Effect of brine solution on antioxidants of HDPE geomembranes

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ABSTRACT
High density polyethylene (HDPE) geomembranes (GMBs) are used as the primary bottom liner for brine storage and evaporation ponds. The brine arising from the processing of waters recovered from shale or coal gas extraction often contains sodium chloride (NaCl), sodium carbonate (NaHCO₃) and sodium bicarbonate (Na₂CO₃) at very high concentrations. This paper describes an experimental examination of the ageing of four different GMBs immersed in brine solution at four different temperatures to monitor the depletion rate of antioxidants/stabilizers added to the GMB formulation to protect the GMB both during manufacturing and subsequently when deployed in the field. The depletion rate of antioxidants depends on several factors, including the amount and type of antioxidants/stabilizers, GMB temperature, the GMB exposure conditions, the diffusion/extraction of antioxidants from the GMB, and the chemical composition of the fluids with which the GMB is in contact. There is a paucity of published research examining the chemical compatibility of HDPE GMB with brine solution. The tests are intended to provide insight regarding the antioxidant depletion rate and its impact on the time to nominal failure of HDPE GMB and therefore will help to provide an estimate of the service life of four different HDPE GMBs immersed in a brine solution.

RÉSUMÉ
Les Géomembranes (GMBs) en Polyéthylène Haute Densité (HDPE) sont utilisées comme principal revêtement de fond pour le stockage de la saumure et pour les bassins d'évaporation. La saumure provenant des eaux récupérée à partir de l'extraction des gaz de schiste ou de charbon contient souvent du chlorure de sodium (NaCl), du carbonate de sodium (NaHCO₃) et du bicarbonate de sodium (Na₂CO₃) à des concentrations très élevées. Ce document décrit un examen expérimental du vieillissement de quatre GMBs immergées dans une solution de saumure à quatre températures différentes afin de contrôler le taux de diminution des antioxydants et des stabilisateurs dont le rôle est de protéger les GMBs pendant leur fabrication et par la suite lorsqu'elles sont déployées sur le terrain. Le taux de diminution des antioxydants dépend de plusieurs facteurs, notamment la quantité et le type d'antioxydants et de stabilisateurs, la température des GMBs, les conditions d'exposition des GMBs, la diffusion et l'extraction des antioxydants de la GMB et la composition chimique des fluides avec lesquels la GMB est en contact. Il n'y a eu jusqu'à présent de recherche examinant la compatibilité chimique du Polyéthylène Haute Densité (HDPE) des GMBs avec une solution de saumure. Les essais sont destinés à donner une idée du taux d'épuisement des antioxydants et de son impact sur le temps de dégradation du Polyéthylène Haute Densité (HDPE) des GMBs. Ils contribueront à fournir une estimation de la durée de vie des quatre GMBs HDPE immergées dans une solution de saumure.

1 INTRODUCTION

The main design function of high density polyethylene (HDPE) geomembranes (GMBs) is used to minimize the migration of pollutants into the surrounding environment. For example, HDPE GMBs are essential for minimizing the migration of contaminants by advection or diffusion (Rowe et al. 2004). Modern HPDE geomembranes typically have a medium density polyethylene resin, 2-3% carbon black and antioxidants/stabilizers which are added to the GMB formulation to protect the GMB both during manufacture and subsequently when deployed in the field (Hsuan and Koerner 1998). Chemical aging consists of three conceptual stages (Hsuan and Koerner 1998): (a) antioxidants depletion (Stage I); (b) an induction period between antioxidant depletion and the onset of measureable polymer degradation (Stage II); and (c) degradation affecting the physical properties of the GMB with nominal failure being deemed to have occurred when a property of interest decreases to 50% of its original value. The rate of antioxidant depletion in Stage I depends on several factors, including the amount and type of antioxidants/stabilizers, GMB temperature, the GMB exposure conditions, the chemical composition of the fluids with which the GMB is in contact, the type and thickness of GMB protection layer, and the diffusion/extraction of antioxidants from the GMB. There has been considerable research into antioxidant depletion from HDPE GMBs to investigate these issues (e.g., Sangam and Rowe 2002b; Müller and Jacob 2003; Rimal et al. 2004; Rowe et al. 2008; Rowe et al. 2009; Rimal and Rowe 2009; Schiers 2009; Rowe et al. 2010a; Rowe et al. 2010b; 2012; 2013; Ewais and Rowe 2012; 2014).

2 A BRINE SOLUTION

The brine arising from processing of waters recovered from shale or coal gas extraction often contains sodium chloride (NaCl), sodium carbonate (Na₂CO₃) and sodium bicarbonate (NaHCO₃) at concentrations of the order of 200,000 ppm total dissolved solids (TDS) (Table 1). Also, due to the heavy demand for natural gas liquids (NGLs) during the winter, there is a need for practical NGLs storage methods. One such method is in salt cavern within deep salt bed deposits, made by dissolving the salt deposits underground. The extracted brine solution goes
into the brine storage ponds leaving a large empty space in the formation to store liquefied petrochemicals (e.g., NGL’s). These brine storage ponds typically have a salt concentration of the order of 10,000 ppm TDS or higher (Leblanc et al. 2011, Tan et al. 2012).

Brines attract solar radiation and can heat to temperatures of 90°C (Leblanc et al. 2011) without active temperature control and even with active temperature control they may be at temperatures of 55°C or higher (Gassner 2011, Leblanc et al. 2011).

3 EXPERIMENTAL INVESTIGATION

3.1 Exposure Conditions

The four different 1.5 mm HDPE from the two different manufacturers used in this study (denoted as MxAa-15, MxC-15, MyE-15, and MyEW-15). GMB samples 100 mm by 180 mm were cut, immersed in four-liter glass containers containing the brine solution, separated by 5 mm glass rods. The containers were placed in ovens at 85, 75, 65, and 40°C. The brine was replaced every month to avoid any buildup of antioxidants (Rowe et al. 2008, Rowe et al. 2010a). Specimens from the GMBs studied are taken periodically to test the changes in GMB properties with ageing were monitored in accordance with Std-OIT ASTM standard method.

Table 1. Initial Std-OIT of GMBs examined (ASTM3895)

<table>
<thead>
<tr>
<th>GMB</th>
<th>MxAa-15</th>
<th>MxC-15</th>
<th>MyE-15</th>
<th>MyEW-15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal thickness</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Upper surface colour</td>
<td>BLACK</td>
<td>BLACK</td>
<td>BLACK</td>
<td>WHITE</td>
</tr>
<tr>
<td>Std-OIT (DSC)</td>
<td>91.4±0.22</td>
<td>164±1.4</td>
<td>161±1.1</td>
<td>177±0.61</td>
</tr>
</tbody>
</table>

3.2 Experimental Procedure

Laboratory accelerated ageing tests were conducted by immersing the coupons in brine (Table 2) to examine the ageing of the four HDPE GMBs (MxAa-15, MxC-15, MyE-15 and MyEW-15; Table 1).

Table 2. Composition of brine used in this study

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Component</th>
<th>Mass percent</th>
<th>Amount (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride</td>
<td>NaCl</td>
<td>Na⁺</td>
<td>40000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cl⁻</td>
<td>60000</td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>NaHCO₃</td>
<td>Na⁺</td>
<td>14000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HCO₃⁻</td>
<td>36000</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na₂CO₃</td>
<td>Na⁺</td>
<td>21700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO₃²⁻</td>
<td>28300</td>
</tr>
</tbody>
</table>

3.3 Standard Oxidative induction time (OIT) tests

Std-OIT tests (ASTM D3895) were conducted at 200°C and 35 kPa using a differential scanning calorimeter (DSC; TA instruments,Q-100 series). Std-OIT and tests were conducted as an index to monitor the rate of the decreasing change in the available antioxidant for four GMBs. A two parameter exponential model was used to calculate the antioxidants depletion time based on Std-OIT to estimate the Stage I of the nominal failure.

4 PRELIMINARY RESULTS

Figures 1-4 show the depletion of the antioxidants detected by the Std-OIT test depletion in normalized from (i.e., Std-OIT/Std-OIT₀) with time for samples incubated at four temperatures for the four MxAA-15, MxC-15, MyE-15 and MyEW-15. When re-plotted in terms of ln (Std-OIT/Std-OIT₀), the slopes of the depletion curves in Figures 5-8 were then used to construct Arrhenius curves (Figures 9-12) and establish Arrhenius equations for the four GMBs. The data used in these plots is preliminary and will be updated as more information becomes available with time.

The Arrhenius equations generated from Figures 9-12 can be used to estimate the time to Std-OIT depletion at other temperatures (Table 3).

Table 3. Calculated antioxidant depletion times (rounded to 2 significant digits) based on 12 months data.

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>MxAa-15</th>
<th>MxC-15</th>
<th>MyE-15</th>
<th>MyEW-15</th>
</tr>
</thead>
<tbody>
<tr>
<td>70°C</td>
<td>4.9</td>
<td>5.2</td>
<td>4.1</td>
<td>7.1</td>
</tr>
<tr>
<td>60°C</td>
<td>6.2</td>
<td>8.1</td>
<td>5.9</td>
<td>9.2</td>
</tr>
<tr>
<td>50°C</td>
<td>9.4</td>
<td>16</td>
<td>10</td>
<td>13</td>
</tr>
<tr>
<td>40°C</td>
<td>13</td>
<td>28</td>
<td>16</td>
<td>18</td>
</tr>
<tr>
<td>30°C</td>
<td>19</td>
<td>50</td>
<td>26</td>
<td>25</td>
</tr>
</tbody>
</table>

5 CONCLUSION

Based on the preliminary results of the Std-OIT for 12 months aging, the following tentative conclusions have been reached:

- The predicted time to Std-OIT depletion for MxAa-15 GMB ranged from 4.9 years at 70°C to 19 years at 30°C.
- The predicted time to Std-OIT depletion for MxC-15 GMB ranged from 5.2 years at 70°C to 50 years at 30°C.
- The predicted time to Std-OIT depletion for MyE-15 GMB ranged from 4.1 years at 70°C to 26 years at 30°C.
- The predicted time to Std-OIT depletion for MyEW-15 GMB ranged from 4.9 years at 70°C to 19 years at 30°C.
- The predicted time to Std-OIT depletion for MxAa-15 GMB ranged from 4.9 years at 70°C to 19 years at 30°C.
Although MxC-15 had lower initial Std-OIT value (164 min) than MyEW-15 (177 min), it had the longest depletion based on Std-OIT depletion, demonstrating that a high initial value of Std-OIT does not necessarily translate into a longer antioxidants depletion time at moderate temperatures. More research is required to assess the depletion over a longer period of time.

The Std-OIT examined in this paper only captures some of the antioxidants/stabilizers in the GMB. In addition HP-OIT, melt index (MI), tensile properties, stress crack resistance (SCR) and crystallinity are being monitored. These ongoing tests will provide more perspective with regard to the four different GMBs in a subsequent paper.

ACKNOWLEDGEMENTS
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Figure 6. Antioxidant depletion rates (Std-OIT) for MxC-15 immersed in brine at four temperatures

Figure 7. Antioxidant depletion rates (Std-OIT) for MyE-15 immersed in brine at four temperatures

Figure 8. Antioxidant depletion rates (Std-OIT) for MyEW-15 immersed in brine at four temperatures

Figure 9. Arrhenius plot for MxAa-15 immersed in brine at four temperatures.

Figure 10. Arrhenius plot for MxC-15 immersed in brine at four temperatures

Figure 11. Arrhenius plot for MyE-15 immersed in brine at four temperatures
Figure 12. Arrhenius plot for MyEW-15 immersed in brine at four temperatures.

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REFERENCES