Performance benefits of white formulation HDPE geomembranes

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Abstract. High Density Polyethylene (HDPE) Geomembranes have been used in containment applications for the past 50 years. Over this period, Polyethylene Geomembrane formulations have changed markedly with a design need to contain higher risk contaminants stored in more challenging environments. One of the major product developments has seen the emergence of "White Top Layer" Geomembranes. Atarfil would concur, and our most recent immersion and exposure data is compelling. It is not simply the thermal behavior that is beneficial, the additive types required to meet the challenges of stabilizing white layers, also serve significantly better protection when subjected to UV and Immersion Testing. This is translating to significantly longer predictions of Geomembrane performance life.

1 Introduction

High density polyethylene (HDPE) geomembranes have been used as containment application barriers for more than 40 years. Over this period, geomembrane formulations have changed markedly trying to improve liner performance and durability to adapt to higher challenging applications and environments. Many of these demanding applications could be found in the mining industry, where the need for high performance lining systems has become a critical issue to face. HDPE geomembranes has emerged as a key component to address this demand as barrier containment.

One of these product developments, made to enhance HDPE geomembrane performance is the "White Top Layer" geomembranes. White/black HDPE geomembranes are a coextruded material making the white surface an integral part of the membrane which cannot be delaminated or detached from the black base sheet.

The use of white top layer geomembranes is not a recent trend, white HDPE liners are been used widely in a big range of applications and locations. But recently, the use of new stabilization packages together to lower service temperatures due to the higher reflectivity of white surfaces are translating to significantly longer predictions of geomembrane performance life.

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2 Historical performance benefits of white top layer geomembranes

Historically white surfaced geomembranes have been used because the two-color layers (thin white top layer – thick bottom black layer) help to ease identify damage and defects during installation, making visual inspection more reliable.

Cadwallader et al. (1993) found, under clear skies at an ambient air temperature of approximately 30°C, a significant temperature reduction as much as 24°C on white-surfaced HDPE geomembrane compared to a standard black-surfaced geomembrane. As a result, thermal expansion and wrinkling are minimized allowing intimate contact between geomembrane and subgrade. Lower geomembrane temperatures provide an additional benefit, better protection of GCL or soil subgrades from desiccation. In summary, the advantages of use a white coextruded geomembrane on a project include:

- Less wrinkles caused by thermal expansion, therefore lower stress cracking risk of the liner.
- Intimate contact between geomembrane and GCL or soil subgrades. Lower risk of damage to liner which can result from the interaction of wrinkles and earthmoving equipment.
- Improves damage detection due to contrast caused by exposing black underlying layer.
- Decreased moisture evaporation from underlying soil layers, retards subgrade desiccation.

3 Service life of white top layer geomembranes

Geomembrane Liner performance is fundamentally the measure of leaks. The key to establishing the Geomembrane leakage rate risk is to ensure that the polymer properties of the sheet remain the same over the life of the containment, but in all applications, we are trying to establish an acceptable loss of properties over time. Establishing the performance of the sheet, allows an assumption that the liner is effectively "impermeable" for the life of the project (it isn't but close) and leakage expectations can match historical design thinking e.g. 4-5 holes per Hectare caused by onsite factors.

The key condition that threatens this assumption, is whether the liner is exposed or buried. When the Geomembrane is covered, the impacts of air and UV are removed, stresses are more easily quantified, temperature is "consistent" and chemical impacts are the key performance parameter.

For exposed Geomembranes, the synergistic impacts of Temperature, Oxygen, UV, Stress and Chemistry all serve to accelerate liner degradation and cannot be easily measured together. The impact of heat alone causes wrinkles, resulting in increased stresses that are difficult to model and known to accelerate degradation. In general, the options for testing must isolate one or two of these degradation mechanisms and make assumptions as to the impact of other factors onsite. Modern laboratory testing is getting closer to applying multiple site conditions, but elevated temperature is a consistent factor that always accelerates rates of degradation.

As was exposed previously, under clear skies the differences in temperature between top white and black geomembranes are significant. The lower temperature in top white geomembranes will provide longer service life because temperature accelerates degradation mechanisms: oxygen, UV radiation, stress and chemistry exposition. As described in GSI White Paper temperature is critical to lifetime and furthermore is the key to time-temperature-superposition which is the basis of the laboratory incubation methods.

4 UV behavior

In Black HDPE Geomembranes, it is the Carbon Black that provides critical UV resistance and gives the liner its black color. For White layers, Titanium Oxide is the White Pigment that serves “similar” function. The need to ensure Carbon Black type, source and distribution for Black HDPE, remains the same with the Titanium Oxide source. There are a range of Titanium Oxide rutile grades, it is important to select a durable source that has key additives to protect the rutile itself and is compatible with the polymer. The use of these pigments together with special stabilizer additives allows geomembranes to be exposed for years with minimal UV degradation.

The usual way to measure the geomembrane performance versus UV radiation is described by the test methods ASTM D 7238 & ASTM D 5885. This test consists of the aging of the geomembrane in a laboratory weatherometer and the measure of the HP OIT after this accelerated UV exposition. The table below shows the HP OIT retained after the UV exposition of seven samples of top white geomembranes, we can observe that all the values are above 75%. If we use GRI GM13 as reference, the required value of HP Retained is 50%. This fact proves that white geomembranes can perforce as well as black geomembranes in terms of UV resistance.

Table 1. HP OIT % retained after 1600h UV radiation exposition in weatherometer.

Sample	**HP OIT RETAINED**
# 1	89 %
# 2	100 %
# 3	75 %
# 4	78 %
# 4	93 %
# 4	77 %
# 4	75 %
Average	**84 %**

5 Oxidation behavior

The most broadly used tests for assessing the resistance of PE geomembranes to oxidation is to evaluate the quality and interaction of the antioxidants and stabilizer packages that remain post manufacturing. Oxidation causes structural polymer changes and is a key measure to understand performance loss in both the atmosphere and chemical immersions. Antioxidants are needed that will perform at the high temperatures associated with manufacturing, as well as at lower temperatures associated with the service life of the geomembrane. As a result, manufacturers often use a combination of two or more types of antioxidants and stabilizers to provide overall stability.

A good stabilization package for an HDPE geomembrane should comprise at least three antioxidant/stabilizing additives:

- Phosphites
- Hindered Phenols
- Hindered Amines

Each of these antioxidants has a different operating temperature and protects the geomembrane in different phases such as the production process and its service life, as we can see in the following figure.

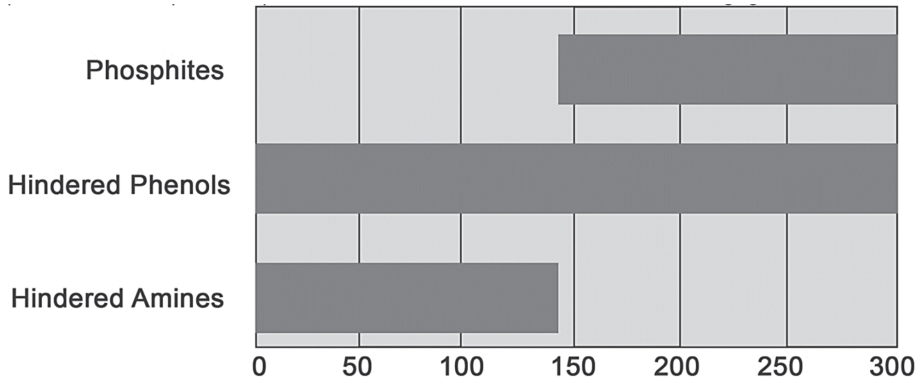

Figure 1. Types of antioxidants and operating temperature range.

There are two tests that allow us to measure the antioxidant content of a geomembrane, the Std OIT (Standard oxidation induction time) and the HP OIT (High-pressure oxidation induction time). The Std OIT is carried out at a temperature of 200°C and a pressure of 35 Kpa, while the HP OIT is carried out at a temperature of 150°C and a pressure of 3500 Kpa. Since HALS (Hindered Amines) are volatile above 150°C, the only way to measure their content in the geomembrane is by means of the HP OIT test.

Table 2. STD & HP OIT % retained after 90 days Oven Aging at 85ºC for two different top white layer geomembrane formulations.

	Number of samples tested	**STD OIT Retained (%)**	**STD OIT Retained (%)**
Formulation 1	23	67 %	94%
Formulation 2	9	84 %	100 %

The results for White Geomembranes can differ markedly to Black, and there are implications for specifications and testing timeframes. It is extremely important to test both OIT and HPOIT to understand the Masterbatch used in White Geomembranes. An overall increase in the total mass of additives is observed with increased standard OIT values, and often there are significantly higher quantities of Hindered Amine Light Stabilizers observed in elevated HPOIT results.

6 Immersion behavior of white geomembranes

Over recent years, Atarfil has conducted multiple immersions of White Geomembranes in excess of 12 months for a range of immersion chemistry that includes actual site and synthesized laboratory liquors.

The studies began with a fundamental aim to demonstrate that White Geomembrane Formulations are comparable to Black Geomembranes in a range of site chemistry. Black HDPE has a much larger project database in terms of project volumes.

The benefit of having both White and Black Layers in the single Geomembrane being tested is that a direct representation of black vs white layers can be established. The results indicate categorically, that when the formulation is designed specifically to the immersion liquor, white performance exceeds black layers in terms of Additive retention. The key additives that were introduced to address the challenges of white layer stabilization are demonstrating better long-term performance.

Immersions have been carried out for the following project types.

- Aluminium - bauxite bayer process residue ponds (red mud)
- Gold/copper/base metals - sulfuric processing/amd containments
- Concentrated brine applications - csg and offshore gas

To estimate geomembrane lifetime in a short time period it is necessary to have a methodology that replicates as close as possible site conditions and accelerates the degradation process in the lab. The steps outlined below need to be followed.

i. Identify the condition on site that the geomembrane will be exposed to.
ii. Incubate geomembrane coupon (portion of a material or laboratory sample) replicating as closed as possible site conditions.
iii. Monitoring of incubated geomembrane coupons. The various coupons will be periodically removed and evaluated according to the selected test methods.
iv. Mathematical modelling. There are several lifetime prediction methods available, however we prefer the GSI proposed Arrhenius Modelling.

Arrhenius extrapolation is a classic method for lifetime prediction of polymers that have been exposed to accelerated testing conditions. The Arrhenius model enables the possibility of extrapolating results obtained for high temperatures in lab, temperature accelerates the degradation mechanisms of polymers, to site specific temperature to estimates geomembrane service life.

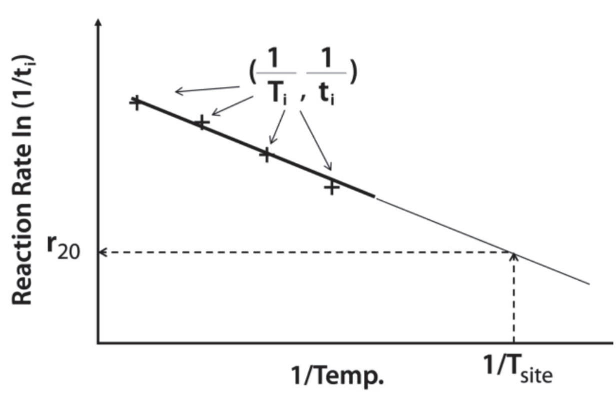

Figure 2. Example of Arrhenius Curve adjustment.

For example, to study the behavior of geomembranes in contact with brine we made an immersion test. In this test coupons were placed in a brine solution:

- 100 g/l NaCl
- 62 g/l NaHCO3
- 50 g/l Na2Co3

At the same time at three temperature 20°C, 60°C and 85°C then the results have been used to conduct lifetime extrapolations via the Arrhenius Curve. The samples were taken after 150, 300, 600, 1200, 2400 and 4800 hours to measure the retained antioxidants by STD OIT and HP OIT.

Table 3. HDPE geomembrane Std OIT and HP retained after immersion in a brine solution for different temperatures and exposition times.

	Std OIT Retained (%)			**HP OIT Retained (%)**		
	20°C	**60°C**	**85°C**	**20°C**	**60°C**	**85°C**
0 h	100 %	100 %	100 %	100 %	100 %	100 %
4800 h	83 %	58 %	27 %	100 %	100 %	100 %
8600 h	93 %	51 %	23 %	95 %	89 %	81 %

7 Case Study

7.1 Description

Yarwun alumina refinery is in the region of Queensland (Australia). It produces more than three million tons of alumina per year, which are exported to customers in Asia, the Middle East and the Pacific region. The Yarwun Refinery includes two Caustic Bladders (No.1 and No.2) near the Fisherman's Landing wharf. In 2018 refinery management decided to replace Caustic Bladder No.1 due to being near the end of its service life. These caustic bladder storage facilities needed a high-performance lining system that was able to operate in contact with a high caustic content solution.

7.2 Solution

Atarfil R&D department created a specific "top white layer" HD geomembrane with a tailored antioxidant package that allowed the geomembrane to be exposed to very high pH, that fact requires outstanding geomembrane endurance properties. Rio Tinto carried out an accelerated performance testing program, run by the external accredited laboratory ExcelPlas, to study the behavior of several geomembrane samples in a concentrated caustic environment. Based on the results of this study, Atarfil geomembrane was the selected product providing a membrane with maximum durability.

Figure 3. White HDPE installation works at Yarwun Refinery Caustic Bladder

8 Conclusions

The historical advantages of white geomembranes, such as reduced temperature and improved damage detection, have been well-documented. Moreover, their extended service life, especially when exposed to environmental factors, is a significant advantage.

Our investigation into UV resistance showed that white geomembranes with titanium oxide pigments perform comparably to their black counterparts. Additionally, the examination of oxidation behavior underlined the importance of antioxidant composition in geomembranes, with potential differences between white and black variants.

The immersion testing results emphasized the superiority of white geomembranes in immersion scenarios, with specific formulations designed for immersion conditions. These findings are reinforced by a practical case study where white geomembranes demonstrated their exceptional durability in a caustic bladder storage facility.

Overall, the adoption of "White Top Layer" geomembranes offers a viable and effective solution for enhancing liner performance, with demonstrated advantages in terms of longevity and environmental resistance. These findings can inform future decisions and considerations in the use of geomembranes in containment applications.

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