Polymer Enhanced Geosynthetic Clay Liners for Bauxite Storage

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Abstract

Polymer modified geosynthetic clay liners (PMGs) are a fairly recent innovation and are seeing use in situations where traditional geosynthetic clay liners (GCLs) do not provide sufficiently low hydraulic conductivity. PMGs have found use in waste impoundments for mining and ore processing operations such as red mud storage facilities, reducing the risks associated with such structures. The chemistry of red mud leachates generated by various mining operations, such as the Bayer process, is well documented. These leachates can have high ionic strengths and elevated pH values compared with other common GCL applications, such as MSW landfills. Our research has shown that new PMGs are compatible with a range of high pH chemistries, such as bauxite liquors, cement kiln dust (CKD) and trona mining. Various types of bentonites sourced from various locations were evaluated with a particular polymer type. The influence of liner design parameters, such as mass per unit area, on the hydraulic conductivity was evaluated. ASTM D6766, *Standard Test Method for Evaluation of Hydraulic Properties of Geosynthetic Clay Liners Permeated with Potentially Incompatible Aqueous Solutions,*[1] can be used to confirm the hydraulic compatibility of GCLs with mining leachates. Research on appropriate termination criteria as well as performance limits will also be presented.

Keywords: Red mud storage, geosynthetic clay liner, polymer modified bentonite, chemical compatibility, hydraulic conductivity.

1.   Introduction

Geosynthetic clay liners (GCL) and polymer modified geosynthetic clay liners (PMGs) are gaining favor for use in industrial waste disposal and ore processing applications. [2-4] The GCLs or PMGs can be a component of a composite liner system that will allow for increased performance (relative to compacted clay), as well as a more environmentally responsible and economical design. The performance advantages afforded by GCL will minimize the risk of leakage into the environment. Additionally, GCLs and PMGs can provide manufactured quality assurance and ease of installation.

Traditional sodium bentonite based GCLs function best in conditions that promote the swelling and sealing power of the hydrated montmorillonite platelets of the clay. However, applications that involve high ionic strength and or high pH conditions can preclude the use of traditional sodium bentonite GCLs due to reduced swelling potential of the bentonite. Trona mining, bauxite mining and CKD storage are applications which have both high dissolved salt concentrations and are also highly alkaline. Trona (also referred to as sodium sesquicarbonate), is mined to produce soda ash that is used in commercial applications/products such as baking soda, glass production, and flue gas desulfurization agents to name a few. In Trona mining, mining process waste water is piped to surface impoundments or ponds. In a similar manner, red mud waste generated by the chemical leaching process of bauxite for aluminum production is storage in tailings dams. Red mud must be stored indefinitely due to the hazardous nature of the waste. Recent high profile red mud storage dam failures have led to improved storage designs utilizing composite liners. Cement kiln dust (CKD) is another highly alkaline type of waste. CKD is a waste product that is removed from cement kiln exhaust gas by air pollution control

devices. Some of the CKD that is not recycled in the cement manufacturing process is typically disposed in landfills, waste piles, or surface impoundments. When this dust mixes with water it can be corrosive and promote the mobility of heavy metals in the soils surrounding a storage facility. Other risks associated with the leaching of CKD is the presence of heavy metals such as arsenic, cadmium, chromium, thallium and lead as wells the presence of dioxin in the dust.

New clay liner technologies have recently been developed to extend the use of a manufactured liner into these aggressive applications. Silica modified bentonites as well as polymer modified bentonite technologies have been successfully used in these applications. A particularly interesting aspect of the engineering and design of the liner has been the type of bentonite which is suitable for use. Studies by Benson[5] et al and Gates[6] et al have found that bentonites with a naturally high concentration of silica can yield lower hydraulic conductivities compared to traditional bentonites that meet traditional performance criteria such as GRI-GCL3. [7] These studies demonstrated the accessory minerals associated with the particular bentonite source can result in different hydraulic performance. For this study, bentonites sourced from the US, China, India and Turkey were mixed with a proprietary polymer treat package and compared for the chemical compatibility with various bauxite, trona and CKD leachates. Also, we sought to understand the influence of mass per unit area on the performance of systems which ranged from 3.7 to 5.3 kilograms per square meter.

2. Experimental

Inductively Coupled Plasma (ICP)
ICP testing was performed on a Thermo Scientific iCAP 7000 Series ICP spectrometer unit equipped with a radial argon torch. The Teva 1.6.5 software was used to collect the data. Prior to testing, the original leachate for the bauxite leachates were diluted 1:100 with deionized water. The trona leachates were diluted 1:1000 with deionized water. The ICP was calibrated with standard electrolyte solution: 5, 50, 100 and 200 ppm prior to analysis. The leachate samples were analyzed for calcium, aluminum, manganese, magnesium, iron, zinc, potassium sulfur, phosphorus, copper and silicon.

Hydraulic Conductivity
Hydraulic conductivity tests on GCL specimens were conducted in a flexible-wall permeameter using a falling headwater / constant tail water method described in ASTM D6766.[1] The GCLs were hydrated with permeant liquid in the permeameter for 48 hr at an effective confining stress of 10 kPa. After prehydration, the effective confining stress was increased to 20 kPa, and the hydraulic gradient was set at approximately 150. Influent for the specimen was introduced using a burette. The permeate was collected in sealed individual vials. Perm testing was conducted for varying lengths of time depending on the hydraulic properties of the sample.

Leachate Characterization
Determination of electrical conductivity (EC) was performed using a Mettler Toledo SevenGo Pro conductivity meter. The EC was expressed as microsiemens per cm (μS/cm). The pH of the leachates and permeates were measured using an Oakton Ion 700 pH meter equipped with an Oakton Acorn model 35811-98 probe. Chloride contents was estimated by QuanTab® Test Strips. The sulfate content estimated by the sulfur content detected by ICP.

Calculations:
Ionic Strength (I):

$$I = \frac{1}{2} \sum_{i=1}^{n} c_i z_i^2$$

The ionic strength, I, of a solution is a function of the concentration of all ions present in that solution, where c_i is the molar concentration of ion i (mol·dm^{-3}), z_i is the charge number of that ion, and the sum is taken over all ions in the solution.

Ratio of Monovalent to Divalent Ions (RMD)

$$RMD = \frac{M_{MV1} + M_{MV2} + M_{MV3} \ldots}{\sqrt{M_{DV1} + M_{DV2} + M_{DV3} \ldots}}$$

Relative abundance of monovalent and multivalent cations was characterized by the RMD of each test solution. The RMD is defined as the ratio of the total molarity of monovalent cations to the square root of the total molarity of multivalent cations at a given ionic strength. ICP data was used to estimate the RMD of the leachate.

Polymer Modified Geosynthetic Clay Liner (PMG)

Samples of PMG-4 were produced by CETCO®. The bentonites were sourced from various regions around the world such as the United States, Tukey, India and China. With the exception of the US bentonite, the clays used were soda ash activated calcium bentonites. The bentonite were all of similar grain size distribution. The clays were granular type clays with a maximum 10% retained on 18 mesh (850 microns) and maximum 15% passing 200 mesh (75 microns). The average inherent moisture content of the bentonite used was 10-12%. The polymer treat package used is a proprietary material developed by CETCO. The PMGs were produced with a range of mass per unit area ranged from 3.7 to 5.3 kilograms per square meter. The inherent water content of the bentonite was included in the mass target and blending calculations. The bentonite and polymer were combined using a proprietary process and incorporated into polypropylene geotextile fabrics typical for geosynthetic clay liners.

Leachates

The Trona leachate T1 were sent from different Trona mines located in Wyoming USA. Synthetic CKD leachates were also prepared in the CETCO labs. CKD1 was prepared by dissolving 50.0 grams of sodium chloride and 14.092 grams of potassium hydroxide in deionized water made to a total volume of 1 liter. CKD2 was prepared by dissolving 4.499 grams of grams of potassium sulfate, 37.717 grams of potassium chloride, 5.974 grams of sodium chloride, 0.823 grams of magnesium chloride, 4.320 grams of calcium chloride and 5.600 grams of potassium hydroxide in deionized water made to a total volume of 1 liter. A synthetic bauxite leachates were also prepared in the CETCO lab. Bauxite liquor B1 was prepared by dissolving 37.139 grams of sodium hydroxide, 45.88 grams of aluminum chloride hexahydrate, 0.27 grams of potassium chloride and 6.60 grams of sodium sulfate in deionized water made to a total volume of 1 liter. A sodium chloride leachate was prepared by dissolving 50 grams of sodium chloride in deionized water made to a total volume of 1 liter. A 50% sodium hydroxide solution was also prepared in deionized water.

3.   Results and Discussion

It is well known that traditional GCL hydraulic conductivity is influenced by several factors such as ionic strength and RMD as well as the particular design parameters of the GCL such as bentonite properties and mass per unit area. Ideal PMG systems would be those that are tolerant to a wide range of leachate chemistries. The swelling pressures generated by hydrated bentonite along with the polymer/solvent and polymer/clay interactions all factor into the performance of the system. As indicated by a large body of work investigating the interactions of ions and macromolecule in solution (known as Hoffmeister effects), we intend to track both the influence of both anions and cations on hydraulic performance. For this work, estimations of the ionic strength and RMD are shown in Table 1 for each leachate. The ionic strengths ranged from 0.86 to 4.16 M. The RMD values are elevated due to the high concentrations of sodium ions typical for these applications. The solutions have varying anion species and relative concentrations range from 100% chloride to a mixture of chlorides, sulfates, carbonates etc. The pH of the systems ranged from 9.7 to 13.3. Elevated pH values are known to an influence on the bentonite based GCLs. The higher ionic strength (imparted by the concentration of hydroxide ions) can reduce the electrostatic repulsion of the montmorillonite platelets. At high pH values, the silicate layer of the montmorillonite can be chemically digest which further reduces the swelling potential of the clay.

Table 1. Leachate Chemistry Estimation.

Ion Conc (mol/L)	High pH Leachate Chemistry					
	CKD1	CKD2	T1	B1	NaCl1	NaOH1
Na^+	0.86	0.10	3.53	0.67	0.86	31.19
Al^{3+}	-	-	-	0.26	-	-
Cu^{2+}	-	-	2.58×10^{-5}	-	-	-
Mn^{2+}	-	-	6.51×10^{-5}	-	-	-
Mg^{2+}	-	8.64×10^{-3}	7.55×10^{-4}	-	-	-
Ni^{3+}	-	-	1.69×10^{-5}	-	-	-
Ca^{2+}	-	0.04	-	-	-	-
K^+	0.25	0.63	8.63×10^{-5}	-	-	-
PO^{4-}	-	-	0.01	-	-	-
SO_4^{-2}	-	0.03	0.11	0.01	-	-
CO_3^{-2}	-	-	0.75	0.08	-	-
Cl^-	0.86	0.70	-	0.02	0.86	-
OH^-	0.25	0.10	1.00×10^{-13}	0.10	-	35.9
F^-	-	-	-	9.5×10^{-3}	-	-
Cl/SO_4 Ratio	No Sulfate	27	No Sulfate	1.5	No Sulfate	No Sulfate
[I] (M)	1.11	0.91	3.54	1.61	0.86	33.52
RMD M^0.5	0.0001	3.35	120.43	1.32	0.0001	0.0001
pH=	13.33	13.33	10.03	12.58	6.48	>14
EC (µS/cm)	194,000	91,000	106,900	54,000	72,900	-

PMG-4 is the fourth of a series of PMG technologies developed by CETCO. The hydraulic conductivity of the various tested geosynthetic clay liners is shown below in Table 2. The samples were tested for varying pore volumes and times. Figure 1 depicts the hydraulic conductivity plotted as a function of hydraulic conductivity. With the exception of the NaCl1 solution, the system exhibited low hydraulic conductivity values ($<1 \times 10^{-8}$ cm/sec) up to 133 000

µS/cm. From this data it appears that solutions with higher chloride ions contents are more aggressive. Interesting, the NaOH1 solution, despite having the most aggressive conditions exhibited a hydraulic conductivity of 1.6×10^{-7} cm/sec. This was most likely attributed to the higher viscosity of that particular leachate.

Table 2. Hydraulic Conductivity Testing Data for PMG-4 samples.

Clay Liner Type	Clay Source	Leachate Code	Flux (m^3/m^2/sec)	Hydraulic Conductivity (cm/sec)	Running Time (hrs)	Pore Volume Flow (PVF)
PMG-4 U	US Western	T1	2.0×10^{-8}	8.4×10^{-9}	2070	65.5
PMG-4 U	US Western	B1	3.6×10^{-9}	1.8×10^{-9}	1132	7.2
PMG-4 T	Turkey	B1	4.2×10^{-10}	2.6×10^{-10}	2232	0.8
PMG-4 T	Turkey	B1	1.1×10^{-9}	5.4×10^{-10}	3679	1.7
PMG-4 T	Turkey	B1	1.9×10^{-9}	7.1×10^{-10}	3702	5.9
PMG-4 I	India	B1	5.6×10^{-9}	2.3×10^{-9}	1385	3.6
PMG-4 I	India	B1	4.9×10^{-10}	2.6×10^{-10}	1552	0.6
PMG-4 U	US Western	B1	6.3×10^{-10}	2.9×10^{-10}	4889	6.7
PMG-4 U	US Western	CKD2	3.6×10^{-10}	1.6×10^{-10}	1610	2.1
PMG-4 U	US Western	CKD1	6.4×10^{-5}	2.9×10^{-5}	0.4	15.0
PMG-4 U	US Western	NaCl1	2.2×10^{-5}	1.0×10^{-5}	1.5	23.2
PMG-4 U	US Western	NaOH1	4.4×10^{-7}	1.6×10^{-7}	73	30.9
GCL	India	B1	6.3×10^{-5}	3.4×10^{-5}	0.5	16.5
GCL	US Western	B1	1.6×10^{-5}	7.3×10^{-6}	2.3	26.5

The leachate chemistry by processing methods such as Bayer process, is well documented, however, changes to methods used in the industry are resulting in higher dissolved salt concentrations. The leachate chosen for this testing is considered representative in terms of ionic strength and RMD. Figure 3 shows the hydraulic conductivity of PMG-4 systems made with different regionally sourced base clays for the bauxite leachate (B1) as a function of pore volume flow (PVF). From the data, the hydraulic equilibrium occurs somewhere between 2 PVF and 7 PVF. In regards to the duration required to reach hydraulic equilibrium, the same data is plotted in Figure 4 as a function of time. The experiments showed similar behavior in that they required approximately 890 hours (37 days) to reach hydraulic equilibrium.
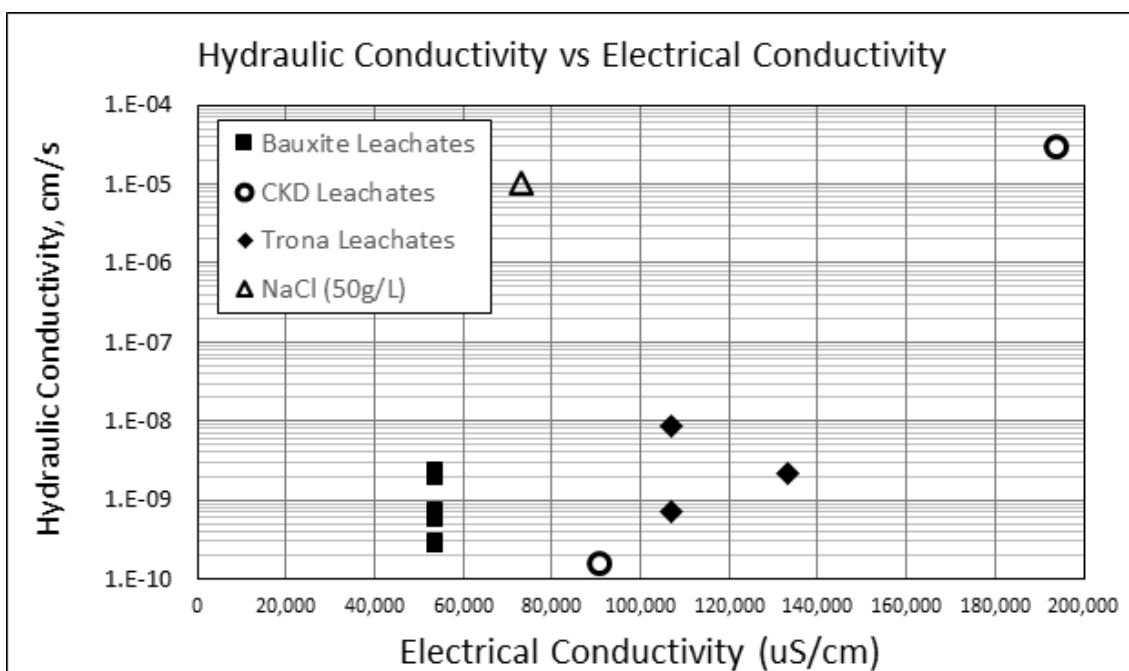
Figure 1. Hydraulic conductivity as a function of electrical conductivity of the PMG-4 system. Hydraulic conductivity as a function of mass per unit area for the PMG-4 system in the synthetic bauxite liquor is plotted in figure 2. The hydraulic conductivity decreases from ~2x10^{-9} cm/sec at 3.7 kg/m^2 for the Indian bentonite to ~3x10^{-10} cm/sec at 4.5 kg/m^2. The Turkish bentonite gave slightly k values at the lower loadings. Higher loadings at 4.9 kg/m^2 did not appear to yield lower k values.
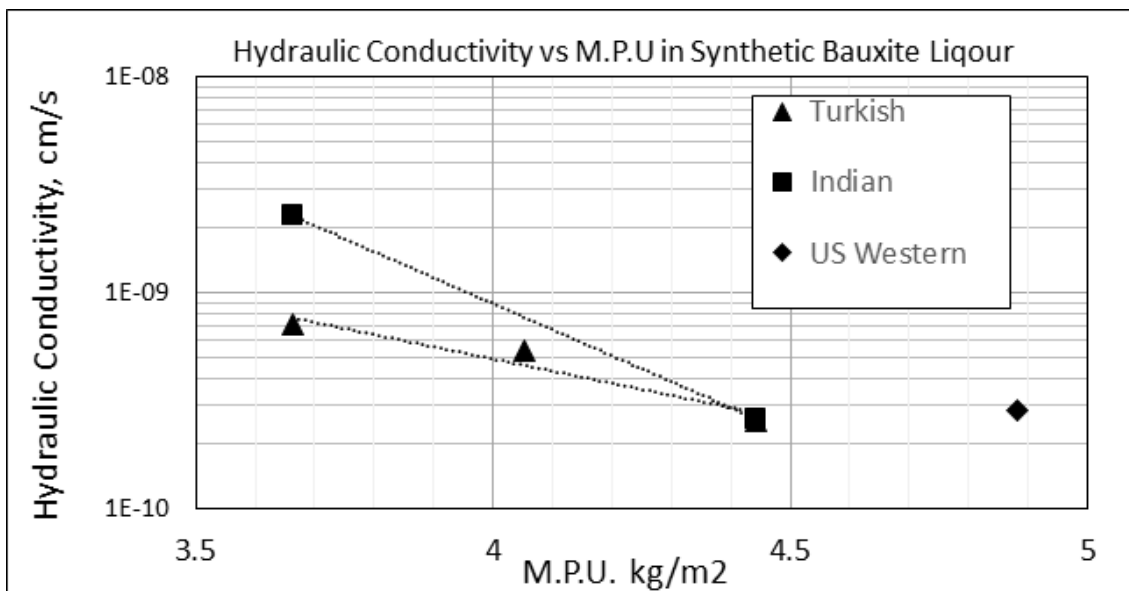
Figure 2. Hydraulic conductivity as a function of mass per unit area.
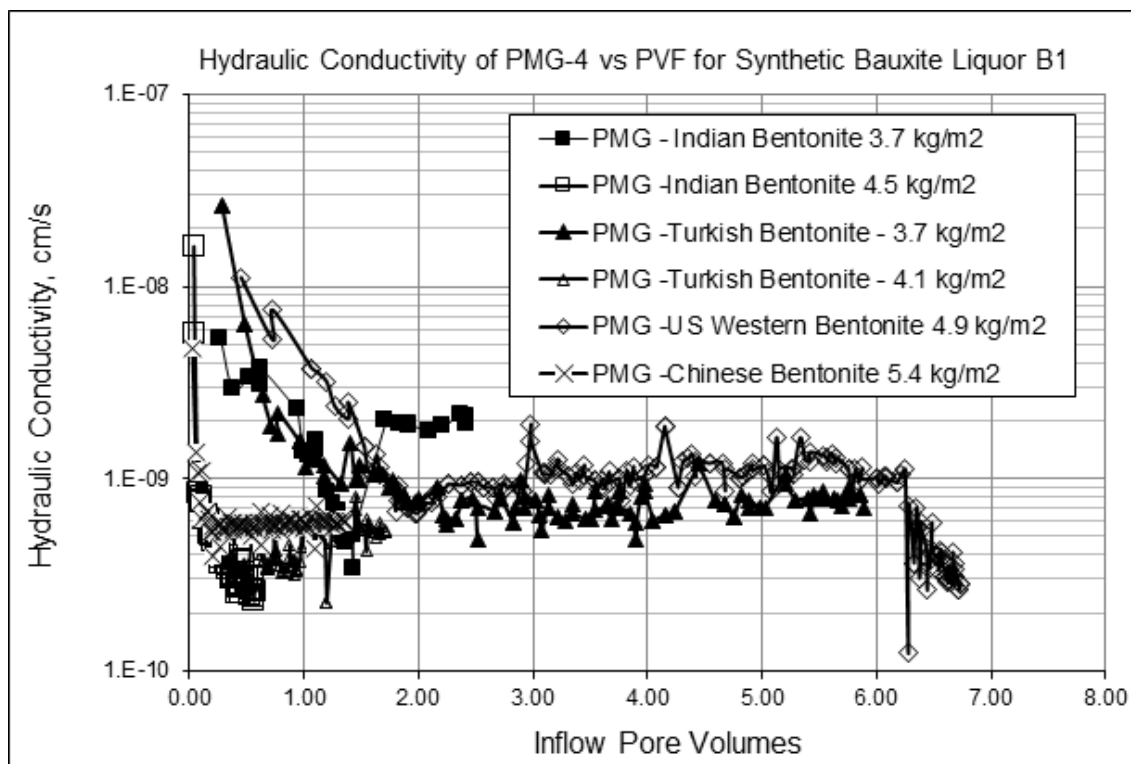
Figure 3. Hydraulic conductivity of the bauxite liquor B1 as a function of PVF for the PMG-4 made with regional clays.
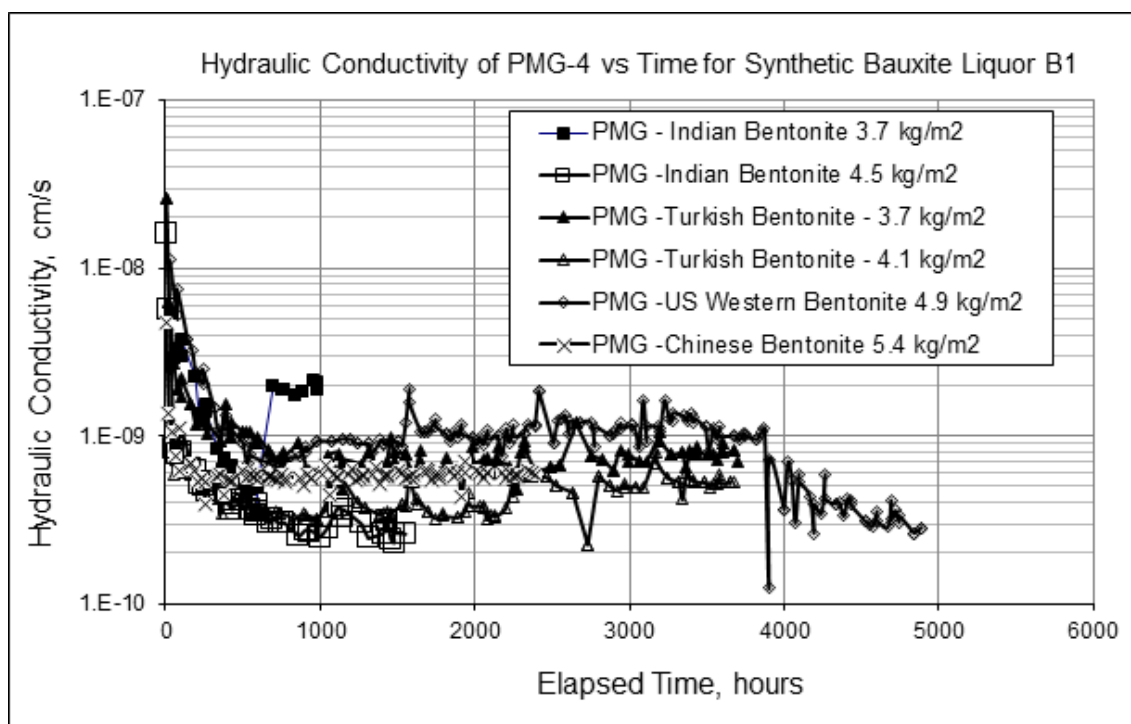

Figure 4. Hydraulic conductivity of the bauxite liquor B1 as a function of time for the PMG-4 made with regional clays.

The chemical equilibrium data was tracked for the trona leachate T1 permeability testing with the PMG-4 U system. The pH and electrical conductivity values, known as traditional indicators for measuring chemical equilibrium, are plotted in Figure 5 as a function of PVF. Also plotted

on the secondary axis is the hydraulic conductivity which reached equilibrium at approximately 53 PVF. Interestingly, the EC and pH measurements did not show large variances from the original leachate and were lower during most of the experiment by a small amount compared to the original leachate. The point of chemical equilibrium can also be tracked by following the changes in the chemistry of the permeate as a function of PVF. The elemental composition of the permeate was determined using inductively coupled plasma. The ions that were investigated in the permeate were those known to be associated with phyllosilicates such as montmorillonite. These ions were chosen so as to give an indication of the chemical digestion of the bentonite itself. Shown in Figure 6 are the plots of the ion concentration changes relative to the molar concentration of the incoming leachate. Interestingly, the concentration of aluminum increased during the entire experiment. Ions such as magnesium, zinc and iron reached a steady state at approximately 20 PVF. Ions such as sodium and silicon did not fluctuate much during the experiment which may indicate the precipitation of the silicon as seen in prior works by Benson et. al.[5] and Gates et. al.[6]
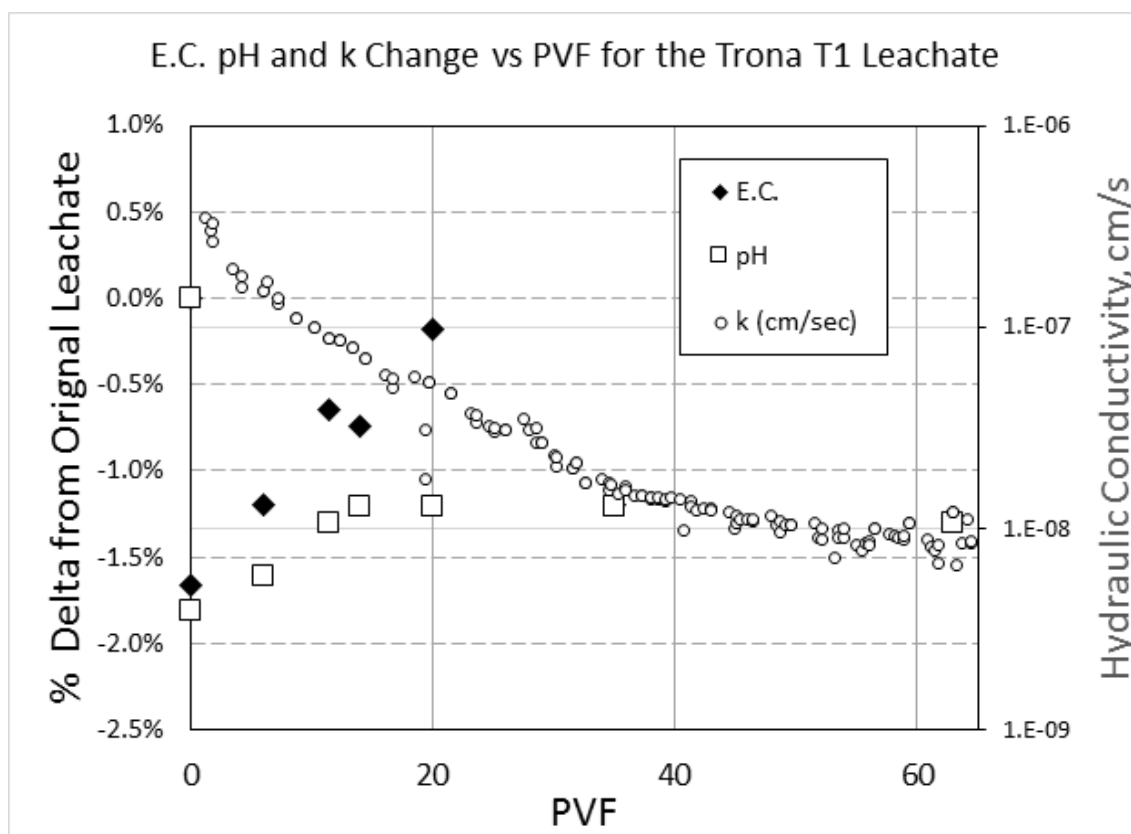

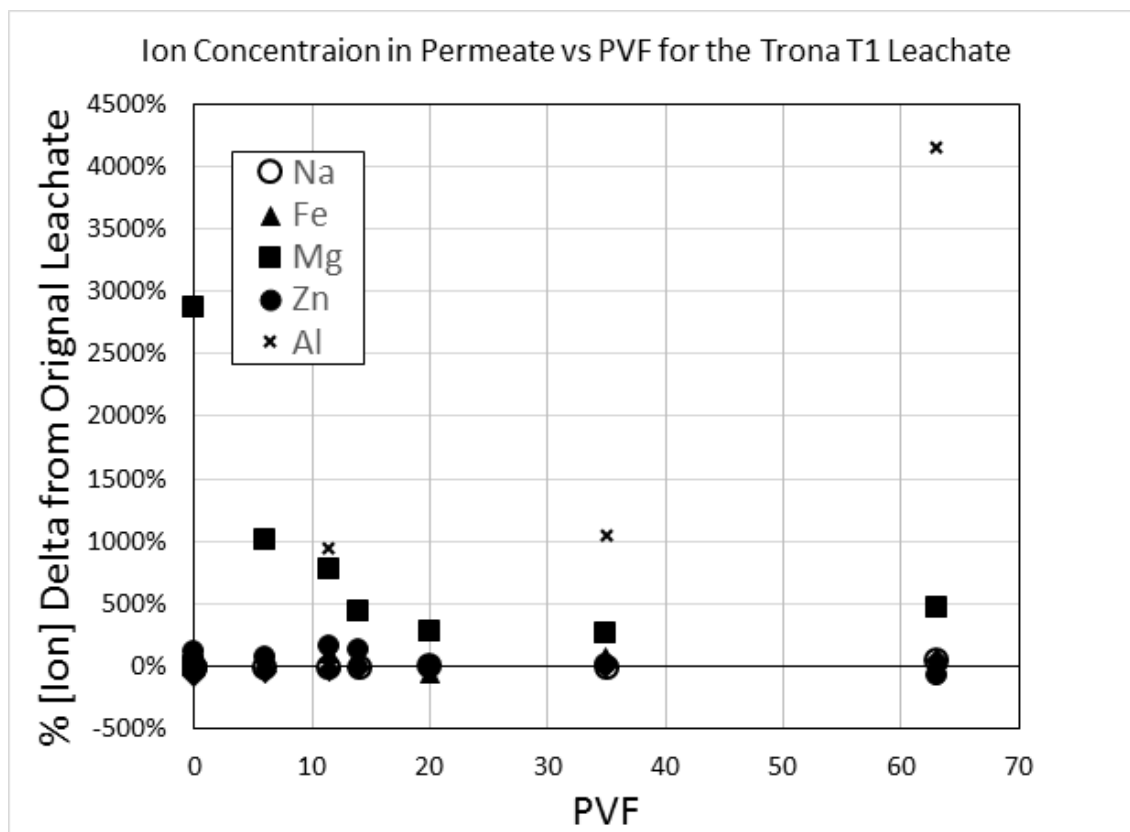**Figure 5. E.C. pH and k Change vs PVF for the Trona T1 Leachate with the PMG-4 U system.**

Figure 6. Relative ion concentration changes vs PVF for the Trona T1 Leachate with the PMG-4 U system.

4.   Conclusion

The hydraulic conductivity of a new polymer modified GCL (PMG-4) was evaluated for high pH leachates. For the PMG-4 system, the maximum electrical conductivity that allowed for low hydraulic conductivities was ~133 000 µS/cm. The regionally source of bentonite did not have a major influence of the hydraulic conductivity. Higher mass per unit area results in lower hydraulic conductivity values for the synthetic bauxite leachate. Depending on the leachate tested, the hydraulic equilibrium occurred at different points in the experiments. For bauxite leachate testing, hydraulic equilibrium occurred at approximately 2 PVF. For trona leachate testing, hydraulic equilibrium occurred at approximately 53 PVF. In addition, the ion chemistry changes as function of PVF was dependent upon the type of ion for the trona leachate. Our work indicates that the ultimate permeability, hydraulic equilibrium and chemical equilibrium is leachate specific. Testing must be conducted to a sufficient pore volume of flow to be confident the system has reached a steady state.

5.   References

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