</tr>
<tr>
<td></td>
<td>LxD20</td>
<td>ASTM D1505</td>
<td>g/cm³</td>
<td>0.936 ± 0.936</td>
</tr>
<tr>
<td>Std-OIT (200°C/35kPa)</td>
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<td>ASTM D3895</td>
<td>min</td>
<td>174 ± 11</td>
</tr>
<tr>
<td></td>
<td>LxD20</td>
<td>ASTM D3895</td>
<td>min</td>
<td>112 ± 1</td>
</tr>
<tr>
<td>HP-OIT (150°C/3500kPa)</td>
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<td>ASTM D5885</td>
<td>min</td>
<td>3700 ± 350</td>
</tr>
<tr>
<td></td>
<td>LxD20</td>
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<td>240 ± 13</td>
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<tr>
<td>MFI</td>
<td>BzS20</td>
<td>ASTM D1238</td>
<td>g/10min</td>
<td>14.95 ± 0.5</td>
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<tr>
<td></td>
<td>LxD20</td>
<td>ASTM D1238</td>
<td>g/10min</td>
<td>18.86 ± 0.7</td>
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<td></td>
<td>LxD20</td>
<td>ASTM D5397</td>
<td>hours</td>
<td>&gt;2600²</td>
</tr>
</tbody>
</table>

² Standard deviation; b Provided by GMB manufacturer; c Test is still running.
RESULTS AND DISCUSSION

Std-OIT

In the PLS with pH = 13.3 (Figure 1), the Std-OIT of the BPO GMB depleted from an initial value of 174 min to an average residual value of 4.0 min in 4.5 months. The Std-OIT of the LLDPE GMB depleted from an initial value of 92 min to an average residual value of 2.0 min in 10 months. Although the LLDPE GMB had a lower initial Std-OIT value, it had longer Std-OIT depletion time.

In the pH = 0.5 mining solution (Figure 2), the Std-OIT of the two GMBs did not deplete to a residual value during 18 months of incubation. The Std-OIT depleted to 56 and 20 min after 18 months for the BPO and LLDPE GMBs, respectively. The equivalent normalized Std-OIT (Std-OITt/Std-OITo) was 0.32 and 0.22 for the BPO and LLDPE GMB, respectively.

The Std-OIT depletion rate from both GMBs in the high pH PLS was faster than in the low pH PLS. For instance, the antioxidant depletion rate of the BPO and LLDPE GMB in the high pH PLS was 0.965 and 0.624 month⁻¹, respectively, compared to 0.065 and 0.104, respectively, in the low pH PLS. This big difference in Std-OIT depletion in both media was attributed to the stability of hindered phenols in both solutions. The hindered phenols which play a major role in the Std-OIT depletion contain ester bridges in their structure (Scheirs 2009). The ester groups are chemical compounds derived from an acid, so they undergo catalyzed hydrolysis in a basic medium (Scheirs 2009, Abdelaal & Rowe 2015; Morsy & Rowe 2017). The results show a difference in the relative performance of the two GMBs in the two incubation media, where the antioxidant depletion rate of the BPO GMB was faster than the LLDPE GMB in the high pH PLS and the opposite was observed in the low pH PLS. This shows that the relative performance of an antioxidant package (phenols and phosphites) stabilizing a GMB varies from one incubation media to another and from one product to another.

HP-OIT

The LLDPE GMB was not stabilized with HALS resulting in a relatively low initial HP-OIT value of 240 min compared to the BPO GMB stabilized with HALS that had a relatively high initial HP-OIT value of 3700 min. Modern GMBs are stabilized with HALS to protect exposed liners from UV light (Scheirs 2009). However, in some cases they may contribute to delaying the oxidative degradation of the GMB (Abdelaal and Rowe 2015). HALS is effective in limiting the oxidative ability of peroxy radicals. HALS react with peroxy radicals yielding nitroxides (Geuskens and Nedelkos 1987). The nitroxide radicals scavenge the alkyl radicals in a reaction cycle called Denisov cycle. This cycle is a two-step cycle: 1) nitroxide radicals scavenge alkyl radicals forming alkylxoyamine, 2) the peroxy radicals are scavenged by alkylxoyamine generating nitroxides, and the cycle is repeated (Gijsman et al. 1993). HALS are oxidized faster by peroxy radicals than by hydroperoxides (Geuskens and Nedelkos 1987).

In the basic PLS, the HP-OIT of the BPO GMB depleted to a substantially high residual value of about 3100 min corresponding to a normalized value (HP-OITt/HP-OITo) of 0.85 only two months after the onset of incubation. For the LLDPE GMB, the HP-OIT depleted to an average residual value of 50 min corresponding to a normalized value of 0.2 after 7.5 months of incubation. In the acidic PLS, the HP-OIT of the BPO GMB depleted to an average residual value of 2750 min corresponding to a normalized value of 0.74 after 6 months of incubation. The HP-OIT of the
LLDPE GMB depleted to a normalized value of 0.48 and did not reach the residual value during the 18 months incubation duration. These results show that in both solutions, the depletion of the HP-OIT of the BPO was faster than the LLDPE but to significantly higher residuals values than those measured for the LLDPE without HALS.

The Std- OIT and HP-OIT depletion of the LLDPE GMB (without HALS) was faster in the basic PLS compared to the acidic PLS. For the BPO GMB (stabilized with HALS), the HP-OIT depleted to the residual value in the basic PLS faster than the acidic PLS. Furthermore, the observed average residual value in the basic PLS was higher than in the acidic PLS indicating that more antioxidants were depleted in the acidic media. Since HALS are basic, they are more stable in basic media compared to acidic media, and therefore the HP-OIT of the GMB stabilized with HALS depletes to a high residual value after short incubation time (Abdelaal & Rowe 2015). The initial slight reduction in HP-OIT may be due to the physical extraction of the relatively low molecular weight antioxidants followed by no further reduction in the HP-OIT values due to the immobility of the relatively high molecular weight HALS in the basic media.

![Figure 1](image-url) Figure 1. Variation of normalized Std-OIT (Std-OIT\_t/Std-OIT\_o) with time in the high pH pregnant leach solution (pH=13.3) at 85°C.
Figure 2. Variation of normalized Std-OIT (Std-OIT_t/Std-OIT_o) with time in the low pH pregnant leach solution (pH=0.5) at 85°C.

Figure 3. Variation of normalized HP-OIT (HP-OIT_t/HP-OIT_o) with time in the high pH pregnant leach solution (pH=13.3) at 85°C.
Figure 4. Variation of normalized HP-OIT (HP-OIT/HP-OIT₀) with time in the low pH pregnant leach solution (pH=0.5) at 85°C.

CONCLUSIONS

The performance of 2.0 mm BPO and LLDPE GMBs was assessed with respect to antioxidant depletion at 85°C in two solutions representing the upper and lower pHs found in heap leaching applications. Results of antioxidants depletion based on Std-OIT and HP-OIT can be used as an initial indicator for the longevity of the two GMBs in this application. However, longevity of a GMB depends also on the polymer resin whose performance could be assessed by monitoring the degradation of MFI, tensile, and SCR properties. Since this paper only examines antioxidants depletion over 18 months, more testing is needed to fully assess their relative performance. Based on the results presented herein, the following preliminary conclusions have been reached:

- The initial SCR values of both the BPO and LLDPE GMBs were high relative to the SCR of HDPE commonly reported in literature.
- Std-OIT depletion in the heap leaching basic solution examined (pH=13.3) was faster than in the acidic solution (pH=0.5) for the two GMBs. For instance, the antioxidant depletion rate from the BPO GMB was 0.965 month⁻¹ in the basic solution compared to 0.065 month⁻¹ in the acidic solution.
- Std-OIT depletion from the BPO GMB was faster than the LLDPE GMB in the basic solution. In contrast, the Std-OIT depletion from the BPO GMB was slower than the LLDPE GMB in the acidic solution.
- HP-OIT depletion from the BPO GMB was faster than the LLDPE GMB in both high and low pH pregnant leachate solutions.
- In the high pH PLS, the HP-OIT of the BPO GMB stabilized with HALS depleted to a higher residual value in a shorter incubation time than for the low pH PLS.
- The HP-OIT of the LLDPE GMB (without HALS) reached the residual value in the high pH PLS faster than in the low pH PLS.
This paper has focused on the relative performance of the two GMBs immersed in PLS based on the antioxidants depletion detected by the Std-OIT and HP-OIT test. The degradation of physical properties, after antioxidants depletion, may show different relative performance for the two GMBs. The longevity of the BPO and LLDPE GMBs at 65, 75, and 85°C will be discussed in a subsequent publication after a longer incubation time has elapsed and the degradation of physical properties of the GMBs has been detected.

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