

Antioxidant depletion from a HDPE geomembrane immersed in unsaturated tailings pore waters and heap leaching solutions

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ABSTRACT

Tailings dams and heap leach pads projects are among the mining applications that extensively use polyethylene geomembranes to prevent the migration of fluids to the surrounding environments. The pH of acidic heap leaching solutions are typically at or below 2.0, while tailings pore waters from pre-filtered or unsaturated tailings may range between 2.0 and 4.5. In this paper, antioxidant depletion from a high-density polyethylene (HDPE) geomembrane immersed in synthetic tailings pore water solutions is examined over a 5-month period. Immersion solutions involve a pH 4.0 solution at 85°C, 75°C and 65°C, and a pH 2.0 solution at 85°C simulating pore waters from unsaturated Cu-Zn sulphide-rich tailings. Preliminary antioxidant depletion rates and extrapolation to field temperatures are presented for pH 4.0 tailings and compared to previously published data of the same geomembrane immersed in heap leach environments with pH of 1.25 and 2.0.

RÉSUMÉ

Les projets de barrages de résidus et de lixiviation en tas font partie des applications minières qui utilisent largement des géomembranes en polyéthylène pour empêcher la migration des fluides vers les environnements environnants. Le pH des solutions acides de lixiviation en tas est généralement égal ou inférieur à 2.0, tandis que les eaux interstitielles des résidus provenant de résidus préfiltrés ou insaturés peuvent varier entre 2.0 et 4.5. Dans cet article, l'épuisement des antioxydants d'une géomembrane en polyéthylène haute densité (PEHD) immergée dans des solutions d'eau interstitielle de résidus synthétiques est examiné sur une période de 5 mois. Les solutions d'immersion impliquent une solution à pH 4.0 à 85°C, 75°C et 65°C, et une solution à pH 2.0 à 85°C simulant les eaux interstitielles de résidus insaturés riches en sulfure de Cu-Zn. Les taux préliminaires d'épuisement des antioxydants et l'extrapolation aux températures sur le terrain sont présentés pour les résidus à pH 4.0 et comparés aux données publiées précédemment de la même géomembrane immergée dans des environnements de lixiviation en tas avec un pH de 1.25 et 2.0.

1 INTRODUCTION

Unsaturated tailings disposal has been adopted worldwide as an alternative solution for mitigating the risk of failures associated with saturated tailings impoundments. Essentially, they consist of a dry cake material with typically 50 to 85% saturation that is compacted into dense and stable stacks (often termed "dry stacks") requiring no dam or associate tailings pond for confinement (Consoli et al., 2022; Davies, 2011).

Filtered tailings provide attractive benefits over thickened, slurried tailings, such as (Davies et al., 2010; Lupo and Hall, 2011): occupation of less space since stacked material is denser, thus reducing the environmental footprint of the facility; improved stability due to high solids content; and the possibility of continuous reclamation, making final reclamation of the mine faster. Although the amount of tailings-derived pore waters seeping from the impoundment is less compared with traditional slurry disposal, environmental containment is still a concerning design factor.

Geomembranes (GMBs) have been considered in the design of tailings storage facilities for the control of fluid migration (Tuomela et al., 2021). High-density polyethylene (HDPE) or linear low-density polyethylene (LLDPE) GMBs with thickness of 1.5-2.5 mm are typically used as liners to the tailings dam wall (McLeod, 2016) or

placed over in-situ or compacted soil on the base (Lupo and Morrison, 2007). The compatibility of a GMB with the tailings effluent it will come into contact with is a major factor affecting GMB degradation over time.

Degradation of polyethylene GMBs conceptually happens in three stages (Hsuan and Koerner, 1998). Stage I refers to the depletion of antioxidants, that is, the components added to GMB formulation to delay accelerated oxidation stages. After antioxidants deplete, oxygen will then begin to attack the polymer, leading to Stage II, wherein degradation effectively begins although with no measurable impacts on its physical or mechanical properties, and finally Stage III, where degradation is severe enough to change the GMB properties.

The quantification of GMB chemical durability in tailings dams applications must then start with the assessment of antioxidant depletion. This can be achieved in a laboratory environment through a combination of oven immersion tests at different temperatures (ASTM D5322, 2017) and monitoring of the GMB oxidative induction time (OIT), which indicates the relative amount of antioxidants present in the GMB at a given time. Standard oxidative-induction time (Std-OIT) (ASTM D3895, 2019) and high-pressure oxidative-induction time (HP-OIT) (ASTM D5885, 2020) 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°).

Little information is currently available with respect to antioxidant depletion of GMBs in tailings solutions. E Silva et al. (2021) presented the first five months of Std-OIT data from a 1.5 mm HDPE GMB immersed in a pH 7.0 solution simulating arsenic-bearing pore water from saturated gold mine tailings. Immersion temperatures included 85°C, 75°C and 65°C. The unaged Std-OIT value from the examined GMB decreased 60%, 78% and 84% after five months of incubation at 65, 75 and 85°C, respectively. For the incubation time considered, the early time Std-OIT depletion rate in the pH-neutral tailings solution was greater than in synthetic heap leaching solutions with pHs of 0.5 and 13.5.

Unsaturated tailings allow the access of oxygen to sulphide minerals, which then increases the extent of oxidation reactions and leads to pore water with high concentration of metals and sulfate and pH that may range between 2.0 and 4.5 (Acero et al., 2007; Al et al., 2000). Since chemistry and pH at the bottom of an unsaturated tailings storage facility differ from traditional saturated impoundments, compatibility of GMBs in unsaturated tailings pore water deserves separate consideration.

This paper therefore reports antioxidant depletion from the same GMB examined by E Silva et al. (2021) but now immersed in synthetic pore water solutions with acidic pH and elevated concentrations of metals and sulfates. Performance of the GMB is compared with that in the pH-neutral pore water previously reported. The difference between antioxidant depletion in unsaturated tailings versus acidic heap leaching environments is then addressed to provide an insight of GMB performance in two very different mining applications.

2 MATERIALS AND METHODS

Two-sided exposure tests (ASTM D5322, 2017) are used in this study to assess GMB chemical compatibility. In this immersion technique, 200 x 95 mm coupons are placed in 4 L glass jars filled with synthetic chemical solutions mimicking the effluents expected in the field. Coupons are separated with glass rods to ensure that the immersion solution is in contact with both surfaces of the GMB. The jars are subsequently heated to different elevated temperatures (65°C, 75°C and 85°C in this study) to accelerate the ageing of the GMB. Samples are taken at different incubation durations to assess changes in GMB properties over time. Data collected at elevated temperatures are then modelled to allow extrapolation of the GMB degradation to lower field temperatures.

Only results based on the Std-OIT testing are presented in this paper, in other words, attention is aimed at Stage I of GMB degradation. The GMB examined is a black, 1.5mm-thick, HDPE with hindered amine light stabilizers, or HALS (Table 1). The immersion solutions are pH 2.0 and pH 4.0 solutions simulating pore waters from tailings highly affected by oxidation of sulfide minerals (Table 2). The immersion liquid was replaced with fresh solution every 1.5 months to avoid the build-up of antioxidants leached from the GMB.

Composition of unsaturated pore water solutions was based on geochemical data collected at the Kidd Creek copper-zinc sulfide deposit, Ontario (Al et al., 2000, 1994).

Sulfide oxidation within the residue at Kidd Creek generated low-pH conditions in the pore water and increased concentrations of Cd, Mg, Mn, Zn and SO₄, as well as Al, Co, Fe, Cu, Pb and Ni, although to a less extent.

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, 2019)	Min	154 \pm 5
HP-OIT (150°C/3500IPa) (ASTM D5885, 2020)	Min	960 \pm 17

¹SD = Standard deviation

²Provided by GMB manufacturer based on their test results

Table 2. Composition of the unsaturated tailings pore water solutions (concentration values in mg/L, unless otherwise noted).

	PW-1	PW-2
pH	2.0	4.0
Aluminum	5.5	5.5
Calcium	452.0	452.0
Cadmium	42.8	42.8
Copper	2.6	2.6
Iron	19.4	19.4
Lead	1.1	1.1
Magnesium	3000	3000
Manganese	887	887
Nickel	6.6	6.6
Potassium	40.4	40.4
Sodium	68.6	68.6
Zinc	1430	1430
Chloride	16.3	16.3
Sulfates	17,580	16,870
Sulphuric acid ^a (mL/L)	0.4	0.01

^aFor pH adjustment

3 RESULTS AND DISCUSSION

3.1 Antioxidant depletion in various tailings incubation media

Preliminary results of antioxidant depletion based on Std-OIT from the HDPE GMB immersed in pH 2.0, pH 4.0 and pH 7.0 tailings solutions at 85°C are compared (Figure 1). Data from the pH 2.0 and 4.0 solutions are best fitted using a second order exponential decay function, also termed a 4-parameter model (Abdelaal and Rowe, 2014). For comparison purposes, the same model is used to fit

antioxidant depletion data in the pH 7.0 solution, which yields a different depletion rate than the one reported by E Silva et al. (2021) based on a 3-parameter model.

For the five months incubation duration, decreasing the pH of unsaturated tailings from 4.0 to 2.0 resulted only in a slightly faster Std-OIT early-time depletion rate (Table 3). When compared to tailings pore water in saturated conditions, the difference in Std-OIT depletion rate is very small, and potentially insignificant. The initial Std-OIT value of the GMB examined is relatively high, but it decreased approximately 80% within the incubation time considered. The residual Std-OIT value reached after five months is fairly similar between the three tailings solutions.

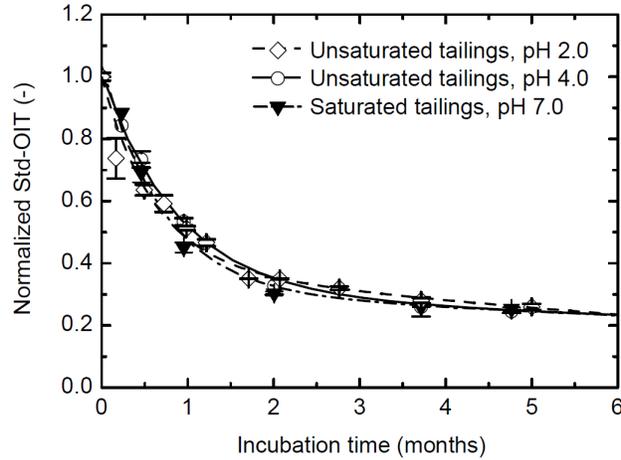


Figure 1. Variation of normalized Std-OIT with incubation time at 85°C for pH 2.0, 4.0 and 7.0 tailings solutions.

Table 3. Antioxidant depletion rates for different tailings solutions at 85°C.

Incubation media	Early-time depletion rate at 85°C (month ⁻¹)
Unsaturated tailings, pH 2.0	1.67
Unsaturated tailings, pH 4.0	1.14
Saturated tailings, pH 7.0	1.41

3.2 Modeling Std-OIT data and extrapolating depletion rates to lower temperatures

The 4-parameter model used to fit antioxidant depletion data in the pH 4.0 tailings solution involves superimposing two exponential functions, and can be described as (Abdelaal and Rowe, 2014):

$$\frac{OIT_t}{OIT_0} = a \times e^{-s_1 t} + b \times e^{-s_2 t} \quad [1]$$

where OIT_t is the normalized Std-OIT value at time t , OIT_0 is the normalized unaged Std-OIT value (in other words, unity), s_1 (month⁻¹) is the early-time antioxidant depletion rate, s_2 (month⁻¹) is the late-time antioxidant depletion rate,

a and b are the amplitudes of the exponential decays (note that the sum of a and b is unity).

The 4-parameter model is also used to fit the 75°C and 65°C Std-OIT depletion data in pH 4.0 tailings (Figure 2). There is a substantial difference between the early- and late-time depletion rates at different temperatures (Table 4). Also, depletion rates increase with increasing temperature.

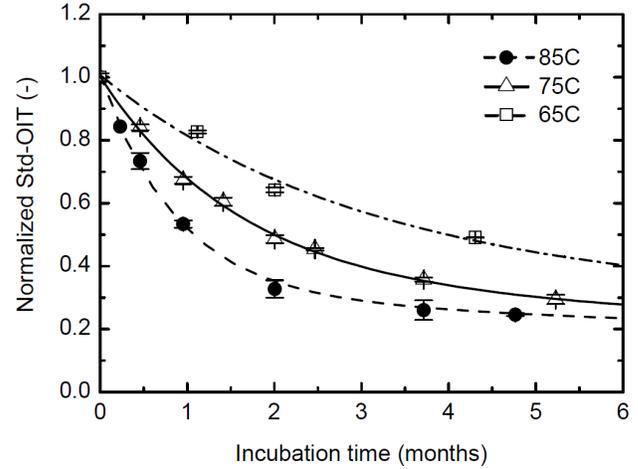


Figure 2. Variation of normalized Std-OIT with incubation time in pH 4.0 tailings at different temperatures.

Table 4. Antioxidant depletion rates and exponential fitting parameters for different incubation temperatures.

T (°C)	a	Early time-depletion rate, s_1 (month ⁻¹)	b	Late time-depletion rate, s_2 (month ⁻¹)
65	0.62	0.37	0.38	0.02
75	0.67	0.64	0.33	0.03
85	0.70	1.14	0.30	0.05

The depletion rates s_1 and s_2 in Table 4 are then plotted against the inverse of the incubation temperature in an Arrhenius plot (Figure 3). Arrhenius modelling is used according to the following equation (Hsuan and Koerner, 1998):

$$S = A e^{-\left(\frac{E}{RT}\right)} \quad [2]$$

$$\ln(S) = \ln(A) - \left(\frac{E}{RT}\right) \quad [3]$$

where S is the OIT depletion rates (values listed in Table 4), E is the activation energy (or the slope of the Arrhenius regression line) under the present test conditions (kJ/mol), R is the universal gas constant (8.31 J/mol), T the test temperature in absolute Kelvin degrees (K) and A is a constant known as collision factor.

The resulting activation energies for incubation in pH 4.0 tailings were 56 and 36.1 kJ/mol for the early- and late-time depletion rates, respectively. The discrepancy is a

result of the depletion rates from the 4-parameter model being quite different.

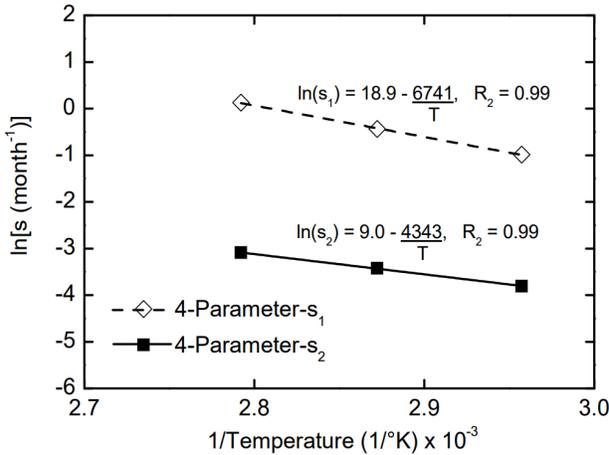


Figure 3. Arrhenius plots for incubation in pH 4.0 tailings solution.

The Arrhenius plots in Figure 3 are used to extrapolate the depletion rates s_1 and s_2 to field specific temperatures of interest, for instance, 40°C and 20°C. Next, the amplitude a from Table 4 is linearly correlated to the incubation temperature and extrapolated to the target field temperatures (see Abdelaal and Rowe 2014, Method A). Since the sum of a and b is unity, parameter b can easily be computed (Table 5).

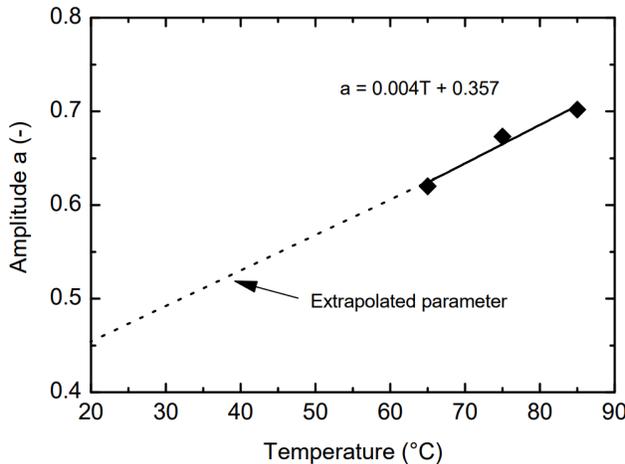


Figure 4. Extrapolation of the amplitude a .

Table 5. Extrapolated depletion rates and exponential fitting parameters for lower field temperatures.

T (°C)	a	Early time-depletion rate, s_1 (month ⁻¹)	b	Late time-depletion rate, s_2 (month ⁻¹)
20	0.44	0.017	0.56	0.003
40	0.52	0.075	0.48	0.008

3.3 Comparison with heap leaching environment

The first five months of Std-OIT depletion from the GMB immersed in pH 4.0 tailings at 85°C are compared to the data obtained from immersion in heap leaching solutions with pHs of 1.25 and 2.0 at the same temperature (Figure 5). These two heap leach solutions simulate effluents found in copper, nickel and uranium heap leach pads, and have the same concentration of metals (Rowe and Abdelaal, 2016). Chemistry also involves elevated concentration of metals and sulfates, but much higher than the unsaturated pore water solution examined herein (e.g., sulfates concentration is ~2.7 higher in the heap leach solutions).

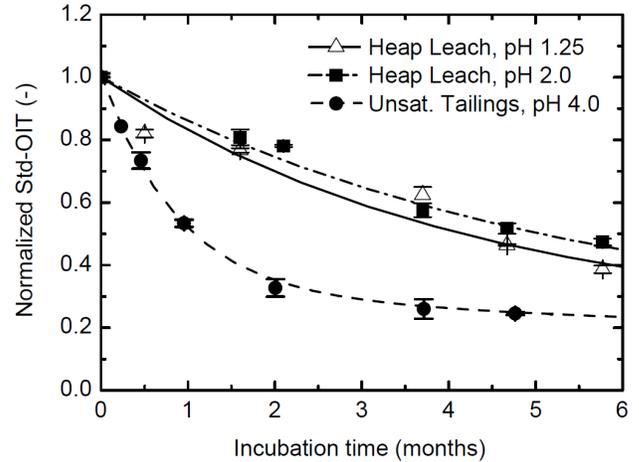


Figure 5. Variation of normalized Std-OIT with incubation time at 85°C for the pH 4.0 unsaturated tailings solution and pH 1.25 and 2.0 heap leaching solutions.

The early-time Std-OIT depletion rate in pH 4.0 tailings was approximately four and five times faster than the heap leach solutions with pHs of 1.25 and 2.0, respectively. As previously reported (Rowe and Abdelaal, 2016), the higher concentration of metals in the heap leaching solutions might have hampered the diffusion of antioxidants and, thus, slowed antioxidant depletion. Since pH alone does not seem to have played a role (the difference in antioxidant depletion rate between the pH 4.0 and pH 2.0 tailings solutions having the same metal concentration is relatively small, vide Table 3), the decreased performance of antioxidants in tailings might be related to the chemistry of those two solutions. Further investigation is necessary to assess if this is simply due to lower metal concentrations in tailings relative to heap leaching or an effect of a particular chemical constituent (e.g., Hornsey et al., 2010).

Using the depletion rates and exponential fitting parameters at lower temperatures (Table 5), the ageing time (t) in Equation 1 required to deplete the unaged Std-OIT value (i.e., 154 min) to any residual value can be computed. For the GMB immersed in the pH 4.0 tailings solution, the Std-OIT residual value reached at the end of five months of incubation at 85°C is 35 min. Similar residual value was reached at 75°C and 65°C but at longer times than the five months reported herein.

The calculated depletion times in pH 4.0 tailings are much shorter compared to pH 1.25 and 2.0 heap leaching solutions (Table 6). Since results from the GMB immersed

in the unsaturated tailings solution were only reported for a 5-month period and three incubation temperatures (relative to 36 months and five incubation temperatures in heap leaching solutions), predictions might change as additional data becomes available.

Table 6. Predicted antioxidant depletion times at 20°C and 40°C for the pH 4.0 tailings solution and pH 1.25 and 2.0 heap leaching solutions.

T (°C)	Incubation media	Std-OITr (min)	Depletion rate (month ⁻¹)	Time to Std-OITr (yrs)
20	Heap Leaching, pH 1.25 ^a	54	0.004	97
	Heap Leaching, pH 2.0 ^a	58	0.003	110
	Tailings, pH 4.0	35	0.017; 0.003	28
40	Heap Leaching, pH 1.25 ^a	44	0.016	25
	Heap Leaching, pH 2.0 ^a	47	0.012	25
	Tailings, pH 4.0	35	0.075; 0.008	9

^a From Rowe and Abdelaal (2016)

4 CONCLUSIONS

Degradation of antioxidants can be of great concern for the long-term performance of GMBs in tailings dams applications. Thus, preliminary antioxidant depletion detected by Std-OIT testing from a 1.5 mm HDPE GMB immersed in unsaturated tailings pore water solutions was reported in this paper. Immersion solutions involved a pH 4.0 solution at 85°C, 75°C and 65°C, and a pH 2.0 solution at 85°C. Arrhenius modelling was used to extrapolate the depletion rates in pH 4.0 tailings to lower field temperatures, and the ageing time required to deplete the unaged Std-OIT value to the residual value after 5-months incubation was calculated and compared to depletion times in heap leaching solutions previously published. For the conditions examined and data collected up to the time writing, the following can be concluded:

- Decreasing the pH from 4.0 to 2.0 in unsaturated pore waters with the same metal concentrations resulted only in a small, slightly faster, change in early-time Std-OIT depletion. For the 85°C incubation temperature and considering a 4-parameter model fitting the data, depletion rates in unsaturated tailings are not significantly different than that in a pH-neutral pore water solution from saturated arsenic-bearing gold mine tailings.
- At 85°C, Std-OIT depletion rates from the GMB immersed in pH 2.0 and 4.0 tailings were faster than in the heap leach solutions with pHs of 1.25 and 2.0. For instance, the early-time depletion rates were 1.67 and 0.2 month⁻¹ for immersion in pH 2.0 tailings and pH 2.0 heap leach solutions, respectively.

- Predicted antioxidant depletion times in lower field temperatures were significantly lower for pH 4.0 tailings (based on a 5-month period) compared to low-pH heap leaching (based on a 36-month period). For instance, it was 28 years at liner temperature of 20°C in the pH 4.0 tailings solution versus 97 and 110 years in the heap leach solutions with pHs of 1.25 and 2.0.

The effect of decreasing pH from 4.0 to 2.0 and changing pore water chemistry to that of saturated mine tailings with pH 7.0 might become more evident for antioxidants detected by HP-OIT testing. Updated results will be presented in the oral presentation at the conference. The full set of results will be published in a subsequent paper when they have been run a sufficient time to draw clear conclusions.

Results presented in this paper are specific to the geomembrane and tailings solutions examined. Since pore water chemistry and pH significantly vary depending on the nature of metal sources and flow regime, other tailings effluents may affect the long-term performance of HDPE GMBs differently. Also, a generic GMB formulation might be better suited than others to a particular mining application, that is to say, not all HDPE's will perform the same way.

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