Polymer Enhanced Geosynthetic Clay Liners for Extreme Leachate Chemistries

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ABSTRACT: Geosynthetic clay liners (GCLs) have been used for a quarter-century as a substitute for the compacted clay component of composite lining systems in various industrial applications. For waste storage, the primary use of GCLs has been as a component in the composite liner system of municipal solid waste landfills. GCLs have seen limited use in other applications that involve high salinity and/or high-/low-pH leachates due to the chemical compatibility limitations of the base bentonite. Research into blends of bentonite clay with tailored polymer systems has shown that the chemical compatibility can be extended to leachates with high-pH (>10) and low-pH (<4) solutions. The compatibility of these bentonite clay blends with tailored polymers was evaluated using site-specific leachate permeability tests for four different cases. The low-pH leachates involved in these studies were representative of those encountered in phosphogypsum storage, copper heap leach processing and other applications.

Keywords: GCL, pH, polymer, permeability, leachate

1 INTRODUCTION

Geosynthetic clay liners (GCLs) are gaining interest for use in industrial waste disposal and ore processing applications. GCLs can be an economical choice as a component of a composite liner system. The use of GCLs can allow for a more environmentally responsible design which will minimize the risk of leakage into the environment. Additionally, GCLs can provide manufactured quality assurance and ease of installation. Prior studies have shown that the incorporation of a GCLs into a liner design provides added protection for a geomembrane when exposed to the high normal stresses of the ore (Athanassopoulos & Smith, 2013).

Enhanced ore extraction techniques, such as heap leaching, have become popular in recent years due to the steep increases in the prices of precious metals. Heap Leaching is an ore processing technique where run-of-mine or crushed and/or agglomerated ores are stacked over an engineered impermeable leaching pad and exposed to a lixiviant solution which is collected after percolation through the ore (Zanbak, 2012). Additionally, the processed ore can be stored in stacks, disposed of in tailings impoundments or the heap can be decommissioned in place. These waste cells can represent a challenge for long-term management due to the chemical composition of the ore, potential radioactivity and other factors that could impact the geophysical stability of the pad.

For ores like phosphate rock, uranium, nickel, and copper ores, extraction conditions involve leachates with high ionic strength and low pH, and in some cases high temperatures. These extreme conditions represent a compatibility challenge for traditional bentonite based GCLs, since the swelling/gelling capacity of bentonite is reduced in aggressive leachates. New GCL products that offer improved chemical compatibility with mining and coal ash leachates have recently been developed, which are referred to as polymer-modified GCLs (PMG). The polymer-clay technology can be tailored to provide low hydraulic conductivity against a wide range of aggressive leachates, as demonstrated for coal ash and red mud storage applications (Donovan et al., 2016; Benson and Athanassopoulos, 2015).

The purpose of this study is to evaluate a new type of polymer-modified GCL for use in low-pH applications such as copper heap leaching and phosphogypsum stacks. The intent of the study is to determine the minimum required duration of the hydraulic conductivity testing to reach chemical equilibrium between the original leachate and the collected permeate. In addition, the study will evaluate the impact of the leaching solution on the chemical stability of the materials of construction (bentonite and polymer). The permeate was tested for evidence of polymer loss or clay acidolysis. For these studies, two phosphogypsum (P-GYP) leachates were chosen as well as two copper leaching solutions.

2 EXPERIMENTAL TESTING METHODS

2.1 *Inductively Coupled Plasma (ICP)*

ICP testing was performed on a Thermo Iris Intrepid ICP-OES unit equipped with a radial argon torch. Teva 1.6.5 software was used to collect the data. The leachate and permeate samples were diluted 1 to 100 with DI water. The ICP was calibrated with standard electrolyte solution: 5, 50, 100 and 200 ppm prior to analysis.

2.2 *Hydraulic Conductivity*

Hydraulic conductivity (permeability) tests on GCL specimens were conducted in a flexible-wall permeameter using a falling headwater/constant tailwater method described in ASTM Standard Test Method D6766. The GCLs were hydrated with permeant liquid in the permeameter for 48 hours 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 graduated burette. The permeate was collected in individual vials. Hydraulic conductivity testing was conducted for varying lengths of time depending on the hydraulic properties of the sample.

2.3 *Leachate Characterization*

Determination of electrical conductivity (EC) was performed using a Mettler Toledo SevenGo Pro conductivity meter. The EC was expressed as milliSiemens per centimeter (mS/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 content was estimated by QuanTab$^{®}$ Test Strips. The sulfate/bisulfate content was estimated by the sulfur content [S] detected by ICP. As ion selective chromatography was not available, the sulfuric acid, sulfate, and bisulfate contents were estimated using the equations one through three. The dissociation constant (K_{a1}) of $2.6x10^{6}$ was used for sulfuric acid.

$$H_2SO_4 \approx \frac{[H^+]^{^2}}{2.4 \times 10^6} \qquad (1)$$

$$HSO_4^{-1} \approx [H^+] \qquad (2)$$

$$SO_4^{-2} \approx [S] - ([H_2SO_4] + [HSO_4^{-1}]) \qquad (3)$$

2.3.1 Total Organic Carbon (TOC):

A Shimadzu TOC-V CSN Total Carbon Analyzer was used to estimate the TOC of the leachate and permeate samples. The same dilution ratios mentioned in the ICP section were used for the TOC testing.

2.3.2 Ionic Strength (I):

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 (Equation 4). To estimate the concentration of sulfate (SO_4^{-2}) and bisulfate ions (HSO_4^{-2}), the pH was used to determine the percentage of each species calculated given the Ka_1 and Ka_2 values of $2.4x10^6$ and $1.0x10^{-2}$ respectively.

$$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2 \qquad (4)$$

2.3.3 Ratio of Monovalent to Divalent Ions (RMD)

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 (Equation 5). ICP data was used to estimate the RMD of the leachate.

$$RMD = \frac{M_{MV1} + M_{MV2} + M_{MV3} \ldots}{\sqrt{M_{DV1} + M_{DV2} + M_{DV3} \ldots}} \qquad (5)$$

2.4 Polymer Modified Geosynthetic Clay Liner (PMG)

Samples of PMG-A were produced by CETCO®. The bentonite used was granular western sodium bentonite. The polymers used in the PMG-A material and the total polymer loading is proprietary CETCO® information.

2.5 Leachates

The leachates tested were prepared using reagents purchased from Sigma Aldrich Corporation, with the exception of the "P-GYP #2" leachate which was supplied from an actual phosphogypsum processing facility.

3 RESULTS AND DISCUSSION

The hydraulic conductivity results for PMG-A in the various leachates is shown in Figure 1. The data is plotted as a function of pore volume flow (PVF). In general, the hydraulic conductivity starts higher and decreases with subsequent pore volumes. Hydraulic equilibrium occurs at >3 pore volumes for most samples. The P-GYP #1 test was different in that it exhibited a decreasing trend with time where the k stabilized at ~25 PVF.

The lowest hydraulic conductivity was observed for the phosphogypsum leachates. Interestingly, despite having the high chloride concentrations and the highest electrical conductivity (178 mS/cm), the P-GYP-1 system had the lowest hydraulic conductivity at $1.2x10^{-9}$ cm/sec. The hydraulic conductivity for the P-GYP 2 test started low and remained low, which is most likely due to the lower ionic strength and higher pH compared to the P-GYP-1 leachate. Despite the similar chemical composition of the copper leachates, the hydraulic conductivity of PMG-A in the Copper #1 leachate was higher than in Copper #2. Comparing the two leachates, the Copper #1 leachate has a lower pH (1.18) and slightly higher electrical conductivity (62 mS/cm) which may explain the hydraulic conductivity results.

Figure 2 shows the hydraulic conductivity as a function of time. The hydraulic conductivity reached a plateau between 100 and 625 hours. The longest test duration was 11,000 hours, which was for the P-GYP #1 leachate.
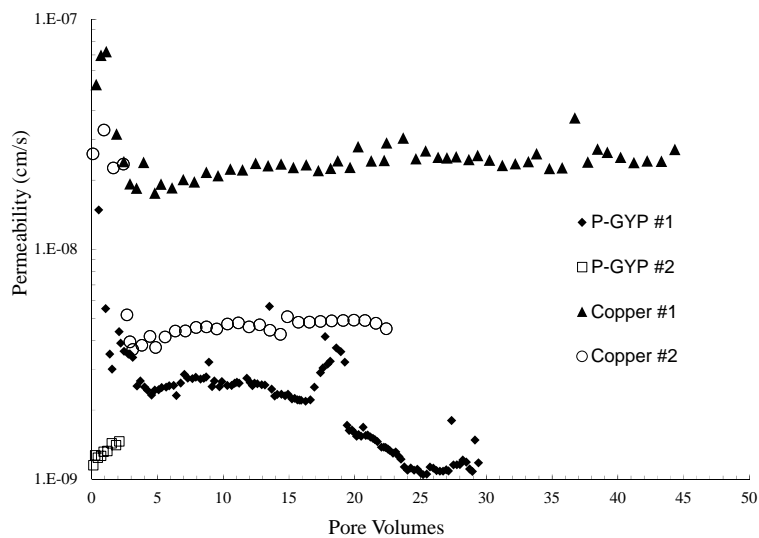

Figure 1: Hydraulic conductivity with pore volumes of flow.

Several tests, including pH, EC, and TOC, were conducted to follow chemical equilibrium during the hydraulic testing. The permeate pH was tested and compared to the original leachate. In general, the early permeate samples had higher pH values. After approximately 10 PVF, the pH values reached an equilibrium. The response of electrical conductivity showed the opposite trend. The EC values decreased initially and gradually increased at the higher PVF values. The copper #1 leachate samples plateaued at values higher than the original leachate, which may indicate chemical changes to the system. The TOC testing showed trends similar to the pH testing. The organic content of the early leachate samples was elevated relative to the incoming leachate, which indicates that a small quantity of mobile polymer is leaving the system early on. After 10 PVF, the organic content of the leachate approaches that of the incoming leachate.
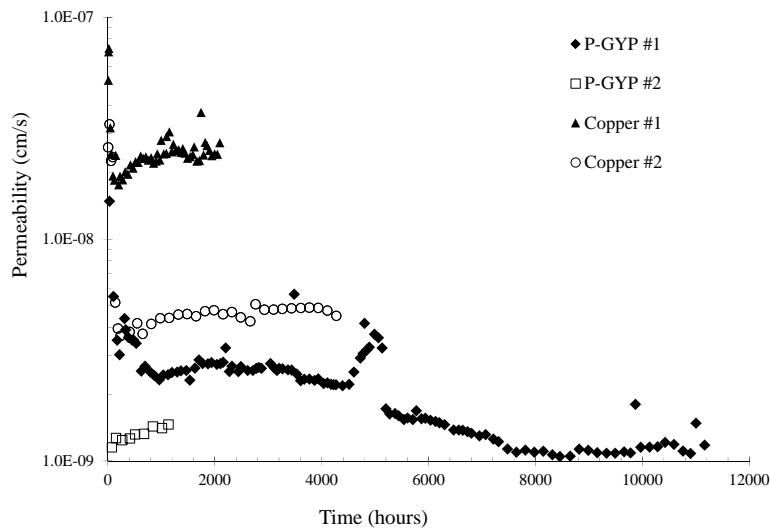
Figure 2: Hydraulic conductivity with time.

Figure 3 shows the relationship between hydraulic conductivity and ionic strength in the acidic leachates. As the ionic strength increases, so does the hydraulic conductivity. Table 1 compares the original leachate chemistry with the last permeate sample taken during the hydraulic conductivity testing. The data shows good agreement between in original leachates and the permeate chemistries for those samples with PVF values of greater than 10. The P-GYP #2 leachate testing showed elevated concentrations of ionic species, indicating that the testing has not reached equilibrium.
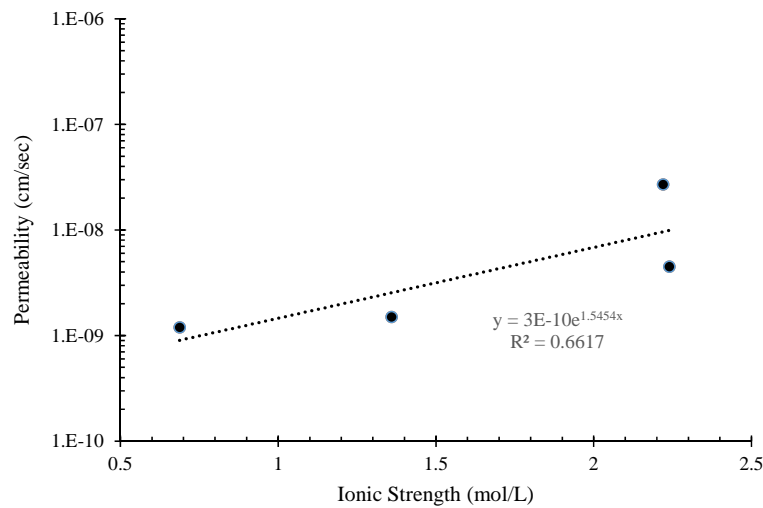

Figure 3: Hydraulic conductivity with ionic strength.

Table 1: Chemical Analysis of Original Leachates at Varying Pore Volume Flow

Parameter	Units	P-GYP #1		P-GYP #2		Copper #1		Copper #2	
		Influent	Effluent*	Influent	Effluent*	Influent	Effluent*	Influent	Effluent*
Ionic Strength (I)	Mol/L	0.55	-	1.29	-	1.7	-	1.76	-
RMD		2.29	-	0.749	-	0.329	-	0.247	-
PVF*	-	-	25	-	2.1	-	35.76	-	21.62
k	(cm/sec)	-	1.2×10^{-9}	-	1.5×10^{-9}	-	2.7×10^{-8}	-	4.5×10^{-9}
pH	-	0.54	0.59	1.78	2.7	1.18	1.15	1.44	1.47
EC	mS/cm	178.1	139.6	25.1	19.64	62.9	70.1	56.8	56.2
TOC	ppm	160.9	227	2,767	10,490	148	125.5	137.9	107.7
Cl	ppm	15,900	14,200	326	306	9,900	11,100	9,000	12,200
Na	ppm	2,022	2,213	2,911	11,444	2,805	2,797	3,164	3,438
Ca	ppm	235	263	1055	1990	653	727	689	725
Al	ppm	32	690	52	901	2,457	2471	2335	2,628
Mn	ppm	0.196	1.2	23	111	2,687	2611	2334	2,530
Mg	ppm	500	713	326	1097	6,253	6159	6474	7,023
Fe	ppm	30	202	55	32	1.29	32	0.95	62
Zn	ppm	0.24	1	9.8	16	0.57	0.8	0.48	1
K	ppm	343	377	489	521	926	938	973	1,068
SO_3^{-2}	ppm	8,995	10,178	6,731	22,736	38,424	38,065	39,122	41,891
PO_4^{-3}	ppm	506	638	22,138	34,844	2,508	2,450	2,711	2,891
Cu	ppm	0.01	0.03	0.01	0.831	0.51	0.31	1,392	1,509
Si	ppm	1.935	94	776	283	3.5	104	1.3	110

* Effluent characteristics measured at indicated pore volumes of flow through specimen.
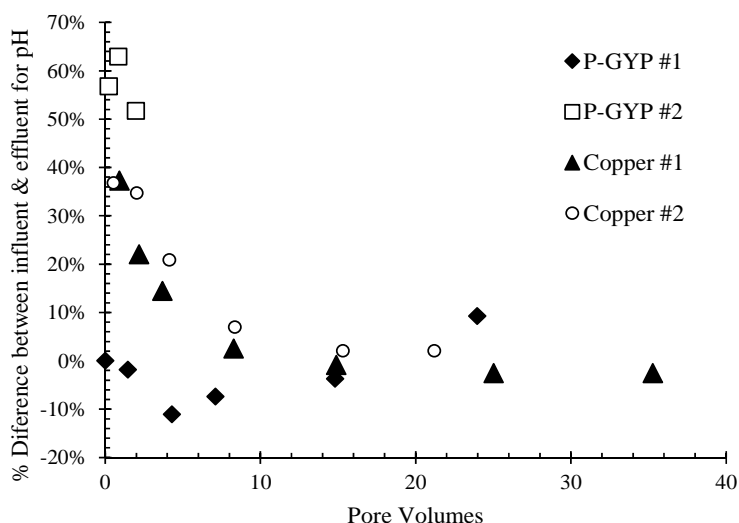

Figure 4: Relative pH difference between leachate and permeate with pore volumes of flow.
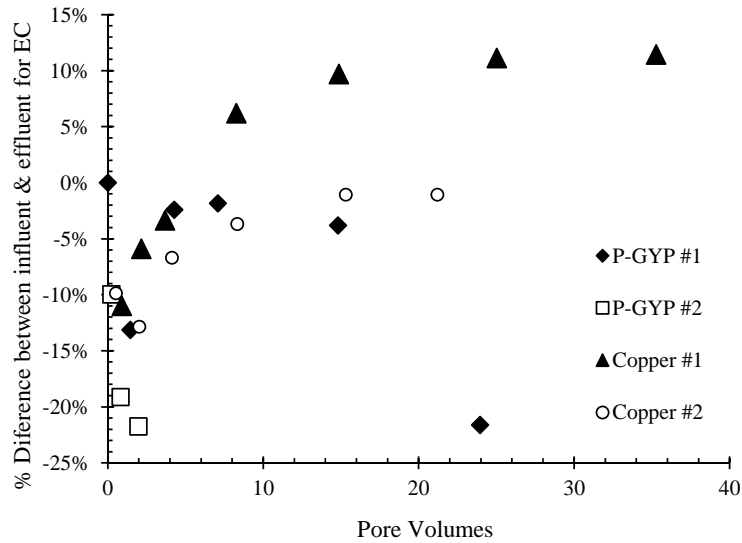
Figure 5: Relative EC difference between leachate and permeate with pore volumes of flow.
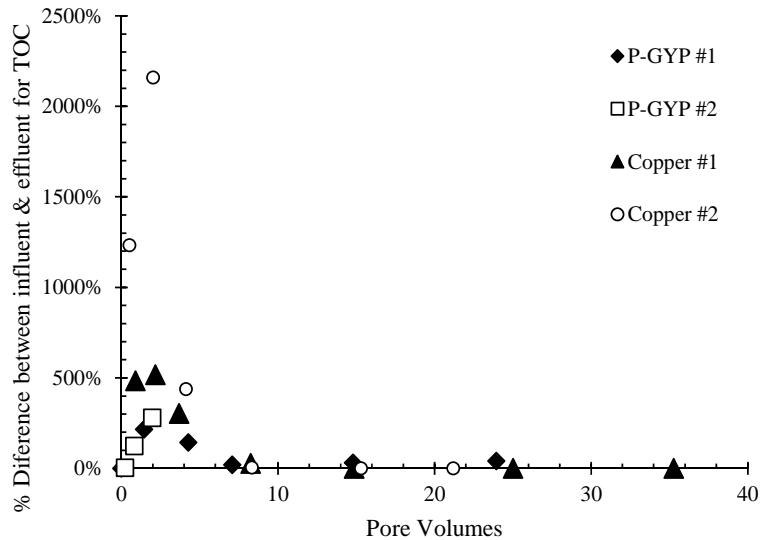

Figure 6: Relative TOC difference between leachate and permeate with pore volumes of flow.

To determine the impact of the low pH solutions on the bentonite/polymer blends, the elemental composition was evaluated as a function of PVF. The first series of charts, shown in Figure 7, relates the changes in concentration of ions related to the bentonite clay such as silicon, zinc, iron, manganese and aluminum. The different leachates exhibited different trends. The P-GYP #1 leachate exhibited higher initial concentrations of manganese, but reached a steady state for all ions around 4 PVF. As seen in Table 2, the initial concentration of silicon in the leachate was 2 ppm whereas the steady state concentration is ~100 ppm, indicating some elution of clay related species during the testing. P-GYP #2 leachate testing did not exhibit the same magnitude of clay-ion release, potentially a result of the higher pH value. The copper leachates exhibited similar trends in that large amounts of iron were released early on, but the chemistry of the leachate reached steady state at ~15 PVF. The steady state concentration of silicon in both of these examples was approximately 100 ppm.
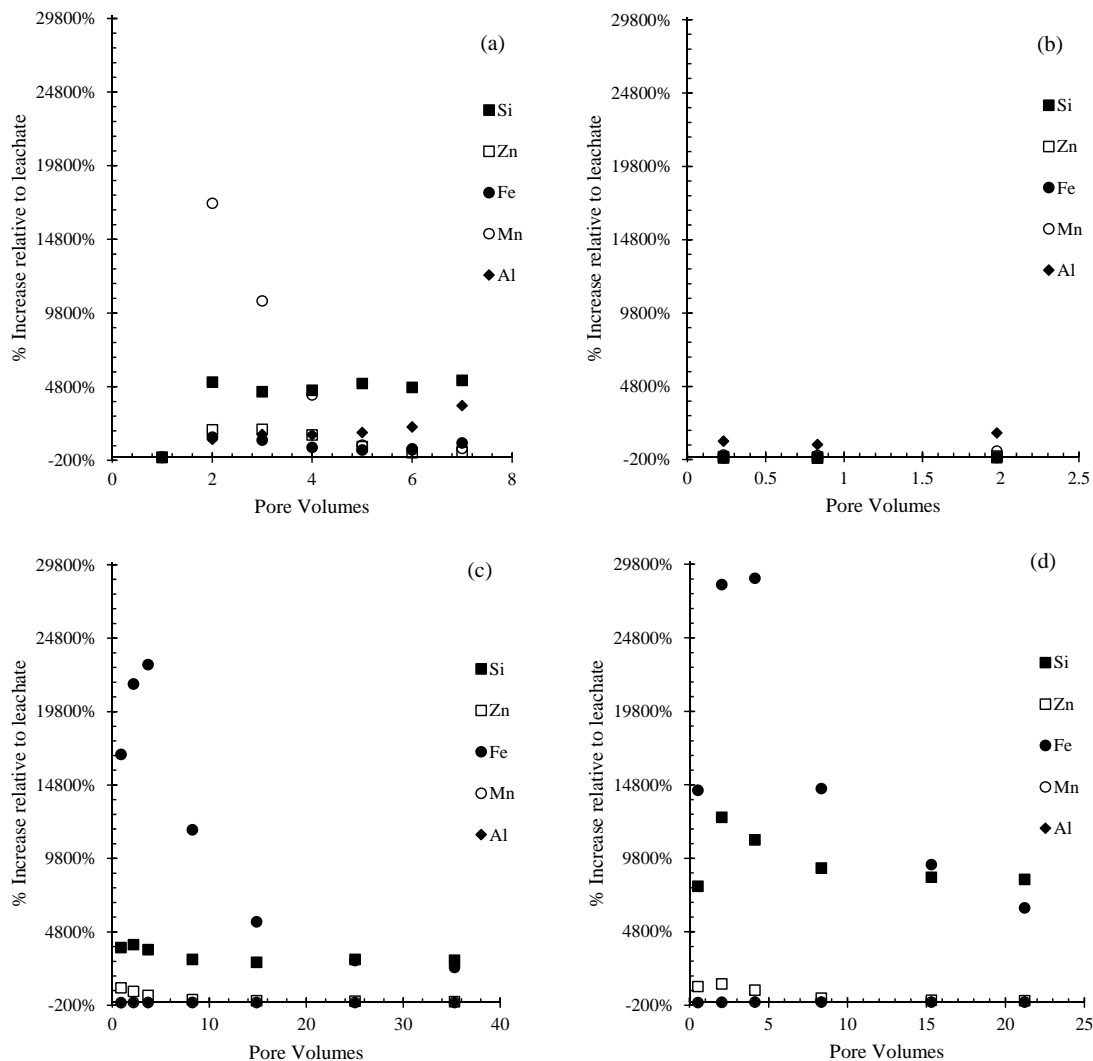
Figure 7: Relative concentration of clay-related ions as a function of pore volumes of flow for: (a) P-GYP #1, (b) P-GYP #2, (c) Copper #1 and (d) Copper #2.

Figure 8 illustrates the changes in ion concentration for other elements such as sodium, calcium, magnesium, potassium and phosphorous. The trends show that the early permeate samples have elevated concentrations of the ions of interest, where the steady-state concentrations were reached between 5-10 PVF.
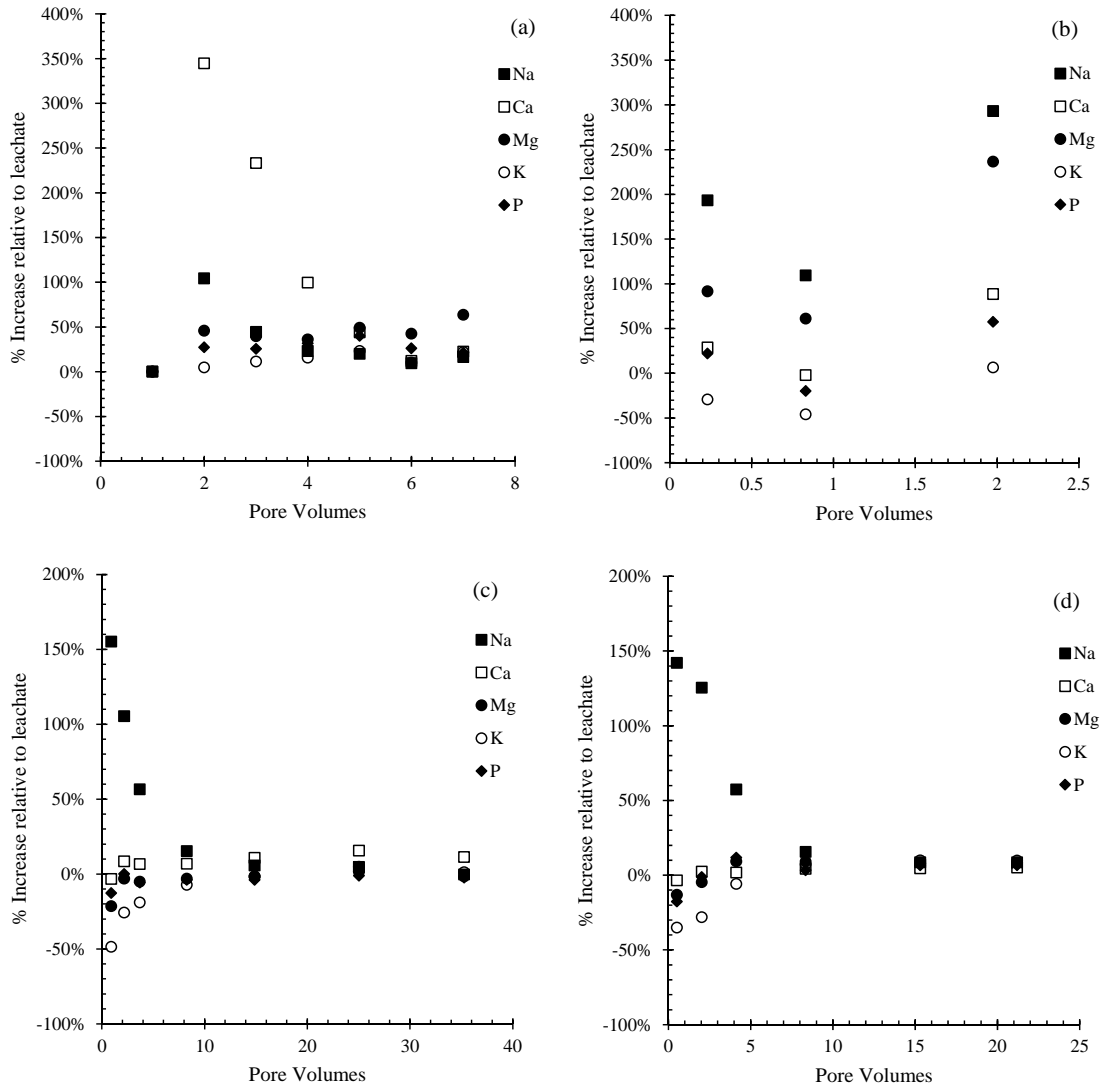
Figure 8: Relative concentration of common ions as a function of pore volumes of flow for: (a) P-GYP #1, (b) P-GYP #2, (c) Copper #1 and (d) Copper #2.

4 CONCLUSION

The hydraulic conductivity of a new polymer modified GCL (PMG-A) was tested against a range of low-pH leachates. The hydraulic conductivity values ranged from 2.7×10^{-8} to 1.2×10^{-9} cm/sec. Stable hydraulic conductivity values were observed up to 11,000 hours. As the ionic strength of the leachate increased, the hydraulic conductivity also increased. The chemistry of the permeates reached a steady-state prior to approximately 15 PVF. Some evidence of minor polymer elution was observed early in the experiments. Element analysis of the leachates indicate a small but measureable increase in elements related to the bentonite portion of the GCL, which indicates some effect of the low-pH on the clay.

5 REFERENCES

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