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Antioxidant Depletion of a HDPE Geomembrane in Arsenic-Bearing Tailings

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ABSTRACT
The design of saturated tailings impoundments often relies on geomembrane liners at the base and upstream face of the storage facility to prevent the movement of tailings-derived water into the adjacent groundwater flow system. The geomembrane must be chemically compatible with the tailings pore water to ensure its long-term performance in protecting the environment. In this paper, antioxidant depletion from a high density polyethylene (HDPE) geomembrane is examined using standard oxidative induction time over a 5-month period through immersion tests. The geomembrame is immersed in a synthetic pH-neutral pore water solution with elevated arsenic simulating pore waters from carbonate-associated gold mine saturated tailings. Antioxidant depletion rates for tests conducted at 85°C, 75°C and 65°C are presented and preliminary extrapolations at field temperatures are provided using Arrhenius modelling.

RÉSUMÉ
La conception des bassins de résidus saturés repose souvent sur des revêtements géomembranes à la base et à la face amont de l'installation de stockage pour empêcher le mouvement des eaux dérivées des résidus dans le système d'écoulement des eaux souterraines adjacent. La géomembrane doit être chimiquement compatible avec l'eau interstitielle des résidus pour assurer sa performance à long terme en matière de protection de l'environnement. Dans cet article, l'appauvrissement en antioxydants d'une géomembrane en polyéthylène haute densité (PEHD) est examiné en utilisant un temps d'induction oxydative standard sur une période de 5 mois grâce à des tests d'immersion. Le géomembranes est immergé dans une solution synthétique d'eau interstitielle à pH neutre avec un arsenic élevé simulant les eaux interstitielles des résidus saturés de mines d'or associés aux carbonates. Les taux d'appauvrissement des antioxydants pour les essais menés à 85°C, 75°C et 65°C sont présentés et des extrapolations préliminaires aux températures sur le terrain sont fournies à l'aide de la modélisation d'Arrhenius.

1 INTRODUCTION

Disposal of tailings from mineral extraction has historically relied on in situ soils or rocks to limit the migration of contaminated fluids. However, increasing awareness of environmental damages caused by the release of toxic metals and the legislation on basal structures becoming stricter have made the use of geomembranes (GMB) liners an attractive option to make storage of mine tailings more secure (Rowe et al., 2017; Tuomela et al., 2021). Arsenic species in tailings, in particular, are known for its association with sulfide minerals in gold-silver ore deposits (Jamieson, 2014), and thus is of great concern to biotic and human health.

Tailings impoundments involve GMB liners at the base and upstream face of the storage facility to prevent the movement of tailings-derived pore waters. In these waters, the distribution of metals and sulfate varies depending on the nature of the flow regime and particularly on the locations of the metal sources. Near the unsaturated surface of the impoundment, pore waters are highly affected by sulfide oxidation and/or dissolution of minerals and therefore a moderately acidic pH as well as high ion concentration is expected (Al et al., 2000). In deep saturated tailings with low dissolved oxygen (most likely where the GMB liner is placed), sulfide minerals tend to be stable due to the reduced conditions and do not oxidize (Dold, 2014). Thus, pore water pH likely remains around neutrality and with decreased concentrations of metals and sulfate (Al et al., 2000; Lange et al., 2009; Lindsay et al., 2009; Othmani et al., 2015).

Storage of tailings in the conventional "slurry-like" consistency associated with saturated conditions is still the most common practice worldwide, which requires construction and maintenance of the retention structures as well as management of an immense amount of water. The aggressiveness of pore water chemistry and pH along with high overburden stresses involved in these facilities can be considered among the most aggressive service conditions of GMBs in waste containment and mineral resource extraction applications.

Immersion tests conducted at different temperatures have been used to examine the effect of GMB formulation, elevated temperatures, chemical constituents of the leachate, and GMB thickness on the durability of the GMB liner (Abdelaal et al., 2014; Ewais et al., 2014; Jeon et al., 2008; Li et al., 2021; Rowe and Shoaib, 2017; Rowe et al., 2008; Rowe and Ewais, 2014; Thiel and Smith, 2004). Most of this work examined HDPE GMBs in different leachate solutions simulating municipal solid waste landfills. Few studies examined synthetic mining solutions such as high pH solutions found in silver and gold heap leaching

(Abdelaal and Rowe, 2017, 2014; Morsy et al., 2019; Morsy and Rowe, 2017) and low pH leachates (Rowe and Abdelaal, 2016) simulating copper, nickel and uranium heap leach pads in short-term to explore their antioxidant depletion in these applications.

The chemical compatibility of GMBs immersed in fluids similar to tailings-derived pore waters has not yet been addressed, so the key question of how pore water pH and chemistry affect GMB degradation behaviour remains unanswered. The present study provides a preliminary answer to this question, as antioxidant depletion from a high-density polyethylene (HDPE) GMB immersed in a synthetic tailings pore water solution with elevated arsenic content is reported. The experimental programmee that has been initiated and is presently ongoing is described in the following sections.

2 TESTING METHOD

Immersion tests are used in this study to accelerate the ageing of the GMBs in the laboratory and examine the chemical durability in the mine tailings solution of interest. In this test method, 200x95 mm GMB coupons are immersed in 4L glass jars filled with synthetic solutions that mimic the fluids expected in the field. The coupons are separated using glass rods to ensure that the immersion solution is in contact with all the surfaces of the GMBs. The jars are then incubated at different elevated temperatures (65°C, 75°C and 85°C for this study) to accelerate their degradation in the laboratory. The GMB is sampled at different incubation durations to explore the changes in the GMB properties over time. When enough data is collected at different elevated temperatures to assess the three degradation stages of the GMBs, Arrhenius modelling (Koerner, 2012) is used to allow extrapolation of the GMB degradation at lower field temperatures.

Quantification of the three degradation stages of the GMB (Hsuan and Koerner, 1998) involves monitoring different mechanical and physical properties using a variety of index tests (i.e., examining the changes in properties of interest relative to the initial value of unaged materials). Antioxidant depletion (Stage I) is described in terms of the oxidative induction time (OIT) and indicates the relative amount of antioxidant present in the GMB at different incubation durations relative to the unaged GMB. Standard oxidative-induction time (Std-OIT) (ASTM D3895, 2014) and high-pressure oxidative-induction time (HP-OIT) (ASTM D5885, 2017) are conducted in parallel to assess the depletion of antioxidants with different functioning temperature ranges stabilizing the GMB (e.g., hindered amines have an effective temperature range up to 150°C, while hindered phenols have a temperature range above 150°). Nevertheless, only results based on Std-OIT are presented herein to assess the depletion of antioxidants.

The GMB examined is a black, 1.5mm-thick, HDPE with hindered amine light stabilizers (HALS). The initial properties of the GMB based on ASTM index tests are presented in Table 1. The immersion fluid is a pH-neutral solution (Table 2) that simulates pore waters from carbonate-associated gold mine saturated tailings (Lange et al., 2009). The solution was changed periodically to ensure a constant pH during the testing period and to prevent the build-up of antioxidant concentrations in the solution.

Table 1. Initial properties of the tested GMB

Property	Unit	Value (mean $\pm$ SD[1])
Designator	-	MxC15
Nominal thickness (ASTM D5199, 2012)	mm	1.5
Resin density[2] (ASTM D1505, 2018)	g/cm^3	0.936
Crystallinity (ASTM E794, 2018)	%	51
Std-OIT (200°C/35kPa) (ASTM D3895, 2014)	Min	154 $\pm$ 5
HP-OIT (150°C/3500lPa) (ASTM D5885, 2017)	Min	960 $\pm$ 17

[1]SD = Standard deviation

[2]Provided by GMB manufacturer based on their test results

Table 2. Composition of the tailings pore water solution

	Concentration (mg/L except for pH)
pH	7.0
Aluminum	5
Arsenic	5.4
Calcium	117
Cadmium	7
Iron	1.5
Magnesium	60
Manganese	1.7
Potassium	12
Sodium	731
Ammonium	6
Chloride	1000
Bicarbonate	233
Nitrate	6

3 RESULTS AND DISCUSSION

Figure 1 depicts preliminary results of antioxidant depletion based on Std-OIT from the GMB immersed at three different temperatures (85°C, 75°C and 65°C). As seen in previous works (Abdelaal et al., 2011; Hsuan and Koerner, 1998), the exponential decay trend is evident. Additionally, the OIT depletion rate increases with incubation time.

Although the initial Std-OIT value of the GMB examined is relatively high, it decreased to 30 min (approximately 20% of the initial value) within only two months at 85°C. At 75°C and 65°C, similar residual value was reached but at longer times than the 5 months incubation duration presented herein.

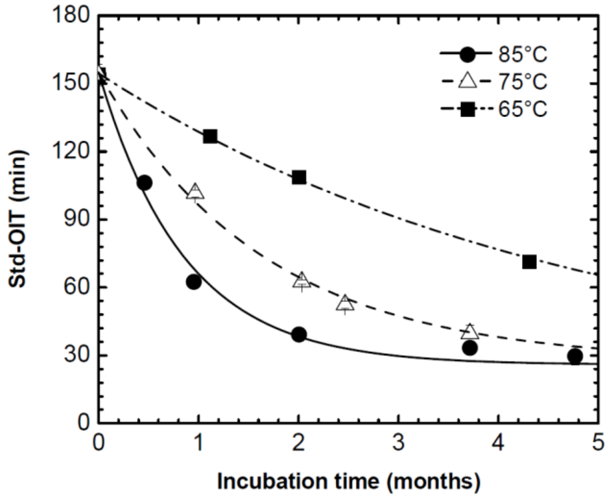

Figure 1. Std-OIT value versus incubation time at different incubation temperatures.

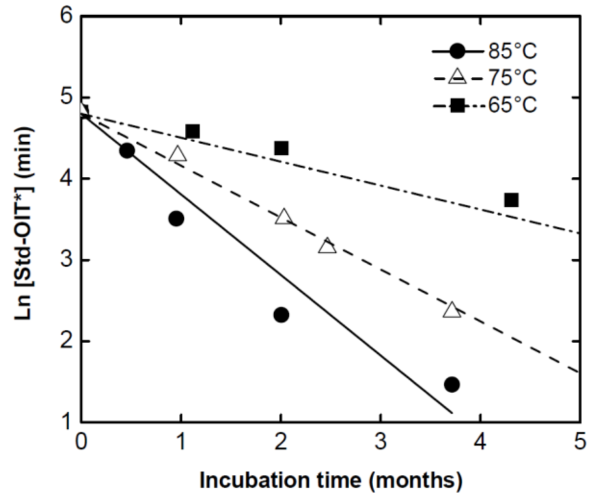

Figure 2. Ln(Std-OIT*) versus incubation time at different incubation temperatures.

The Std-OIT results for immersion in the As-bearing pore water solution are fitted using a three-parameter (first order) exponential decay function considering a high Std-OIT residual value (Rowe and Abdelaal, 2016). In such case, the three parameters (initial OIT, depletion rate and residual OIT) are used to describe the change in the Std-OIT value with time as follows:

$$OIT_t = ae^{-st} + OIT_r \quad [1]$$

where OIT_t (min) is the OIT value at time t, a (min) is the exponential fit parameter (= $OIT_o - OIT_r$), s (month^{-1}) is the antioxidant depletion rate, t is the incubation time (month), and OIT_r (min) is the residual OIT value (taken as 29min for the incubation time considered). The three-parameter model given by Equation 1 can be transformed into a two-parameter model:

$$OIT_t^* = OIT_o^* e^{-st} \quad [2]$$

where OIT_t^* = ($OIT_t - OIT_r$) and OIT_o^* = ($OIT_o - OIT_r$). By taking the natural log of Equation 2 it follows that:

$$ln(OIT_t^*) = ln(OIT_o^*) - st \quad [3]$$

The variation of $ln(OIT_t^*)$ with incubation time at 65, 75 and 85°C is presented in Figure 2. The depletion rate (s) of Std-OIT at each incubation temperature can be obtained from the slopes of the lines, and are listed in Table 3.

Table 3. Std-OIT depletion rates at different temperatures

Incubation Temperature (°C)	s (min/month)
85	0.992
75	0.639
65	0.295

In order to extrapolate OIT depletion rate down to site-specific temperatures, Arrhenius modelling is used according to the following equation (Hsuan and Koerner, 1998):

$$S = A\, e^{-\left(\frac{E}{RT}\right)} \quad [4]$$

$$\ln(S) = \ln(A) - \left(\frac{E}{RT}\right) \quad [5]$$

where S is the OIT depletion rate (values listed in Table 3), E is the activation energy under the present test conditions (kJ/mol), R is the universal gas constant (8.31J/mol), T the test temperature in absolute Kelvin degrees (K) and A is a constant known as collision factor.

The relationship between $\ln(S)$ and inverse temperature is shown in Figure 3.

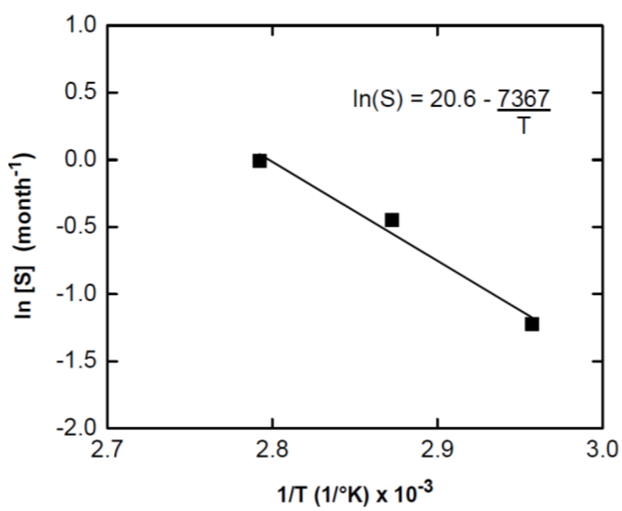

Figure 3. Arrhenius plot of the antioxidant depletion for the GMB immersed in the As-bearing tailings solution.

Using the equation depicted in the Figure 3, the OIT depletion rates at lower temperatures (and, hence, the ageing time required to deplete the antioxidants from the GMB) can be calculated. Table 4 presents the predicted antioxidant depletion rates and times for the GMB and immersion solution examined.

Table 3. Std-OIT depletion rates at different temperatures for immersion in the As-bearing tailings solution

Temperature (°C)	Antioxidant depletion rate ($month^{-1}$)	Antioxidant depletion time (yrs)
50	0.112	3.6
40	0.054	7.4
30	0.025	16
20	0.011	37

To compare the examined mine tailings solution with heap leaching solutions previously used for incubation of the same GMB, Figure 4 shows the antioxidant depletion at 85°C in the As-bearing tailings solution (Table 2), low pH pregnant liquor from copper, nickel and uranium heap leach pads (Rowe and Abdelaal, 2016), and high pH pregnant liquor from gold and silver heap leach pads (Abdelaal and Rowe, 2017). Table 4 shows the antioxidant depletion rates for these three mining solutions.

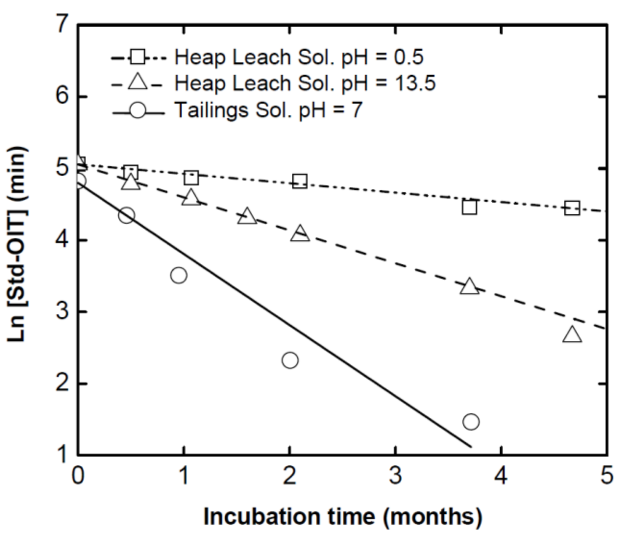

Figure 4. Std-OIT depletion for the GMB examined herein in different mining immersion fluids at 85°C.

Table 3. Antioxidant depletion rates in different incubation solutions

Incubation Solution	Antioxidant depletion rate ($month^{-1}$)
Heap leach pH 0.5	0.131
Heap leach pH 13.5	0.459
Mine tailings pH 7.0	0.992

Compared with the synthetic heap leaching solutions having very low and high pH, the antioxidant depletion rate in the mine tailings solution with pH 7.0 was the fastest during the first five months of incubation (2.2 times faster than the heap leach solution with pH 13.5 and 7.6 times faster than that with pH 0.5). For the heap leach solution with pH 0.5, the calculated antioxidant depletion times at 50, 40, 30 and 20°C Were 15, 28, 54 and 110 years, respectively (Rowe and Abdelaal, 2016). For the heap leach solution with pH 13.5, the predictions were 9, 17, 25 and 72 years, respectively (Abdelaal and Rowe, 2017). The calculated antioxidant depletion times are longer in both heap leach environments than in the pH-neutral tailings pore water. Nevertheless, given the preliminary nature of data from the GMB immersed in the mine tailings solution being established only at 85, 75 and 65°C for a 5 months period (relative to 36 months in heap leaching solutions), predictions in the mine tailing solutions may slightly change as more data becomes available in the future.

4 CONCLUSIONS

The focus of this paper was to present preliminary results for antioxidant depletion from a 1.5 mm HDPE GMB in a pH-neutral mine tailings solution with elevated arsenic content. Accelerated ageing tests at 85, 75 and 65°C are used to increase the rate of oxidative reactions and then Arrhenius modelling is used to extrapolate the antioxidant depletion rate to temperatures expected in the field. From the data collected up to the time of writing, the following can be tentatively concluded:

- At test temperatures of 75 and 85°C, the best fits obtained for the Std-OIT data (Figure 1) allowed the evaluation of an OIT_r value based on the data collected during the first 5 months. For the examined mine tailings solution, this value is approximately 29min. Updated results beyond the time frame reported in this paper indicate that the same OIT_r value has been reached at 65°C.

- The predicted antioxidant depletion times to the residual value indicated (i.e., $OIT_o \rightarrow OIT_r$) were about 3.6 years at 50°C, 7.4 years at 40°C, 16.1 years at 30°C and 36.9 years at 20°C. For the same GMB immersed in a heap leach solution with pH 0.5, antioxidant depletion times were 15, 28, 54 and 110 years for 50, 40, 30 and 20°C, respectively. When considering a pH 13.5 heap leaching solution, depletion times are 9, 17, 25 and 72 years for the same temperatures. At least for the limited testing period considered in this paper, the simulated tailings environment showed shorter antioxidant depletion stage than in heap leaching solutions.

This paper only reported antioxidant depletion detected by Std-OIT tests, but HP-OIT tests are also being used to analyze the rate at which antioxidants with different functioning temperature ranges will deplete. Additionally, different mechanical and physical properties are also being monitored to assess the duration of Stages II and III of the

GMB degradation. Such discussions are reserved for future publications.

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