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ANTIOXIDANT DEPLETION FROM HDPE AND LLDPE GEOMEMBRANES IN CHLORINATED WATER

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ABSTRACT

Chlorine has the third highest electronegativity of all chemical elements (after fluorine and oxygen); thus, chlorine is a very strong oxidizing agent. This paper investigates the rate of antioxidant depletion from different geomembranes immersed in chlorinated water at 85°C. Free chlorine is introduced to the incubation solution by mixing sodium hypochlorite with deionized water with a chlorine loading simulating those in potable water reservoirs. Four different geomembranes are tested: two composed of high density polyethylene (HDPE) and two linear low density polyethylene (LLDPE). The preliminary antioxidant depletion rates of these geomembranes are compared. In addition, a comparison is made between the preliminary antioxidant depletion rate from one of the LLDPE geomembranes in chlorinated water and other incubation media.

Keywords: Geosynthetics, geomembrane, chlorine, antioxidant depletion, HDPE, LLDPE.

1. INTRODUCTION

Geomembranes are used in the containment of liquids and gases, and act as diffusive barriers for organic contaminants in a wide range of engineering applications including landfills, mining facilities, and potable water reservoirs. Geomembranes are used in potable water reservoirs to prevent the leakage of disinfected water to the surroundings. Chlorine is added to water for disinfection of pathogenic microorganisms harmful to human health (Kim et al. 2002). However, since chlorine is a very strong oxidizing agent (Fair et al. 1948; Yu et al. 2011), consideration of its effect on the degradation of geomembranes used in potable water reservoirs is important. Studies of the performance of polyethylene pipes conveying chlorinated water has shown rapid antioxidant depletion from the pipe (Hassinen et al. 2004; Lundback et al. 2006; Castagnetti et al. 2011). Devilliers et al. (2011) showed that increasing the chlorine concentration in chlorinated water accelerates the oxidation process. However, very few studies have examined the performance of geomembranes exposed to chlorinated water. Mills (2011) reported the formation of cracks in the geomembrane liner of a potable water reservoir just six months after installation; the cracks were formed in the side of the geomembrane exposed to water. Abdelaal and Rowe (2014b) reported that the rate of antioxidants depletion from an HDPE geomembrane immersed in chlorinated water was six times faster than immersion in synthetic leachate with industrial surfactant. Scheirs (2009) proposed the following degradation mechanism for geomembranes exposed to chlorinated water: (i) the depletion of antioxidants from the surface layer of geomembrane, then (ii) degradation of the surface layer which becomes brittle, then (iii) formation of micro-cracks

on the surface layer, and then (iv) propagation of cracks through the whole thickness of geomembrane at the locations of tensile stresses/strains until brittle failure of the geomembrane occurs.

This paper presents the preliminary results of antioxidant depletion from four different geomembranes based on the results of standard oxidation time test (Std-OIT). These results are a part of an extensive study monitoring the behavior of eleven different types of geomembranes (HDPE, LLDPE, and blended PE) immersed in chlorinated water.

2. TESTING PROGRAM

Geomembrane samples were cut into 190 x 90 mm coupons. The coupons (separated by 5 mm glass rods) were placed in glass jars. Chlorinated water was then added to the jars followed by incubation of these jars in an oven at 85^{o} C. The chlorinated water is prepared by mixing 70 ml of sodium hypochlorite (NaClO) with 14 liters of distilled water. The chlorine concentration in immersion test was boosted 600 times in order to obtain the same average mass loading of chlorine per unit surface area of geomembrane in the immersion test as in a potable water reservoir (Abdelaal and Rowe, 2014b). Since the free chlorine is consumed to deplete the antioxidants stabilizing the geomembranes and by evaporation, the chlorinated water in jars was replaced every 10 days. Table 1 shows the initial properties of geomembranes studied in this paper.

Table1. Initial properties of geomembranes used (mean± standard deviation)

Property	GMB1	GMB2	GMB3	GMB4
Type	HDPE	HDPE	LLDPE	LLDPE
Designator	MyE15	MyEW15	LxD15	LxE15
Thickness (mm) (ASTM D5199)	1.5	1.5	1.5	1.5
Color	Black	White	Black	Black
Std-OIT (minutes) (ASTM D3895)	160±1.3	177±0.6	191±5.0	156±5.0
HP-OIT (minutes) (ASTM D5885)	1128±25	580±17.2	350±13	885±25

3. RESULTS AND DISCUSSION

Oxidation is a chemical reaction which leads to degradation of physical and mechanical properties of geomembranes. Oxidation reactions are divided into four stages (Hsuan et al., 2008; Scheirs, 2009): (a) initiation reactions, (b) propagation reactions, (c) chain branching reactions, and (d) termination reactions. Oxidation reactions are initiated by removal of a hydrogen atom from the chain of the hydrocarbon polymer and a chain free radical is formed. The free radical reacts with oxygen, forming peroxy radicals, which remove an additional hydrogen atom, forming a hydroperoxide group. The hydroperoxide group decomposes into more free radicals, which extract more hydrogen atoms. Oxidation of hydrocarbons is an auto-oxidation process which, once it is initiated, propagates and progresses.

The induction period is the time after the oxidation has begun but before measurable degradation of its physical and mechanical properties has occurred. Antioxidants are added to the geomembrane to delay the start of the induction period.

Std-OIT tests (ASTM D3895) were performed using a differential scanning calorimeter (DSC). The Std-OIT for HDPE GMB1 and GMB2 (initial values in Table 1) decreased to 33 and 70 minutes, respectively, after 20 days of immersion in chlorinated water (Figure 1), which is equivalent to 20% and 39% of the initial Std-OIT value, respectively.

For LLDPE GMB3 and GMB4, the Std-OIT decreased to 50 and 75 minutes (26% and 48% of the initial Std-OIT value) after 32 days of immersion in chlorinated water, respectively (Figure 2). The depletion rates of antioxidants from GMBs 1, 2, 3, and 4 were 6.42, 5.40, 4.35, and 2.55 min/day, respectively.

Although the initial Std-OIT of GMB3 was 22% more than that of GMB4, the antioxidant depletion rate of GMB3 is 1.7 times that of GMB4 and so, after 32 days, the retained Std-OIT of GMB3 was only 67% of that of GMB4. However, for HDPE geomembranes, GMB1 with the lower initial Std-OIT and higher depletion rate had depleted to 20% of the initial value while GMB2 had depleted to 39% of its initial value after 20 days.

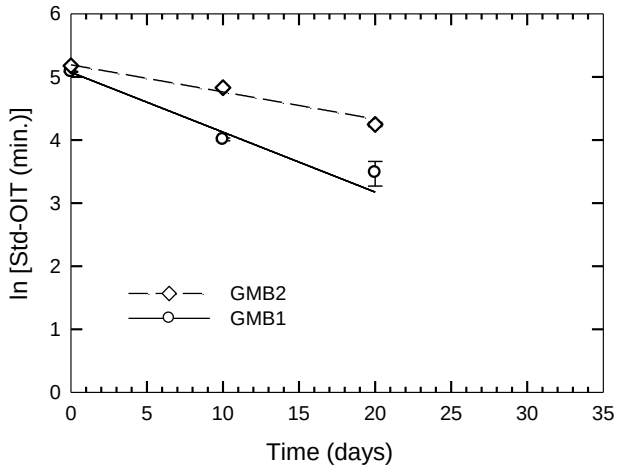

Figure 1. Std-OIT depletion from two HDPE geomembranes.

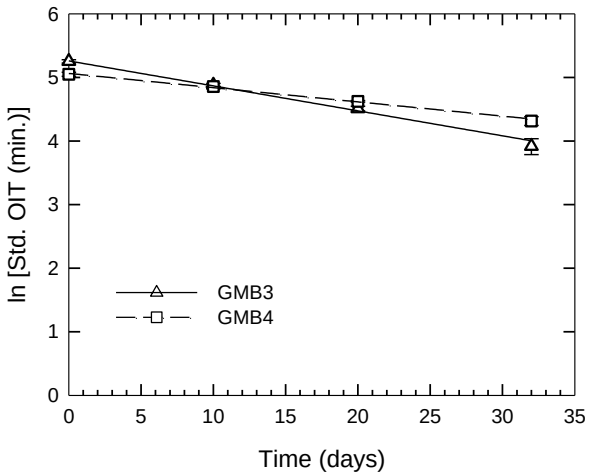

Figure 2. Std-OIT depletion from two LLDPE geomembranes.

4. COMPARISON BETWEEN THE ANTIOXIDANT DEPLETION RATE FROM GMB3 IMMERSED IN CHLORINATED WATER AND OTHER SOLUTIONS

Figure 3 shows the Std-OIT depletion from LLDPE GMB3 in chlorinated water, distilled water, and extremely low and high pH solutions. The rate of Std-OIT depletion from GMB3 immersed in chlorinated water was 2.95, 7.40, and 12.2 times the depletion rate for the same geomembrane when immersed in high pH mining solution (pH=13.5), distilled water, and low pH mining solution (pH=0.5), respectively.

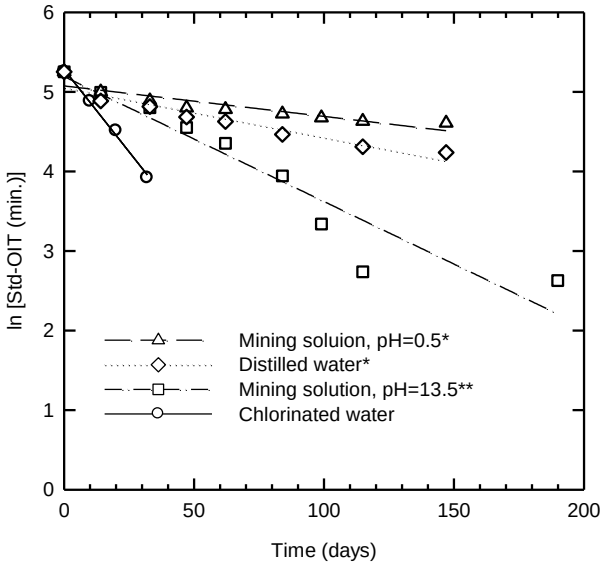

Figure 3. Rate of antioxidants depletion from GMB 3 in different solutions.

* Data from Abdelaal et al. (2012)

** Data from Abdelaal and Rowe (2014a)

5. CONCLUSIONS

The depletion of antioxidants (as detected by the Std-OIT test) from HDPE and LLDPE geomembranes immersed in chlorinated water has been investigated. The chlorinated water caused depletion of antioxidants from different types of geomembranes with different antioxidants package (as evident from different initial Std-OIT and HP-OIT values) in a very short time. Based on the results presented herein, the following preliminary conclusions have been reached:

- The rate of antioxidant depletion from the two HDPE geomembranes investigated was higher than for the two LLDPE geomembranes examined.
- GMB4, with the lowest initial Std-OIT among the four tested GMBs, had the slowest Std-OIT depletion and had the highest Std-OIT value after 20 days of immersion. This shows that, while a high initial Std-OIT usually is preferred (other things being equal), the type of antioxidant and thus its resistance to chlorinated water may govern the time to antioxidant depletion.
- Antioxidant depletion from LLDPE GMB3 immersed in chlorinated water was very fast compared with other incubation media, such as distilled water and mining solutions. For instance, the rate of antioxidant depletion from GMB3 in chlorinated water was three times faster than in a high pH mining solution (pH=13.5).

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