

Effect of chlorinated water on the antioxidant depletion of HDPE geomembrane without HALS

Fady B. Abdelaal & R. Kerry Rowe

GeoEngineering Centre at Queen's-RMC, Queen's University, Ellis Hall, Kingston, ON, Canada.

ABSTRACT: This study investigates the compatibility of a high-density polyethylene geomembrane to chlorinated potable water applications using immersion tests. The geomembrane examined was stabilized with hindered phenols and phosphites but does not contain hindered amine light stabilizers (HALS) in its antioxidant/stabilizer package. The chlorine is introduced to the incubation solution as sodium hypochlorite that produces free chlorine when mixed with water. Many trials were conducted in order to maintain chlorine concentration at elevated temperatures and to ensure the same mass loading of chlorine on the geomembrane surface area to mimic the chlorine loading in the field. Results are presented in terms of oxidative induction time (OIT) using the standards OIT test. The results show a large increase in the antioxidant depletion rates when chlorine is introduced to water. Incubation of the geomembranes in chlorinated water was presented at different elevated temperatures and Arrhenius modelling was performed to extrapolate antioxidant depletion stage at lower field temperatures.

Keywords: Chlorine, potable water, Geomembranes, antioxidants

1 INTRODUCTION

According to Koerner (2012), polyethylene (PE) geomembranes (GMB) are estimated to represent 80% of the GMB industry. PE resins are produced with densities varying from 0.88 to 0.96 g/cm³ (Scheirs 2009), with the difference in resin density being related to the manipulation of the length of the side chains that control the polyethylene chain packing. High density polyethylene (HDPE) GMBs are used as the bottom liners of different geoenvironmental applications due to their high chemical resistance to a wide range of chemicals. HDPE GMBs comprises 96-97.5% MDPE resin, 0.5% additives (e.g., antioxidants, UV stabilizers) and 2-3% carbon black (Hsuan and Koerner 1998) but the addition of carbon black raises the final product density to HDPE range as defined by ASTM D 883.

Oxidative degradation of HDPE GMBs has detrimental effects on its physical and mechanical properties and can eventually jeopardizes its main function as a hydraulic barrier layer. According to Hsuan and Koerner (1998), HDPE GMBs encounter three stages of degradation until the nominal failure in a selected engineering property is reached. The degradation stages of the GMB start in Stage I by losing the antioxidants and stabilizers in the GMB then passes through an induction time (Stage II) before the GMB starts to exhibit a decrease in its physical and mechanical properties with time in Stage III until nominal failure characterized by 50% loss in a selected engineering property.

Chlorine is usually used as a disinfectant in water to kill bacteria and microbes. In most disinfected drinking water, chlorine is present at concentrations of 0.2-1 ppm (White 1978). In several standards, HDPE pipes are approved to transport drinking water exposing the pipe to chlorine levels of 0.1-0.4 ppm (Mitroka et al. 2013). Since the chlorine molecule has a high electronegativity, it is considered a strong oxidizing agent that makes the PE susceptible to oxidative degradation. PE pipes exposed to free chlorine encounter degradation in their mechanical properties that can drastically shorten their service lives (Veibke et al. 1996; Hassinen et al. 2004; Wheltron et al. 2009; Mitroka et al. 2013). Several investigators (e.g., Hassinen et al. 2004; Azhdar et al. 2009; Castagnetti et al. 2011; Yu et al. 2013) showed that the antioxidants in polyethylene pipes were rapidly chemically consumed by the action of chlorinated water. In HDPE pipe studies, accelerating aging has been involved either increasing free chlorine concentrations

(e.g., 4000~10,000 ppm; 0.4-1%) at room temperatures or by increasing the temperatures of the chlorinated water and using circulation loops to ensure constant chlorine levels within the incubation solution (Devilliers et al. 2011).

HDPE GMBs are also used in lining reservoirs for potable water that has been treated with chlorine. The exposure of the GMB liner to chlorinated potable water raises questions as to their service life in this application. According to Mills (2011), there were series of failures in thermoplastic olefin materials in North America and Australia for liners and floating covers in contact with chlorine. Mills (2011) showed that at very high sodium hypochlorite content, the stabilizers in the GMB were deactivated leading to oxidation and stress cracking failure of the specimens.

The objective of this study is to investigate the impact of chlorine, as used in potable water reservoirs applications, on antioxidant depletion from a HDPE GMB using accelerating ageing conditions.

2 MATERIALS AND TESTING METHODS

The tested GMB is a 1.5 mm thick commercially available HDPE manufactured in 2005 using resin from Pétromont (S-7000). High performance liquid chromatography indicated the presence of hindered phenols (primary) and phosphites (secondary) antioxidants. No hindered amine light stabilizers (HALS) were detected.

A series of index tests were conducted on the GMB specimens to quantify its initial properties (Table 1). After incubation of the GMB specimens, antioxidant depletion stage was monitored using standard oxidative induction time (Std-OIT; ASTM D 3895) that can capture antioxidants, such as those detected in the examined GMB, with effective temperatures above 200°C.

Both free and total chlorine contents in the incubation fluid were measured using a Hatch[®] pocket colorimeter. The colorimeter can detect chlorine range from 0.02 and up to 8 ppm. For higher chlorine concentrations, the solution was diluted and measured using the colorimeter and then adjusting the concentration using the dilution factor.

Table 1. Index properties of the tested GMB

Properties	Method	Unit	Values (Mean ± SD)
Standard oxidative induction time	ASTM D 3895	min	100 ± 2
High-pressure oxidative induction time	ASTM D 5885	min	260 ± 10
Melt index (190°C/21.6 kg)	ASTM D 1238	g/10min	15.9 ± 0.3
Single point stress crack resistance	ASTM D 5397	hours	720 ± 130
Machine direction break strength		kN/m	47.3 ± 1.8
Machine direction break strain	ASTM D 6693	%	822 ± 30
Cross machine direction break strength	(Type IV)	kN/m	46.7 ± 1.8
Cross machine direction break strain		%	874 ± 46

3 RESULTS AND DISCUSSIONS

3.1 Incubation solution

Disinfection of water can be done by introducing chlorine gas (Cl₂) or by adding bleach such as sodium hypochlorite (NaOCl) (Mills 2011). NaOCl is produced by adding chlorine gas to an aqueous solution of sodium hydroxide (Wallis-Lage 2010). In the presence of water, both Cl₂ and NaOCl generate free chlorine (HOCl and ClO⁻) that is responsible for the disinfection and the oxidizing action (Eng et al. 2011).

Introducing free chlorine to water was examined by either using a chemical grade NaOCl or household bleach (Clorox[®]). Both resulted in the increase of the free chlorine concentration in the incubation solution (Figure 1a). However, at same concentrations, the free chlorine was higher for NaOCl than the bleach. In addition, since the household bleach is expected to contain unknown additives that may affect the results, it was decided to use the chemical grade NaOCl in the experiments presented in this study.

To investigate the degradation of the GMB when exposed to chlorine in the laboratory, accelerating ageing was conducted using jar immersion tests. In these experiments, 16 GMB coupons 20x10 cm in size were incubated in 4-liter glass jars filled with 3.5 liters of chlorinated water. The target test temperatures varied from room temperature to 85°C and the target free chlorine content varied between 0.5 and 5

ppm. However, prior to the incubation, several parameters were investigated to verify the target testing conditions.

The main challenge in these experiments was to maintain a fixed chlorine loading during incubation mimicking potable water reservoirs conditions. At 85°C, Figure 1b shows a rapid decrease in the free chlorine content with incubation time for three different jars with different initial free chlorine content. At an initial concentration of 0.5 ppm free chlorine, all the free chlorine was depleted in less than two hours and even increasing the initial chlorine content 10-fold (i.e., to 5 ppm), the free chlorine content decreased to undetectable levels at around 9 hours. Even with recharging the chlorine content every 9 hours, the average chlorine content would be less than 3 ppm in these experiments. Thus, to maintain the target average chlorine levels in the immersion solution, the initial chlorine content needed to be boosted.

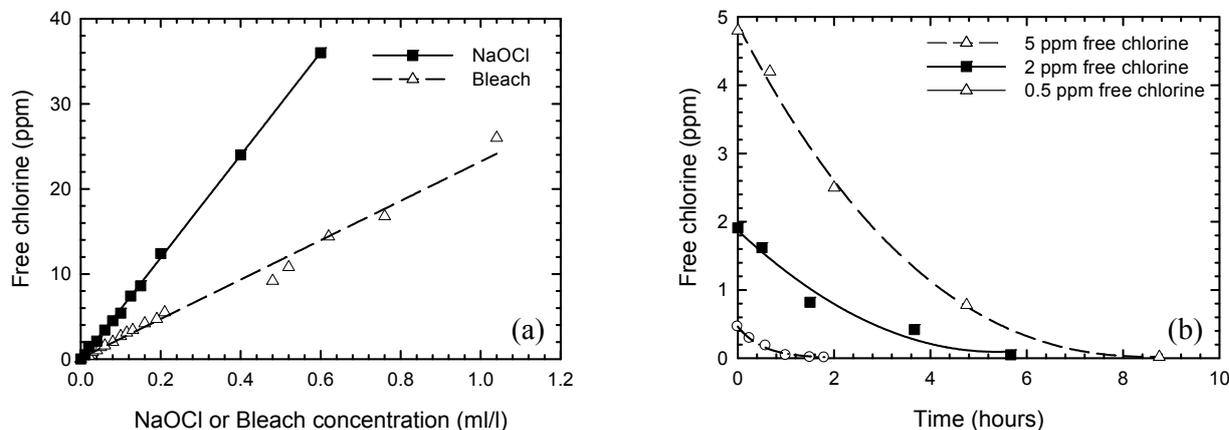


Figure 1. (a) Effect of sodium hypochlorite and bleach on the free chlorine concentration. (b) Depletion of different concentrations of free chlorine with time at 85°C.

Figure 2a shows the decrease of chlorine content in immersion jars containing water boosted with 22 ppm free chlorine and unaged GMB specimens at three different elevated temperatures. The free chlorine was completely depleted after 72, 120, and 200 hours of incubation at 85, 75, and 65°C, respectively and hence, the average chlorine concentration was between 6~7 ppm at these temperatures. The decrease in temperature results in less consumption of chlorine and hence, recharging the chlorine content could be done at longer intervals at lower temperatures.

At 85°C, the Std-OIT of the GMB was checked and compared to samples incubated in reverse osmosis water to check the effect of an average chlorine content of 6.5 ppm maintained for 7 days. There was no significant difference between the Std-OIT of specimens immersed in water and chlorinated water solution. This raises the question: why such a rapid depletion of chlorine but little effect?

One possible explanation for the rapid consumption of chlorine in the jars was the presence of a large number of GMBs coupons with high surface area available to consume the free chlorine content. To investigate the effect of temperature and the GMB surface area, two jars containing water with 5 ppm initial free chlorine content were incubated at 85°C. One jar was only filled with chlorinated water and the other was filled with the same volume of solution and having 16 GMB coupons having total surface area of 0.64 m². For the jar without GMBs, the chlorine content was totally consumed in 120 hours while the jar containing the GMBs depleted all its chlorine content in only 8 hours (Figure 2b). This implies that the high ratio of GMB surface area to volume of solution, typical of immersion tests, was the primary factor causing the very fast consumption of the chlorine in the jars. Thus, while the initial concentration of chlorine in the 6.5 ppm test reported in the previous paragraph was realistic, the initial mass of free chlorine per unit surface area of the GMB was very low; especially compared to a water reservoir application. Thus, the low effect of chlorine reported in the previous paragraph was because the mass of free chlorine per unit area of geomembrane surface was unrealistically low.

It follows that to get realistic results, one needs to consider an available mass of chlorine similar to what might be expected in a water reservoir application based on the volume of chlorinated water at a representative concentration per unit area of the exposed GMB surface. For example, considering a specific water reservoir of 10 million liters capacity lined with GMB and the ratio of the GMB surface area to volume of chlorinated water (SA/V) was 0.3 m²/m³, to maintain this SA/V ratio in jar immersion tests, this means that the GMB surface area corresponding to 3.5 liters of solution should be reduced to 0.0011 m² (i.e. 0.64/0.0011~600 times). This corresponds to a 3 cm x 1.8 cm GMB piece immersed in 3.5 liters of chlorinated water.

To investigate the effect of chlorine loading, two jars with the same chlorine loading were incubated at 85°C. The first jar was loaded with 1 ppm free chlorine content with only a 3 cm x 1.8 cm GMB coupon while the other jar contained 16 coupons of GMB with total surface area of 0.64 m² but the chlorine content was boosted 600 times (i.e., to 600 ppm) to maintain the same mass of free chlorine per unit area. Specimens of the GMB from both jars were tested after different times of incubation in Std-OIT test. The results showed that the depletion of antioxidants from both jars were similar up to full depletion (discussed in the next section). Thus boosting the chlorine concentration in the jar immersion tests to provide a realistic mass of free chlorine per unit surface area of GMB provided a good simulation of OIT depletion observed for a single small coupon in water with 1 ppm chlorine with the same mass of free chlorine per unit surface area selected to be representative of a real field case. Thus, in jar immersion tests, the free chlorine concentration should be boosted to maintain similarity with field condition with high chlorine loading per unit area surface area of GMB.

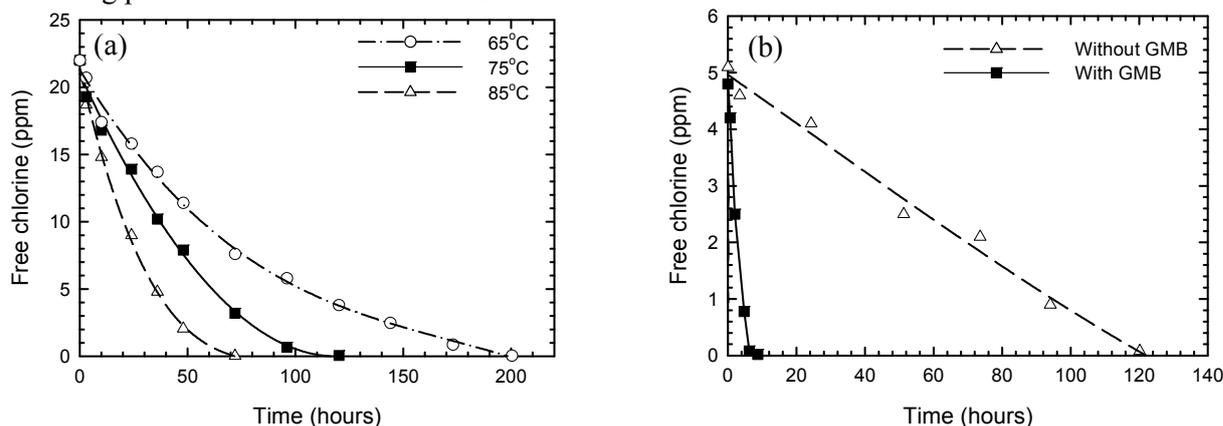


Figure 2. Change of the free chlorine content with time for (a) boosted chlorine content at different elevated temperatures; (b) 5 ppm initial free chlorine content with and without GMB specimens in the jar at 85°C.

3.2 GMB antioxidant depletion

The depletion of antioxidants from the tested GMB was investigated in a solution with free chlorine content boosted 600 times as discussed in the previous section to simulate the chlorine loading of 1 ppm free chlorine in the field (and referred to herein as the “1 ppm free chlorine” case). Figure 3 shows the depletion of Std-OIT of the tested GMB when immersed in 1 ppm free chlorine, synthetic municipal solid waste (MSW) leachate, and reverse osmosis (RO) water at 85°C. The MSW leachate was reduced and contained 5 ml/l industrial surfactant (IGEPAL Ca-720). The fastest Std-OIT depletion was in the 1 ppm free chlorine followed by the MSW leachate. The slowest depletion was for the RO water. After almost one month of incubation in the chlorinated water solution, Std-OIT was fully depleted to ~1% of the initial Std-OIT value while in leachate and water, Std-OIT was reduced only to 20 and 70% of the initial values, respectively. The rate of depletion of antioxidants in the 1 ppm free chlorine solution was almost 6 times faster than the leachate with surfactant. This shows the detrimental effect of chlorine on the depletion of the GMB antioxidants detected by Std-OIT test.

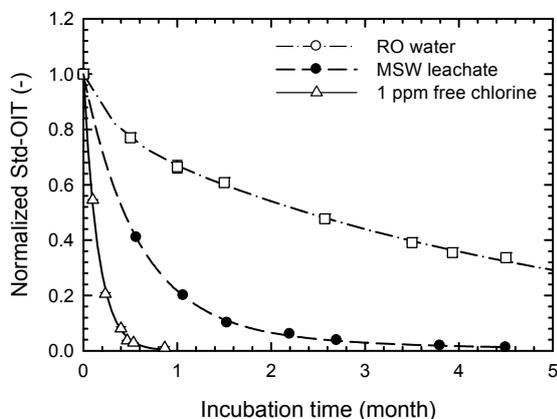


Figure 3. Variation of normalized Std-OIT with time at 85°C in different incubation solution. The RO water and MSW leachate data are from Rowe et al. (2010a) and Rowe et al. (2010b), respectively.

Figure 4a shows the depletion of Std-OIT with time at five different temperatures (25, 40, 65, 75, and 85°C) for the GMB samples incubated in 1 ppm free chlorine solution. The antioxidant depletion was modeled using a first order exponential relationship (Hsuan and Koerner 1998) for the case with low residual Std-OIT values that can be written as:

$$(Std - OIT_t) = (Std - OIT_o) \times e^{-st} \quad (1)$$

where: $Std-OIT_t$ (min) is the OIT value at time t , $Std-OIT_o$ (min) is the initial OIT = 100 min, s is the antioxidant depletion rate (months⁻¹), and t is the exposure time (months).

The Arrhenius model (Figure 4b) was established using different depletion rates obtained at the five incubation temperatures to predict the antioxidant depletion stage length at different temperatures. According to Koerner et al. (1992), the Arrhenius equation can be written as:

$$s = Ae^{-(E_a/(RT))} \quad (2)$$

where s (month⁻¹) is the antioxidant depletion rate, T (K) is the temperature, E_a (J.mol⁻¹) is the activation energy, A , (month⁻¹) is a constant called collision factor, $R = 8.314$ (J.mol⁻¹.K⁻¹) is the universal gas constant.

Using the predicted depletion rates at temperatures of interest from the Arrhenius plot, the length of the antioxidant depletion stage can be predicted by substituting residual Std-OIT value of 0.5 min for ($Std-OIT_t$) in Equation 1. With an activation energy of 76 kJ/mol, the calculated times for antioxidant depletion for this GMB immersed in a 1 ppm free chlorine solution were 23, 5, 2, and 0.5 years at 20, 35, 45, and 60°C, respectively (Table 2). At 35°C and above, the short durations of antioxidant depletion stage implies that the GMB is prone to chemical attack by chlorine relatively quickly and the expected lifetime (i.e., time to nominal failure) of the tested GMB in presented incubation solution is questionable and requires further investigation.

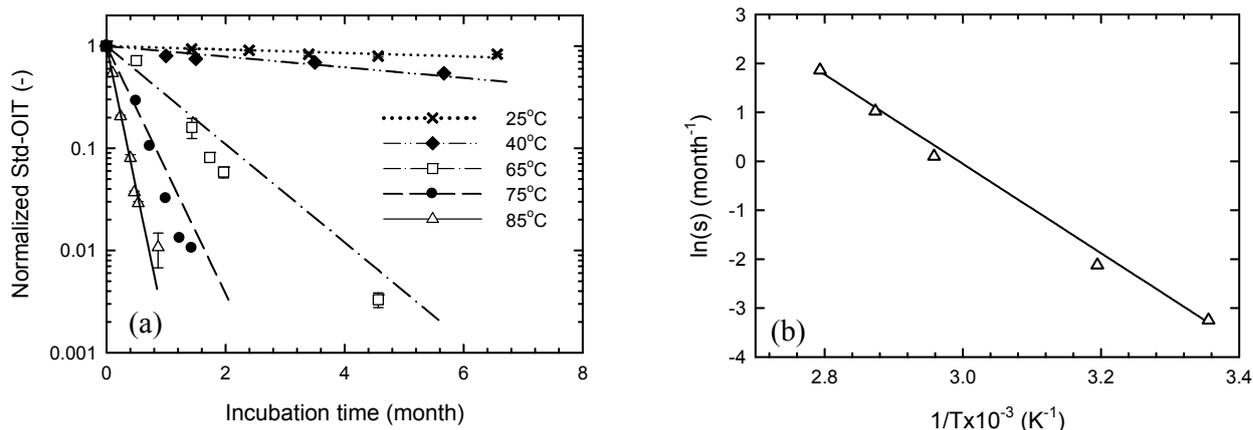


Figure 4. For GMB incubated in 1 ppm free Chlorine: (a) Variation of normalized Std-OIT with incubation time at different temperatures. (b) Arrhenius plot for the antioxidant depletion stage.

Table 2. Antioxidant depletion stage predictions for incubation in 1 ppm free Chlorine

Temperature (°C)	Antioxidant depletion stage prediction (years)*
20	23
35	5
45	2
55	0.8
60	0.5

*Residual OIT = 0.5 min

4 CONCLUSIONS

The effect of chlorine used as a disinfectant in potable water applications on antioxidant depletion from a commercially available HDPE GMB was investigated. To design the incubation solutions, several trials were required to obtain a chlorine loading representative of field conditions. Based on immersion tests presented in this study, the following conclusions were reached:

1. The free chlorine content of the chlorinated water solution examined depleted with time due elevated temperatures and consumption by the GMB.
2. Simulating potable water reservoirs lined with HDPE GMB using jar immersion tests required boosting the free chlorine content to maintain the field ratio of the mass of free chlorine in the water to the surface area of GMB in immersion jars. A control test of a 1ppm free chlorine and a small GMB sample (with mass of free chlorine per unit surface area of GMB representative of field conditions) gave results similar to those using the boosting technique.
3. Immersed in a solution simulating 1 ppm free chlorine, the depletion of the antioxidants in the tested GMB was 6.5 times faster than in MSW leachate with surfactant at 85°C.
4. Based on Arrhenius modeling, the estimated antioxidant depletion stage was predicted to vary between 23 and 0.5 years at 20 and 60°C, respectively, with an activation energy of 76 kJ/mol for the GMB immersed in solution simulating 1 ppm free chlorine loading.

The results presented in the current study are based on seven months incubation in chlorinated water. This was not sufficient to obtain the final depletion rates at lower temperatures and hence, antioxidant depletion stage predictions are subjected to change in the future when more results are available. The results presented apply to the specific GMB tested in the specific chlorinated water solution examined and do not necessary applies to other GMBs or incubation conditions.

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