Polymer-Free Geosynthetic Clay Liner for Containment of Aggressive Leachates

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INTRODUCTION

In environmental technology and especially in landfill construction, geosynthetic clay liners (GCLs) have been successfully used worldwide for many years as a partial or total replacement of compacted low-permeability soils. This practice reduces construction time, improves the carbon dioxide (CO_2) footprint of the project, and conserves resources. The key to this application is the bentonite used in the GCL. Bentonite is a natural clay consisting mainly of the mineral montmorillonite. This belongs to the group of smectite clay minerals. Montmorillonite is characterized by a large surface area (100-800 m^2/g), a negative net charge, and exchangeable surface cations (Grim 1968). These properties in turn give the bentonite a strong affinity to water, which leads to swelling, sealing, and cohesion properties (Eisenhour & Brown 2009). In contact with liquids which have very acidic or very basic pH values ($11<pH<3$), high ion concentrations, and high electrical conductivities, these properties are diminished. Under such conditions, multivalent cations replace exchangeable monovalent cations (sodium), whereby the osmotic swelling of the bentonite as well as its effective function is reduced or completely eliminated (Gates, Bouazza, & Churchman 2009).

These types of suppressive conditions are found in mining or in deposits of industrial residues, such as those produced in coal burning power plants. In order for GCLs to be applicable in these scenarios, products amended with polymers have been developed in order to improve sealing properties. This practice, however, brings new challenges as current experience with standard geosynthetic clay liners cannot be directly correlated to the polymer amended GCLs.

This paper presents the development and results of a research project that was utilized to produce a polymer-free GCL for the containment of aggressive leachates. Initial index tests were performed on a suite of various bentonites types, followed by hydraulic conductivity (k-value) tests with the GCL permeated with leachates from aluminum mining, coal-fired power production (coal ash) and gold mining industries. This paper also discusses the characteristics of the bentonite within the polymer-free GCL that contribute to its sealing effectiveness.

OVERVIEW OF RECENT GCL TECHNOLOGY

Development of a Geosynthetic Clay Liner with Polymers

The negative influence of aggressive permeant solutions on the sealing behavior of GCLs has been demonstrated in various tests. Ruhl reports a hydraulic conductivity of $2x10^{-8}$ m/s for a GCL in contact with sodium hydroxide (NaOH) solution with a pH value of 13 (Ruhl & Daniel 1997). The research performed by Chen, et al. (2018), clearly indicates the relationship between the ionic strength of CCP leachate and the hydraulic conductivity of Na-B GCLs. As the ionic strength of the CCP leachate increases, the hydraulic conductivity of the GCL increases. In order to decrease hydraulic conductivity and meet regulations under such conditions, alternative GCL configurations were explored.

The concept of amending the bentonite with polymers to achieve improved hydraulic performance began to be realized through the process of producing bentonite-polymer nanocomposites (BPN). Here, bentonite was mixed with a monomer solution in order to minimize void size between bentonite granules and polymers. The product was then dried and ground (Trauger & Darlington 2000). GCLs containing this product showed significantly improved sealing performance against aggressive leachates compared to the conventional sodium bentonite (Na-B) GCLs. These findings opened up new applications for GCLs in challenging environments (Scalia J. , Benson, Bohnhoff, Edil, & Shackelford 2011). For cost reasons, this process was replaced by dry mixing of bentonite and polymers to produce the bentonite polymer composite GCLs (BPC GCLs).

Polymer-Amended Products

However, the presence of polymers within the bentonite presents unique challenges when subjected to typical laboratory tests. For example, during permeability testing of BPC GCLs, polymers may elute from the GCL and clog the permeameter device. The clogging causes inaccurate measurements of the hydraulic conductivity and requires flushing of the permeameter lines (Scalia, Benson, Bohnhoff, Edil, & Shackelford 2014). Polymer-washout, which has a propensity to occur more intensely at the beginning of permeation, can lead to an increase in the quantity and size of flow paths through the GCL, and ultimately, higher hydraulic conductivities. This is particularly evident in the case of more aggressive leachates (Tian, Likos, & Benson 2019). Also, the environmental impact of the washed-out polymers as well as the polymers' long-term resistance to degradation needs to be further understood.

While for natural bentonites, a correlation between the swelling index test and the hydraulic conductivity is proven in multiple studies (Ruhl & Daniel 1997) (Kolstad, Benson, & Edil 2004), no such correlation is shown for polymer-enhanced bentonites (Scalia J., Benson, Bohnhoff, Edil, & Shackelford 2011). This means that it is essential to conduct hydraulic conductivity tests using site-specific leachate for projects considering the use of BPC GCLs in order to understand their sealing capabilities. Additionally, the type of polymer and polymer loading within the bentonite has to be considered for each individual leachate that is expected to permeate the GCL in the field.

For the reasons given above, technical committees have drawn some conclusions on the use of bentonites enhanced with polymers. In the Austrian Standards International ÖNORM S2081, polymers are generally prohibited as additives in clay liners. Quote: "Polymeric additives that influence swelling or permeability may not be used in any of the layers described (author's note: carrier, intermediate and top layer) (ASI 2020)." This goes considerably further than the version of the 2011 standard. Quote: "The swelling and water absorption capacity must be tested on the bentonite without additives (e.g. polymers) and must meet the requirements of Table 1. In case aggregates are used, they must be stated (ASI 2011)."

Internationally, the ASTM D35.04 Working Group for Geosynthetic Clay Liners noted at its meeting in July 2019 that the ASTM tests for Swelling Index and Fluid Loss are not applicable to chemically modified bentonite mats. The reason is that the index tests may have misleading results, which could allow for poorer quality bentonites to be incorporated into the GCLs. Quote: "This test method is not applicable for clays with polymers" (ASTM 2019).

EXPERIMENTAL STUDIES

Evaluation of Leachates

Different variables are used to provide a preliminary understanding of how leachates might negatively impact the sealing capability of GCLs. Primary factors are the pH value, the electrical conductivity (EC), the ionic strength (I), and the ratio between monovalent and polyvalent cations (RMD). RMD is computed with the Kolstad equation displayed below. This ratio influences the ion exchange and thus also the swelling capacity. In general, solutions that are more acidic or basic, that have higher electrical conductivities and ionic strengths, and contain a larger concentration of polyvalent cations will cause a larger suppression of the bentonite's swelling capacity, and consequently, inhibit its ability to form a low permeable barrier. It has been shown that the influence of RMD is greater at low to moderate ionic strengths (< 50 mM) than at higher ionic strengths (> 50 mM) (Kolstad, Benson, & Edil 2004). The Kolstad equation calculates the RMD as the ratio of the total molar concentration of monovalent (Mm) and polyvalent (Md) cations.

$$(1)\ RMD = \frac{M_m}{\sqrt{M_d}}$$

Experimentation

Initial stages of the research project identified a suite of bentonites to be evaluated for their sealing effectiveness against aggressive bulk solutions. The candidates included samples of sodium bentonite from various deposits, polymer activated sodium bentonites, alkaline activated calcium bentonite, and bentonite mixtures. Swell index tests and fluid loss tests were performed on these materials using red mud leachate, which is also referred to as bauxite liquor. After analyzing the index test results, a calcium activated bentonite was selected to be incorporated into a GCL product for further testing. In addition to the polymer-free GCL, conventional Na-B GCLs were tested for their hydraulic conductivity in order to serve as a baseline. Tests were performed within permeameter cells, without applying back pressure, and used permeant solutions such as DI water and several types of aggressive leachates. Prior to permeation, the effective stress was applied to the samples, and they were saturated with the permeant solution for 48 hours without applying a hydraulic gradient. The tests were conducted in accordance with ASTM D6766, and they were terminated when the ASTM criteria was met. Termination criteria in accordance with this method is achieved when the hydraulic conductivity is steady, there's been a minimum of 2 pore volumes of flow, and hydraulic and chemical equilibrium between the influent and effluent has occurred. Chemical equilibrium is determined when the electrical conductivity of the influent and effluent are within +/- 10% of one another (ASTM 2020).

Permeant Solutions

For the research project, hydraulic conductivity tests were carried out with DI water, red mud (RM) leachate, high ionic strength (HS) CCP leachate, and gold extraction process water. The leachates and their chemical composition are outlined in Table 1. The RM leachate was a synthetic replica of a project leachate from an aluminum ore processing plant. The HS CCP leachate was a synthetic solution representative of the CCP leachates produced within a specific phase of the coal combustion process. The HS CCP leachate chemistry was developed from research efforts that evaluated numerous leachates within the Electrical Power Research Institute (EPRI) database (Benson, Chen, & Edil 2014). The composition of process water from gold extraction was taken from literature and also synthetically produced (Ghazizadeh, Bareither, Scalia, & Shackelford 2018).

	Unit	RM*	CCP-HS	Gold
K^{+}	mg/L	-	22.2	17
Na^{+}	mg/L	-	2500	529.6
Mg^{2+}	mg/L	-	140	31
Ca^{2+}	mg/L	-	512	150
Cl^{-}	mg/L	-	1720	450
NO_3^{-}	mg/L	-	-	12
SO_4^{2-}	mg/L	-	4720	990.5
pH	(-)	13.2	8.0 ±0.5	5.7
EC	mS/cm	42	13.9	-
Ionic Strength	mM	~700	174	42
RMD	M-1/2	-	0.98	0.47

Table 1. Compositions and characteristics of the leachates for hydraulic conductivity testing (*unable to disclose leachate chemistry)

Trials with Red Mud Leachate

For the experiments with the red mud leachate, a synthetic solution was used as the permeant that was a replicate of a red much leachate from an actual project (cf. Table 1). Also, conventional Na-B GCLs were also examined with this leachate. Figure 1 shows the progression of the hydraulic conductivity (k-value) over the duration of three tests: one for the newly developed GCL and two for the conventional Na-B GCLs. In Test A, the Na-B GCL was pre-hydrated the RM leachate, and in Test B, the Na-B GCL was pre-hydrated with DI water before it was brought into contact with the RM leachate. Test C pre-hydrated the newly developed GCL directly with the leachate without pre-hydrating with DI water. Figure 1 shows that the Na-B GCL had a relatively high hydraulic conductivity on the order of 10^{-7} m/s when directly permeated with the leachate (Test A), but it achieved a much lower permeability on the order of 10^{-10} m/s when pre-hydrated with DI water (Test B). Nevertheless, the GCL was gradually becoming more permeable as the test continued. The polymer-free GCL resulted in a hydraulic conductivity of 1.9 x 10^{-11} m/s after approximately 130 days of permeation (Test C).

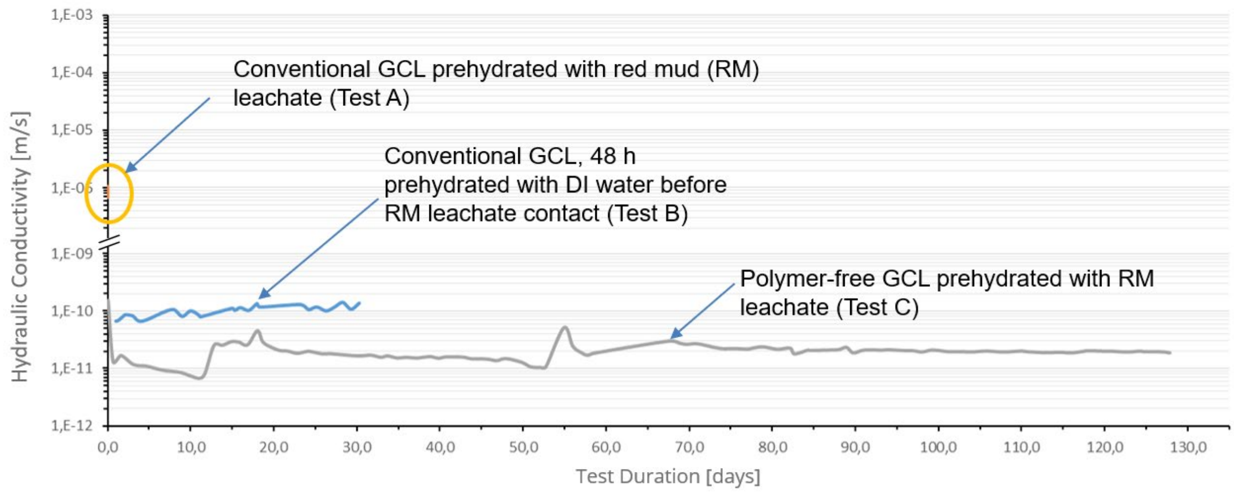

Figure 1. Illustration of the tests with Red Mud leachate permeant. A) Na-B GCL in direct contact with permeant B) Na-B GCL pre-hydrated with DI water C) Novel GCL in direct contact with permeant

Tests with Other Leachates

After the successful permeability test with the red much leachate, further testing was conducted using high ionic strength (HS) CCP leachate, and gold extraction process water. A summary of the permeability test results for the polymer-free GCL is displayed in Table 2. The polymer-free GCL permeated with the HS CCP leachate had a hydraulic conductivity of 1.2 x 10^{-11} m/s with a test duration of 49 days to reach termination criteria. Similarly, the GCL permeated with gold extraction process water resulted in a hydraulic conductivity of 7.6 x 10^{-12} m/s after a test duration of 245 days.

GCL Samples	Leachate	Effective Stress (kPa)	Hydraulic Conductivity (m/s)	PVFs	Days	Trend	Hydraulic Equilibrium
X9-5000	High St.	28	1.2 x 10^{-11} m/s	4.0	49	Steady	Yes
	Gold		7.6 x 10^{-12} m/s	5.2	245	Steady	Yes

Table 2. Permeability test results for the polymer-free GCL permeated with HS CCP and gold extraction process water leachates

As a baseline measurement, conventional Na-B GCLs were tested and had a permeability of 1.7 x 10^{-7} m/s and 3.0 x 10^{-11} m/s when permeated with the HS CCP leachate and gold extraction process water, respectively. Summary of the hydraulic conductivity tests for both the polymer-free GCL and the conventional GCL are displayed in Table 3. The results indicated an improved hydraulic performance of the polymer-free GCL compared with the conventional GCL when permeated with high ionic strength and high pH leachates.

	K-value Polymer-Free GCL [m/s]	K-value Na-B GCL [m/s]
RM	1.9×10^{-11}	8.4×10^{-7}
CCP HS	1.2×10^{-11}	1.7×10^{-7}*
Gold	7.6×10^{-12}	3.0×10^{-11}**

Note: *(Chen, Benson, & Edil 2018), **(Bareither, Zadeh, Conzelmann, Scalia IV, & Shackelford 2017)

Table 3. Comparison of k-values for the polymer-free GCL and conventional Na-B GCL

Polymer-Free GCL Discussion

There are three primary factors that contribute to the polymer-free GCL's effectiveness in containing aggressive leachates. First, is that the specialized bentonite originates from a unique geological deposit. The geologic processes that occurred millions of years ago constituted the bentonite with unique properties that appear to enhance its compatibility with aggressive leachates. Second, after the bentonite is mined and as it is being processed, it passes through an alkaline activation treatment. This alkaline activation enhances the cation exchange, thixotropy, and swelling properties of the bentonite. The third contributor to its effectiveness is its particle morphology, its specific intergrowth structures, and its pore size distribution. The particle morphology refers to the shape and physiochemical nature of the bentonite. The intergrowth structures create various alignment patterns of the bentonite plates that result in an interlocking of the tetra and octahedral clay mineral sheets. Further research studies are planned in order to better understand the mechanisms behind the bentonite's effectiveness against aggressive leachates and its overall geochemistry sensitivity when permeated with various types of solutions.

CONCLUSIONS

The spectrum of leachate types and chemistries in waste impoundments has substantially increased since the conception of using GCLs in waste containment barrier systems. Within this broadened spectrum are leachates with chemical compositions that reduce the sealing effectiveness of conventional GCLs. Therefore, there is a need to develop specialized GCLs that are more effective in their sealing capabilities when permeated with more aggressive solutions. The results of this study indicate that a GCL, without the addition of polymers, has been developed and proven to be a promising addition to the field of waste containment technologies.

There are a wide range of aggressive leachates with variable characteristics in which polymer-free GCLs could be utilized. Therefore, there is the need to continue expanding the current investigation in order to more comprehensively understand the GCLs hydraulic capabilities. Supplemental hydraulic conductivity tests are planned in addition to other investigative methods that will further explore the specialized characteristics of the bentonite.

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