

**EFFECT OF AMMONIUM ON THE HYDRAULIC  
CONDUCTIVITY OF GEOSYNTHETIC CLAY LINERS  
AND MEASUREMENT IN THE  
EXCHANGE COMPLEX OF BENTONITE**

By

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**Approved by:**

A handwritten signature in black ink, appearing to read 'CHB', written over a horizontal line.

8/9/2013

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## ABSTRACT

Geosynthetic clay liners (GCLs) are hydraulic barriers that consist of a thin layer (<10 mm) of sodium bentonite clay encased by geotextiles or geomembranes held together by needle punching or glue. Sodium bentonite, mainly comprised of the mineral montmorillonite, has characteristically high swell and low hydraulic conductivity making it an ideal material to use in waste containment scenarios, including municipal solid waste (MSW) landfills, to decrease the release of contaminants into the environment.

Cation exchange of bound sodium for ammonium ( $\text{NH}_4^+$ ) in nitrogen rich environments, such as municipal solid waste (MSW) containment facilities, can occur over time potentially affecting a GCL's hydraulic performance. This study investigated an alternative method to ASTM D 7503, a standard procedure for determining the exchange complex of clay minerals to allow for the measurement of bound  $\text{NH}_4^+$  via a lithium bromide (LiBr) extraction method. This method was used to determine the bound  $\text{NH}_4^+$  in bentonite from GCLs that were permeated with MSW bioreactor leachates having up to 0.05 M  $\text{NH}_4^+$ . Hydraulic conductivity tests were also conducted with GCLs using varying concentrations of  $\text{NH}_4^+$  (0.005, 0.05, 0.1, 0.5, and 1.0 M) to understand the effect of  $\text{NH}_4^+$  on the hydraulic conductivity of GCLs.

Hydraulic conductivity results represent a snapshot in time as chemical equilibrium (influent  $\text{NH}_4^+$  = effluent  $\text{NH}_4^+$ ) has not been achieved in all tests and therefore may not reflect the long-term equilibrium condition. The current hydraulic conductivity of a GCL relative to that of DI water is 0.9 for 0.005 M  $\text{NH}_4^+$ , 1.6 to 0.05 M  $\text{NH}_4^+$ , and 3.3 for 0.1 M  $\text{NH}_4^+$ . Currently, solutions with typical  $\text{NH}_4^+$  concentrations for MSW bioreactor leachates ( $\leq 0.05$  M) do not significantly alter the hydraulic conductivity of conventional Na-bentonite GCLs (< 1.6 times). Low hydraulic conductivity was observed in a mock  $\text{NH}_4^+$ -bentonite GCL ( $2.9 \times 10^{-11}$  m/s) that indicates that  $\text{NH}_4^+$  in the exchange complex of bentonite has the ability to swell osmotically, and could be related to the low hydraulic conductivity observed in the < 0.1 M  $\text{NH}_4^+$  hydraulic

conductivity tests. The hydraulic conductivity of GCLs permeated with 0.5 and 1.0 M  $\text{NH}_4^+$  solutions (e.g. increased ionic strength) are four orders of magnitude greater than that of the GCL permeated with DI water ( $1.8 \times 10^{-11}$  m/s), indicating that solutions containing  $> 0.5$  M  $\text{NH}_4^+$  can greatly increase the hydraulic conductivity of conventional GCLs.

In a separate study, GCLs containing bentonite with polymer additives and conventional Na-bentonite were studied by permeating GCLs with inorganic salt solutions of varying ionic strength (I) (1.5, 1.0, 0.5, 0.2, 0.05, and 0.01 M) and ratio of monovalent to divalent cations (RMD) (5, 0.5, 0.05, and  $0.005 \text{ M}^{1/2}$ ) to determine effects on hydraulic conductivity, ion exchange and swelling. The purpose of this study is to determine the thresholds of I and RMD at which the hydraulic conductivity of polymer modified bentonite and convention Na-bentonite GCLs increases appreciably. Iso-hydraulic conductivity lines in the I-RMD space will be created to determine the effectiveness of the polymer modified bentonite in GCLs for various environmental conditions. Three GCLs products were tested and include a bentonite polymer nanocomposite (BPN) GCL, a dry polymer mix bentonite GCL, and a conventional untreated Na-bentonite GCL.

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# CHAPTER ONE

## DETERMINATION OF AMMONIUM IN THE EXCHANGE COMPLEX OF BENTONITE VIA A LITHIUM BROMIDE EXTRACTION METHOD

### 1.1 ABSTRACT

ASTM D7503 or the “Standard Test Method for Measuring the Exchange Complex and Cation Exchange Capacity of Inorganic Fine-Grained Soils” is typically used to determine bound cation concentrations and the cation exchange capacity (CEC) for GCLs used in waste containment applications. ASTM D7503 prescribes the use of 1 M  $\text{NH}_4\text{OAc}$  to for bound cation determination, effectively masking any bound ammonium ( $\text{NH}_4^+$ ) occupying the exchange complex of bentonites that have been exposed to high ammonium environments like those found in municipal solid waste (MSW) containment systems. This study uses a 1 M LiBr extraction solution for the determination of bound cations, including ammonium, to understand the cationic make-up of the bentonite exchange complex of GCLs permeated with real MSW leachates.

### 1.2 INTRODUCTION

Geosynthetic clay liners (GCLs) are factory-manufactured clay liners that consist of a layer of bentonite clay encased by geotextiles or glued to a geomembrane and are typically held together with needle stitch punching (Kolstad 2004). Known for their low hydraulic conductivity, GCLs are used to contain leachate solutions, preventing the contaminants from escaping into the environment. GCLs used in municipal solid waste (MSW) containment facilities as manufactured hydraulic barriers are naturally subjected to hydration and permeation by complex chemical solutions.

Investigators have shown that the bound cation composition of the bentonite exchange complex changes overtime and is dependent on the permeant liquid (Rauen 2007, Kolstad 2004, Jo et al. 2001). This process called cation exchange is directly affected by changes in

thermal dynamic conductivity of the permeant liquid or surrounding soil. Based on the chemistry of a given permeant solution a GCLs properties can change over time resulting in an increase of hydraulic conductivity, decrease of clay swell, and the development of larger flow paths when Na-bentonite GCLs undergo cation exchange with multivalent cations, specifically calcium (Jo et al. 2001, Kolstad 2004, Bradshaw and Benson 2013).

Ammonium ( $\text{NH}_4^+$ ) concentrations can be at high (> 0.25 M) in landfill systems due to the lack of degradation within the MSW containment system (Pivato and Raga 2006). Elevated concentrations of  $\text{NH}_4^+$  in leachate that comes in contact with GCLs is thought to affect the hydraulic properties of GCLs in MSW landfills. Pivato and Raga (2006) and Gautier et al. (2010) conducted experiments that measured ammonium adsorption onto bentonite clay that resulted in a modification of the bentonite porosity and flow network with a reduction in crystalline swelling, suggesting that increased  $\text{NH}_4^+$  in the leachate could result in bentonite physiochemical alterations.

### **1.3 BACKGROUND**

To understand the degree of cation exchange that occurs between a GCL bentonite and a solution, exchangeable or bound cations (BC) of the bentonite clay layer are measured in the laboratory using a solution with a known index ion to calculate the exchange complex (ASTM D 7503). The total net negative charge on the mineral surface is called the cation exchange capacity (CEC), measured by displacing an index ion that satisfies all surface charge locations with another salt solution. The amount of displaced index ions is the calculated CEC and should theoretically be equal to the exchange complex. Characterization of the exchange complex, bound cations satisfying the CEC, is confirmed by summing major cations – sodium (Na), calcium (Ca), potassium (K), and magnesium (Mg). The make-up of the cation exchange complex can be used as an indicator of GCL hydraulic performance based on the preponderance of monovalent over polyvalent cations (e.g.  $\text{Ca}^{+2}$ ). The preference for

replacement has been shown with the lyotropic series as being dependent on type of clay and ions that are replaced. Domenico and Schwartz (1998) shows the lyotropic series as:



Natural-Na bentonites are prone to cation exchange because Na is on the lower end of the series, causing bound Na to be more prone to exchange with cations in permeant solutions.

This study investigated the feasibility of using lithium bromide extraction solution to successfully characterize  $\text{NH}_4^+$  in the exchange complex of bentonite clay. The current testing procedure uses an  $\text{NH}_4^+$  index ion in the measurement of bound cations and therefore masks any  $\text{NH}_4^+$  in the clay exchange complex (ASTM D 7503). Clays that have been exposed to high levels of  $\text{NH}_4^+$ , specifically in municipal solid waste containment facilities (0 to 0.05 M) have the potential to undergo cation exchange with exchangeable cations on the soil's mineral surface with cations in the permeant solution. Others discuss the sorption mechanisms of  $\text{NH}_4^+$  to the soil particle surface (Pivato and Raga 2006). The application of this method is discussed and the process for bound cation extraction via a lithium bromide (LiBr) extraction is explained.

## 1.4 LABORATORY METHODS AND MATERIALS

### 1.4.1 Bentonite

The bentonite used in this study came from two different GCL sources: one source was conventional Na-bentonites used in new GCLs and the second was from GCLs that were tested with MSW bioreactor leachates. Conventional Na-bentonite (Na-B<sub>i</sub>) samples were used in the feasibility testing portion of this study. Details of the original bound cation makeup of the bentonite and complete composition of the bioreactor leachates can be found in Rauen (2007). Properties including mineralogy, cation exchange capacity, and swell index for bentonites used in this study can be found in Table 1.1. The cationic makeup of the exchange complex for the bentonites used in this study can be found in Fig. 1.1. 'C' indicates permeant liquid leachate from a conventional landfill, 'BR' from a bioreactor landfill, and 'Na-B<sub>i</sub>' is bentonite used in the

feasibility testing of this study. Note that the sum of the bound cations (i.e. the exchange complex) for the samples permeated with MSW leachates have values much lower than the expected CEC value. This means that there is a cation (or cations) that are in the satisfying the negative surface charge of the bentonite that are not the major bound cations (Na, Ca, Mg, K). These cations are termed unaccounted bound cations.

The bentonite from the second source came from hydraulic conductivity tests originally set-up by Rauen (2007) where GCLs were permeated with leachates from MSW bioreactor (BR) and conventional (C1) landfills until both hydraulic and chemical equilibrium criterion (ASTM D 6766) were satisfied (Bradshaw and Setz, 2013). The original leachate cation chemistry, ionic strength, pH, and electrical conductivity (EC) can be found in Table 1.2 as reported by Rauen (2007). Reported cations include the four major cations (Na, Ca, Mg, K) and one trace cation ( $\text{Fe}^{2+}$ ) in the leachate and  $\text{NH}_4^+$ . Additional cations detected in the solution ( $\text{Zn}^{2+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$ ) resulted in less than 3% change in total ionic strength; therefore, these cations were not considered during analysis and are not reported in this study but can be found in Rauen (2007).

The concentration of unaccounted bound cations of the bentonites permeated with MSW leachates increases as the concentration of  $\text{NH}_4^+$  increases in the MSW leachate permeant solution as seen in Fig. 1.2. There is a direct correlation between the increasing concentration of  $\text{NH}_4^+$  in solution and the unaccounted bound cations ( $\text{CEC} - \text{BC}_{(\text{Na}, \text{K}, \text{Ca}, \text{Mg})}$ ) of the bentonite exchange complex.

#### 1.4.2 Extraction Liquids

Three 1 M-solutions were used to extract bound cations and determine the cation exchange capacity of the bentonites: ammonium acetate ( $\text{NH}_4\text{OAc}$ ), lithium bromide ( $\text{LiBr}$ ) and potassium chloride ( $\text{KCl}$ ). The 1 M  $\text{NH}_4\text{OAc}$  and  $\text{KCl}$  solutions are the standard extraction liquids prescribed in ASTM D7503 whereas the 1 M  $\text{LiBr}$  solution was employed as a substitute for  $\text{NH}_4\text{OAc}$  for determining bound  $\text{NH}_4^+$ . The solutions are prepared by mixing salts with Type II DI

water (per ASTM D1193) in a 1 L volumetric flask to create 1 M solutions. Corresponding salt grade and salt mass is shown in Table 1.3.

### 1.4.3 Chemical Analysis

The chemical analysis for concentrations of Na, Ca, Mg, and K (typical cations found in soil pore water) and of Li (described below) found in testing solutions was completed using a Varian MPX inductively coupled plasma optical emission spectroscopy (ICP-OES) following the U.S. Environmental Protection Agency (USEPA) method 6010B (USEPA, 2007). Calibration curves were created using High Purity Standards of the cation of interest (Na, Ca, Mg, K, and Li) with a starting concentration of 10.0 mg/mL preserved in 1%-4% nitric acid. The matrix solution used to create the ICP calibration curve was the corresponding extraction solution used for bound cation extractions to account for potential interference during the ICP analysis.

Ammonium in the samples was measured via the salicylate method (EPA method 350.1) using high-range nitrogen  $\text{NH}_3$  "Test 'N Tube" vials (Hach Company: Method 10031) by spectrophotometer. The pH of the reacted solutions (via salicylate method) used in the Hach testing kit are below 7 so that all nitrogen in solution is in the ionized- $\text{NH}_3$  form, or  $\text{NH}_4^+$ . The calibration curve was created using ACS Certified ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) dissolved in Type II DI water.

## 1.4.4 Bound Cations, Soluble Cations, and CEC

### 1.4.4.1 Soluble Cation Determination

Soluble cations (SC) were determined according to ASTM D 7503. A 1:50 solid-water ratio (2 g crushed bentonite passing the #10 sieve to 100 g Type II DI water) is tumbled at 30 rpm for 1 hour in an end-to-end shaker. Na, Ca, Mg, K, and  $\text{NH}_4^+$ , are washed from the pore space and the eluent is extracted via vacuum filtration through Whatman No. 42 paper. The

eluent is analyzed with ICP-OES for Na, Ca, Mg, and K cation concentrations. The spectrophotometer and Hach test method were used to measure  $\text{NH}_4^+$  concentrations.

#### **1.4.4.2 Bound Cation Determination**

Bound cations (BC) were determined using the procedure outlined in ASTM D 7503. However, in substitution to using the prescribed 1 M  $\text{NH}_4\text{OAc}$  extraction solution, bentonites were also tested using a 1 M  $\text{LiBr}$  extraction solution. Changes to the standard are highlighted in Table 1.4 with a comparison of the current ASTM D 7503 method and the alternative  $\text{LiBr}$  extraction method evaluated in this study. Suggested changes to ASTM D 7503 that incorporate the  $\text{LiBr}$  extraction method can be found in Appendix 1.

Following the procedure highlighted in ASTM D 7503, a 1:4 solid-liquid ratio (10 g crushed bentonite pass the #10 sieve to 40 mL extraction liquid (i.e. 1 M  $\text{NH}_4\text{OAc}$  or 1 M  $\text{LiBr}$ ) is tumbled at 30 rpm for 5 minutes in an end-to-end shaker. Post-tumbling, the slurry is allowed to equilibrate for 24 hours and then tumbled again for 15 minutes at 30 rpm. The extract is vacuum filtered through Whatman No. 42 filter paper and four 30 mL rinses of the extraction liquid (1 M  $\text{NH}_4\text{OAc}$  or 1 M  $\text{LiBr}$ ) are applied before the bentonite completely drains. This extract is collected in a 250 mL volumetric flask, preserved to pH of 2 with either nitric (for samples from 1 M  $\text{NH}_4\text{OAc}$  extraction) or hydrochloric acid (for samples from 1 M  $\text{LiBr}$  extraction), and then filled to volume with the extraction liquid. The extract is analyzed for major bound cations (Na, Ca, K, and Mg) using ICP-OES and the  $\text{NH}_4^+$  that is collected from the  $\text{LiBr}$  extraction is analyzed using spectrophotometry as described above.

#### **1.4.4.3 Cation Exchange Capacity**

Residual soil remaining on the filter from the bound cation extraction is used in the CEC testing. The soil is then rinsed with three-40 mL portions of isopropanol for both the 1 M  $\text{NH}_4\text{OAc}$  and 1 M  $\text{LiBr}$  extraction procedure to rinse any residual cations out of the soil pores. Next the isopropanol washed soil is rinsed with four-50 mL portions of 1 M  $\text{KCl}$ , replacing the adsorbed cations (ammonium or lithium cations depending on extraction procedure) with K

cations in the interlayer of the soil. The extract is collected in a 250 mL volumetric flask and filled to volume with Type II DI water. If the 1 M  $\text{NH}_4\text{OAc}$  extraction method was used then  $\text{NH}_4^+$  spectrophotometry. If the 1 M  $\text{LiBr}$  extraction method was used then the concentration of lithium in the extract is determined via ICP-OES. The soil CEC can be calculated from the measured concentration of ammonium or lithium in the extract solution and can be found in Appendix 1, assuming that all  $\text{NH}_4^+$  or  $\text{Li}$  bound to the mineral surface was satisfying the total negative charge of the soil and was then exchanged for  $\text{K}$ .

#### 1.4.5 Quality Control – CEC and Exchange Complex

The bound cation concentration is the concentration of cations adsorbed to the mineral surface and is calculated as the difference between the cation concentration determined via the bound cation extraction (either ammonium acetate or lithium bromide method) and the soluble cation concentration. When the bound cations are extracted the soluble cations in the pore space (i.e. not bound to the mineral surface) are also extracted in this process and therefore have to be subtracted so that just the adsorbed cations are accounted in the exchange complex. The exchange complex and the cation exchange capacity should be equal if full cation replacement and measurement has occurred and can serve as a quality control check for the extraction methods. Equation 1 explains this relationship between the exchange complex and CEC equivalence.

$$\text{Exchange complex} = \sum ((\text{BC} + \text{SC}) - \text{SC}) = \sum \text{BC} = \text{CEC} \quad . \quad (1.1)$$

### 1.5 RESULTS AND DISCUSSION

Two conventional Na-bentonites used in new GCLs and 8 bentonites from GCLs permeated with conventional and bioreactor leachates with no to moderate  $\text{NH}_4^+$  concentrations (0 to 0.1 M) were tested for bound cation concentrations and CEC using 1 M  $\text{LiBr}$  solution as an alternative bound cation extraction liquid. Bound cation extractions using  $\text{NH}_4\text{OAc}$  (per ASTM D 7503) were also performed on each of the bentonites as a control. Duplicate CEC tests were

performed using KCl or  $\text{NH}_4\text{OAc}$  in lieu of KCl for samples that were tested for bound cations with LiBr.

### 1.5.1 Feasibility Study

Two sources of conventional Na-bentonites, Na-B<sub>t</sub>1 and Na-B<sub>t</sub>2, used in GCLs were evaluated for feasibility of using a 1 M LiBr solution for extracting bound cations. Triplicates of each extraction method (3 using LiBr, and 3 using  $\text{NH}_4\text{OAc}$ ) were tested. The BC concentrations determined for each extraction method are compared in Fig. 1.3

Bound cations are measured within a factor of 1.4 for the  $\text{NH}_4\text{OAc}$  and LiBr extraction methods. The CEC and sum of bound cations are also within a factor of 1.1 for determination. The one-to-one correlation between the two extraction methods indicates that 1M LiBr is a suitable extraction solution for the measurement of bound cations in bentonite clay.

### 1.5.2 Detection of Bound Ammonium

Bentonites from GCLs permeated with conventional and bioreactor leachates were previously tested for major bound cations (Ca, Mg, K, and Na) according to ASTM D 7503 (Fig. 1.1). The sum of the bound cations (shown in Fig. 1.1) falls short of the measured average CEC (77.9  $\text{cmol}^+/\text{kg}$ ) and outside a range of one standard deviation of the average CEC (+ / - 8.8  $\text{cmol}^+/\text{kg}$ ). The bentonite was re-evaluated for BC concentrations using the LiBr extraction method and the BC concentrations (including  $\text{NH}_4^+$ ) are shown in Fig. 1.4.

In almost all cases (except BR2) when  $\text{NH}_4^+$  is accounted for in the exchange complex the sum of the bound cations falls within the region of one standard deviation of the expected cation exchange capacity. Sample BR2 falls 5  $\text{cmol}^+/\text{kg}$  short of accounting for all the BCs within one standard deviation of the CEC range. There could potentially be another cation present within the exchange complex that was not analyzed for in this study.

## 1.6 CONCLUSIONS

Geosynthetic clay liners are used in a wide variety of containment environments and have the potential to be exposed to solutions containing elevated  $\text{NH}_4^+$  concentrations. The current standard (ASTM D 7503) for the determination of a fine-grained soil's exchange complex and CEC uses an ammonium acetate solution, which does not allow for the measurement of  $\text{NH}_4^+$  (i.e.  $\text{NH}_4^+$  in extraction solution masks  $\text{NH}_4^+$  extracted from the exchange complex). A laboratory feasibility study of the lithium bromide extraction procedure was completed on two conventional Na-bentonites from new GCLs and results demonstrated that bound cations of fine grained soils can be measured as effectively as when using the ASTM D7503 extraction procedure.

In this study the measurement of  $\text{NH}_4^+$  in the exchange complex of GCLs permeated with MSW leachates was achieved by using a 1 M lithium bromide extraction solution in lieu of a 1 M ammonium acetate solution. The proposed addendum to ASTM D 7503 can be found in Appendix 1. Bound cation extractions were completed on bentonites from GCLs that were permeated with MSW leachates containing various concentrations of ammonium (0 to 0.05 M). Initial exchange complex testing indicated a void in characterizing the exchange complex (the sum of the characterized bound cations was well below the measured cation exchange capacity value). Bound  $\text{NH}_4^+$  concentrations were determined using the lithium bromide extraction procedure and when added to the original major bound cation make up the sum of bound cations was within one standard deviation of the average cation exchange capacity.

By using the current ASTM D 7503 bound cation extraction procedure as a base for the new proposed LiBr bound cation extraction method,  $\text{NH}_4^+$  can be measured in the exchange complex of bentonite clays. It is recommended to use the LiBr bound cation and cation exchange capacity extraction procedures (Appendix 1) for fine-grained soils that are exposed to elevated levels of environmental  $\text{NH}_4^+$  to fully characterize the bound cation composition of the soil.

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## 1.8 TABLES

Table 1.1 Properties of Na-bentonite samples used in this study.

Properties		GCLs			Determined Via
		Na-B <sub>r</sub> 1 GCL	Na-B <sub>r</sub> 2 GCL	Rauen (2007)	
Mineralogy	Montmorillonite (%)	84	86	80	XRD, Moore and Reynolds (1989)
	Quartz (%)	9	5	≤ 2	
	Plagioclase (%)	3	3	7	
	Cristobalite (%)	--	3	6	
	Clinoptilolite (%)	2	1	--	
	Augite (%)	--	2	--	
	Illite, Mica, Orthoclase (%)	1	--	≤ 2	
CEC (cmol <sup>+</sup> /kg)		81.0	80.3	78.5	ASTM D7503
Swell Index (mL/2 g)		26.0	28.0	26.3	ASTM D 5890

Table 1.2 Concentration of major cations, ionic strength, pH, and electrical conductivity (EC) of the convention and bioreactor leachates from Rauen (2007) that were used to permeate the GCLs and bentonite analyzed in this study.

Permeant Liquid	Cation Concentration (mM)						Ionic Strength (mM)	pH	EC (S/m)
	Na	NH <sub>4</sub>	K	Mg	Ca	Fe			
Detection Limit	0.19	0.03	0.03	0.03	0.05	0.04			
C1	130	52	21	18	0.1	<0.04	210	8.19	2.25
BR1	43	48	9	3	6	0.1	60	7.96	1.33
BR2	104	41	15	6	0.9	0.1	130	8.02	1.76
BR3	82	28	11	7	0.6	<0.04	110	7.95	1.38
BR4	47	23	8	3	1	0.1	50	7.92	0.89
BR5	78	23	11	5	0.7	<0.04	100	7.77	1.24
BR6	58	7	9	8	2	0.3	100	7.99	1.17
BR7	52	<0.03	8	7	0.5	<0.04	70	7.77	0.95
Range	43-130	<0.03-52	21-Aug	18-Mar	0.1-6	<0.004-0.3	50-210	7.77-8.19	0.89-2.25

Table 1.3 Salt grade and mass used for extraction testing.

Compound Used	Compound source and purity	Mass (g) for creation of 1 M solution dissolved in 1 L Type II DI water*
KCl	Arcos Organics 99.9 % pure	74.6
LiBr	Sigma Co. 99.9 % pure	86.9
NH <sub>4</sub> OAc	MP Biomedicals 99.9 % pure	77.1

\*Refer to Specification D1193

Table 1.4 Comparison of ASTM D7503 and proposed LiBr (this study) bound cation & CEC extraction method.

Step #	Process	ASTM D7503	Alternative LiBr Extraction
1	24-hour soil hydration in extraction solution	Extraction solution: 1 M NH <sub>4</sub> OAc Bound index cation 1: NH <sub>4</sub>	Extraction solution: 1 M LiBr Bound index cation 1: Li
2	Bound and soluble cation determination: index cation 1 replaces originally bound cations from mineral surface and washes soluble cations from soil pores	Extraction solution: 1 M NH <sub>4</sub> OAc Bound index cation 1: NH <sub>4</sub>  Collect extract: Na, Ca, Mg, K measure using ICP-OES or atomic absorption Acid preservation: 10% HNO <sub>3</sub>	Extraction solution: 1 M LiBr Bound index cation 1: Li  Collect extract: Na, Ca, Mg, K measure using ICP-OES or atomic absorption and NH <sub>4</sub> measure using spectrophotometer Acid preservation: 10% HCl
3	Removal of soluble index cation (from step 2) from soil pore water	Rinsing solution: Reagent grade isopropanol	Rinsing solution: Reagent grade isopropanol
4	Cation exchange capacity determination: exchange of index cation 1 for index cation 2	Extraction solution: 1 M KCl Bound index cation 2: K  Collect extract of cation 1: NH <sub>4</sub> Measure using spectrophotometry	Extraction solution: 1 M KCl Bound index cation 2: K  Collect extract of cation 1: Li Li Measure using ICP-OES or atomic absorption

## 1.9 FIGURES

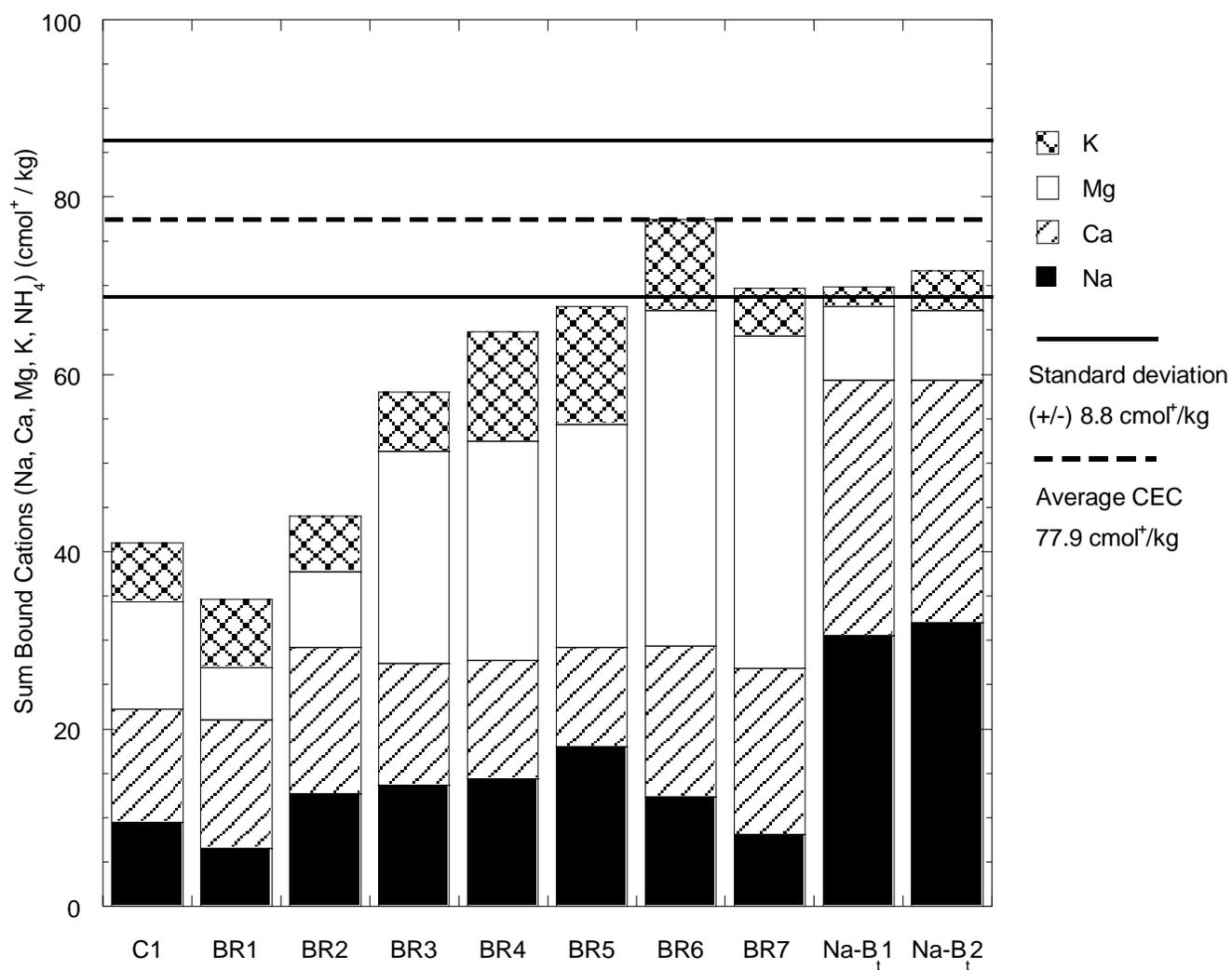


Fig. 1.1

Cationic (Na, Ca, Mg, K) make-up of the exchange complex of bentonites permeated with real MSW leachates and conventional Na-bentonites used in the feasibility testing of this study.

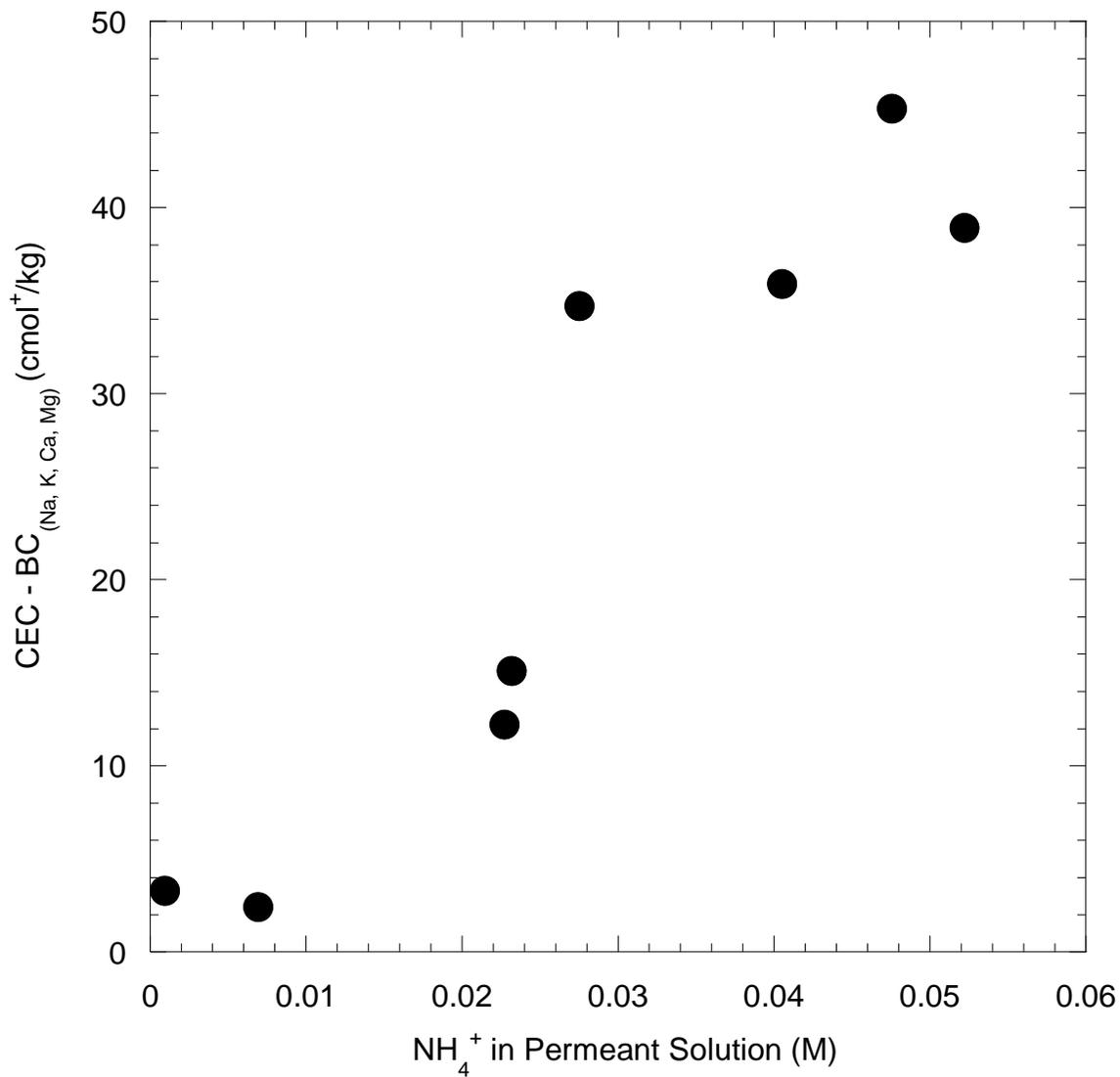


Fig. 1.2 Unaccounted bound cations in exchange complex of bentonites permeated with MSW leachates in relation to  $\text{NH}_4^+$  permeant concentration.

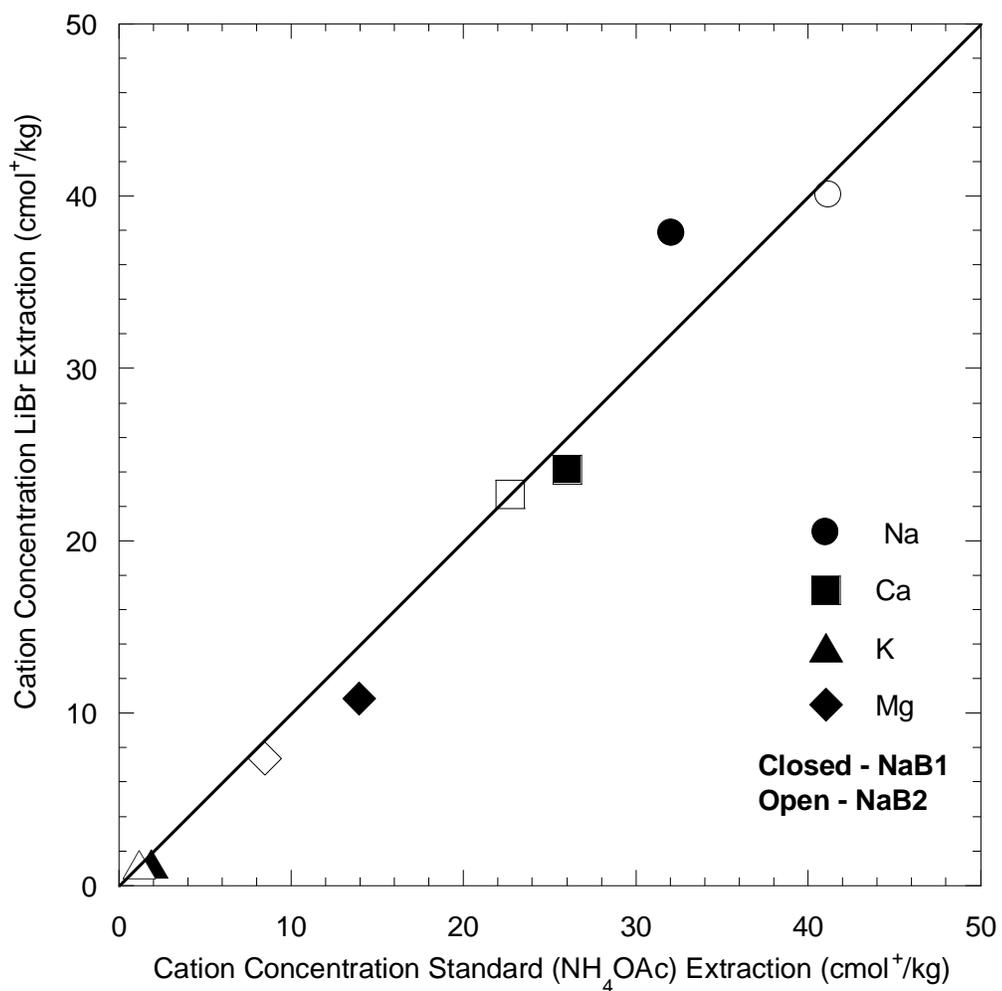


Fig. 1.3 Measured major bound cations (Na, Ca, K, Mg) for LiBr extraction method vs. ASTM D7503 using two natural Na-bentonites.

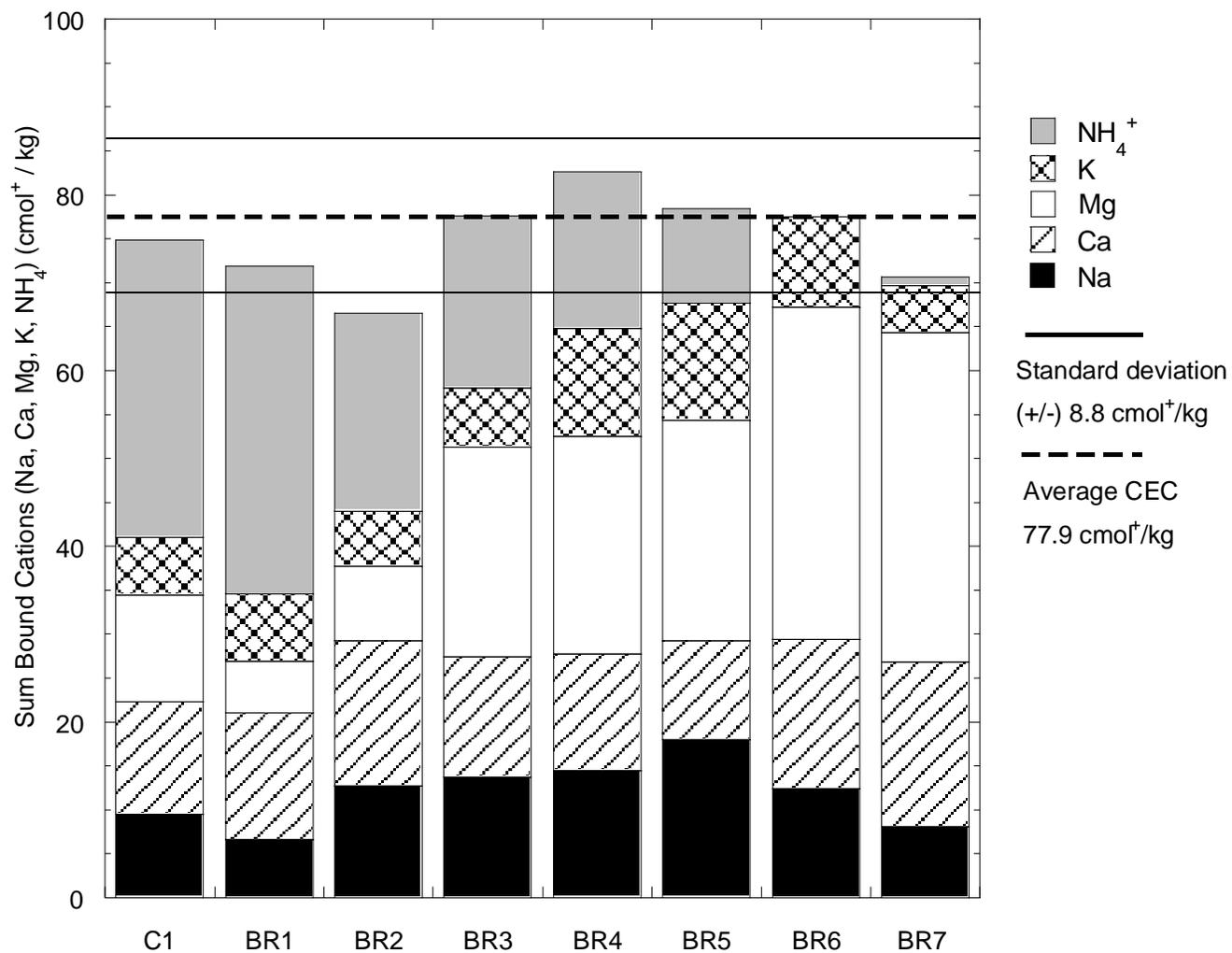


Fig. 1.4 Summary of exchange complex (Na, Ca, Mg, K,  $\text{NH}_4^+$ ) via the LiBr extraction method of bentonites permeated with MSW leachates.

## 1.10 Appendix 1 – Suggested Changes to ASTM D 7503

### ASTM D 7503

Committee: D18.04 - D18.04 - Hydrologic Properties and Hydraulic Barriers

### Standard Test Method for Measuring the Exchange Complex and Cation Exchange Capacity of Inorganic Fine-Grained Soils

#### 1 Scope

- 1.1 This test method describes the procedures for measuring the soluble cations, bound cations, and the cation exchange capacity (CEC) of fine grained inorganic solids using an ammonium acetate ( $\text{NH}_4\text{OAc}$ ) or an alternative lithium bromide (LiBr) matrix solution. Clay minerals in fine-grained soils carry a negative surface charge that is balanced by bound cations near the mineral surface. These bound cations can be exchanged by other cations in the pore water, which are referred to as soluble cations. The cation exchange capacity is a measure of the negative surface charge on the mineral surface. The CEC generally is commonly satisfied by four base cations; calcium (Ca), sodium (Na), magnesium (Mg), and potassium (K). The  $\text{NH}_4\text{OAc}$  testing Method A allows for the measured of these cations in the soil. The LiBr testing Method B allows for the determination of the four base cations as well as ammonium. This test method was developed from concepts described previously in Lavkulick (1981) (1)<sup>2</sup> and Rhoades (1982) (2). In soils with appreciable gypsum or calcite, dissolution of these minerals will release Ca in solution that may affect the measurement.
- 1.2 In this test method, the soluble salts from the mineral surface are washed off with de-ionized water and then the concentration of soluble salts within the extract is measured. The bound cations of the clay are measured by using a solution containing an index ion that forces the existing cations in the bound layer into solution. The total concentrations of bound and soluble cations in this solution are measured. The CEC is measured by displacing the index ion with another salty solution and measuring the amount of the displaced index ion.
- 1.3 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.
- 1.4 All observed and calculated values shall conform to the guide for significant digits and rounding established in Practice D6026. The procedures in Practice D6026 that are used to specify how data are collected, recorded, and calculated are regarded as the industry standard. In addition, they are representative of the significant digits that should generally be retained. The procedures do not consider material variation, purpose for obtaining the data, special purpose studies, or any considerations for the objectives of the user. Increasing or reducing the significant digits of reported data to be commensurate with these considerations is common practice. Consideration of the significant digits to be used in analysis methods for engineering design is beyond the scope of this standard.
- 1.5 The values stated in SI units are to be regarded as the standard, unless other units are especially given.

#### 2 Referenced Documents

##### 2.1 *ASTM Standards:*

- D653 Terminology Relating to Soil, Rock, and Contained Fluids
- D1193 Specification for Reagent Water

D2216 Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass

D3740 Practice for Minimum Requirements for Agencies Engaged in Testing and/or Inspection of Soil and Rock as Used in Engineering Design and Construction

D6026 Practice for Using Significant Digits in Geotechnical Data

E145 Specification for Gravity-Convection and Forced Ventilation Ovens

### 3 Terminology

3.1 For definitions of other term used in this standard, use Terminology D653.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *acid wash, n* – the process of initially rinsing equipment with tap water, followed by a rinse with 10% HNO<sub>3</sub> solution and finally rinsing 3 times with DI water.

3.2.2 *bound cations (BC), n* – cations that are adsorbed (bound) to the mineral surfaces that may be exchanged.

3.2.3 *cation exchange capacity (CEC), n* – the total negative charge on mineral surface to be satisfied by bound cations.

3.2.4 *exchange complex, n* – the collection of bound cations satisfying the CEC.

3.2.5 *fine-grained soils* – any soil with more than 50 % passing the No. 200 US standard sieve.

3.2.6 *inorganic soils, n* – any soil with a loss of ignition (LOI) less than 1%.

3.2.7 *soluble cations (SC), n* – cations in the soil that are not bound to the mineral surface.

### 4 Significance and Use

4.1 Fine-grained soils are used in the waste contaminate systems as barriers to flow and contaminant transport. Liquids contained by these barriers can contain ions that may interact with the mineral surfaces in fine-grained soils.

4.2 The liquid passing through the pores of fine-grained soil can interact with the mineral surface, and affect the physical and chemical characteristics of the soil. This method can be used as part of an evaluation of these interactions.

### 5 Apparatus

5.1 *Drying Oven*, capable of maintaining a uniform temperature of 105 ± 5°C that meets requirements of Specification E145.

5.2 *No. 10 U.S. Standard Sieve*

5.3 *Desiccator*, containing silica gel.

5.4 *Laboratory Balance*, 20 g capacity, ± 0.001 g accuracy and precision.

5.5 *Weighing Paper*, or small weighing dish.

5.6 *End Over End Shaker*, capable of 30 rpm.

5.7 *Capped Containers*, should tightly fit in the end over end shaker holding compartment with capacities larger than 40 mL.

5.8 *500 mL Filtering Flask*, connectable to low-pressure vacuum line, acid washed (See Fig. 1).

5.9 *Flexible Tubing*, appropriate size to connect filtering flask to the low-pressure vacuum line (See Fig. 1).

5.10 *Buchner Funnel*, 55 mm or 90 mm diameter, acid washed (See Fig. 1).

5.11 *Wash Bottle*, for dispensing solutions, new or acid washed.

5.12 *Graduated Cylinder*, for measuring solution portions, acid washed.

5.13 *2.5 μm Ashless Filter Paper* that covers the surface of Buchner funnel.

5.14 *250 mL Volumetric Flasks*, class A flask for precision and accuracy.

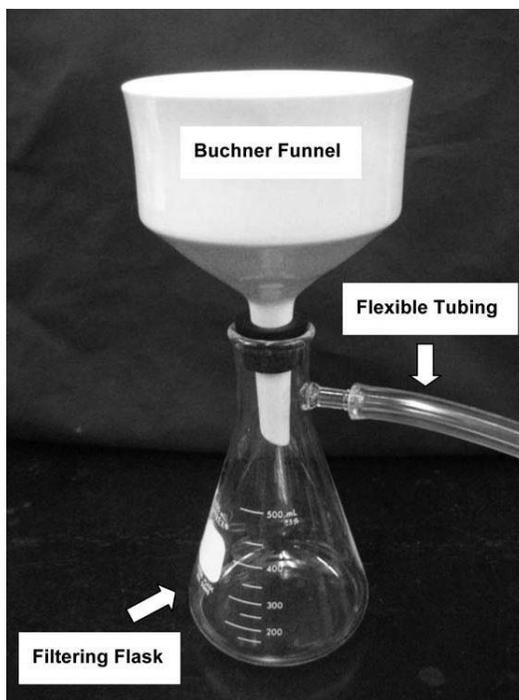


FIG. 1 Experimental Setup for Vacuum Filtration

## 6 Reagents

### 6.1 Reagent Water:

Use only ASTM Type II water as defined in Specification D1193.

### 6.2 Method A Solution:

#### 6.2.1 Ammonium Acetate ( $\text{NH}_4\text{OAc}$ ), 1M:

Dissolve 77.08 g of 99.9 % pure  $\text{NH}_4\text{OAc}$  in Type II DI (see Specification D1193) and fill to volume in a 1000 mL volumetric flask. Adjust the pH of the solution to 7 with ammonium hydroxide or acetic acid. Approximately 1 L of  $\text{NH}_4\text{OAc}$  is needed per 6 samples.

### 6.3 Method B Solution:

#### 6.3.1 Lithium Bromide ( $\text{LiBr}$ ), 1M:

Dissolve 86.85 g of 99.9 % pure  $\text{LiBr}$  in Type II DI water (see Specification D1193) and fill to volume in a 1000 mL volumetric flask. Adjust pH of the solution to 7 with acetic acid or hydrochloric acid. Approximately 1 L of  $\text{LiBr}$  is needed per 6 samples.

### 6.4 Isopropanol:

Reagent grade.

### 6.5 Potassium Chloride, 1M:

Dissolve 74.6 g of 99% pure  $\text{KCl}$  in Type II DI (see Specification D1193) and fill to volume in a 1000 mL volumetric flask. Approximately 1 L of  $\text{KCl}$  is needed per 6 samples.

### 6.6 Ammonium sulfate:

Dry 238 mg of ACS Certified  $(\text{NH}_4)_2\text{SO}_4$  for 4 hours at  $40^\circ\text{C}$ . Make a 200 mg/L stock solution by dissolving the dried compound in 100 mL of Type II DI water and fill to volume in a 250 mL volumetric flask. Prepare calibration standards by diluting the stock solution into concentrations of 10, 20, 40, 50, and 80 mg/L.

### 6.7 Ca, Mg, K and Na:

- 7 Use ICP-grade or AA-grade element standards in an  $\text{HNO}_3$  matrix to prepare quality control spikes in an  $\text{NH}_4\text{OAc}$  matrix (Method A) or in an unpreserved matrix to prepare quality control spikes in a LiBr matrix (Method B). Hazards
  - 7.1 This standard does not address all of the safety concerns associated with its use. The user of this standard is responsible for implementing proper safety precautions and should be aware of any possible health concerns and risks related with the materials and chemicals used while following this standard.
- 8 **Determination of Required Air-Dried Mass of Soil for Analysis**
  - 8.1 Air-dry approximately 30 g of soil (12 g of solid is required for testing) according to the procedures described in Test Method D2216.
  - 8.2 Oven-dry at least 2 g of the air-dry soil to determine the water content following Test Methods D2216.
  - 8.3 Determine total mass of air-dry soil needed to have 2 g of soil solids for determination of soluble cations.
  - 8.4 Determine total mass of air-dry soil needed to have 10 g of soil solids for determination of bound cations.
  - 8.5 Use the oven-dry weight (2 or 10 g) of the soil for all calculations.
- 9 **Determination of Soluble Cations**
  - 9.1 Use only air-dry soil that passes the No. 10 US Standard Sieve.
  - 9.2 Add mass of air-dry soil corresponding to 2 g of soil solids and 100 mL of Type II DI water to a covered container that fits tightly into the shaker.
  - 9.3 Place the containers in an end-over-end shaker and shake for 1 h at 30 rpm.
  - 9.4 Vacuum filter the mixture in each container using 2.5  $\mu\text{m}$  ashless filter paper.
  - 9.5 Transfer the extract to a 100 mL acid washed volumetric flask, preserve with 1 mL  $\text{HNO}_3$  (Method A) or preserve with 1 mL HCl (Method B), and fill to volume.
  - 9.6 Analyze each extract for cation concentration (in mg/L) using inductively coupled plasma spectrometry, atomic absorption, or another suitable method.
  - 9.7 *Method B:*
    - 9.7.1 Analyze the extract for ammonium concentration (mg/L) using a spectrophotometer.
- 10 **Determining of Bound Cations**
  - 10.1 Use only air-dry soil that passes the No. 10 US Standard Sieve.
  - 10.2 Prepare a blank sample for analysis by placing 100 mL of DI water in a covered container.
  - 10.3 Prepare quality control samples for analysis by creating a duplicate and a spike and place in a covered container. Add determined mass of air-dried soil corresponding to 10.0 g of soil solids and 40 mL of Method A or B solution into 100 mL covered container (use a container which tightly fits into the end over end shaker).
  - 10.4 Shake the covered containers for 5 minutes in an end over end shaker at 30 rpm. Agitate the container to rinse the particles from the side of the container and let the mixture stand for 24 hours.
  - 10.5 After 24 h shake the container with the mixture for 15 min at 30 rpm in the end over end shaker.
  - 10.6 Rinse the 500 mL filtering flask and Buchner funnel with Method A or B solution.).
  - 10.7 Place the Buchner funnel over the 500 mL filtering flask and line the Buchner funnel with 2.5  $\mu\text{m}$  ashless filter paper (see Fig. 1).
  - 10.8 Transfer the contents of the shaken container to the Buchner funnel.
  - 10.9 Rinse the container and cap into the Buchner funnel using a squirt bottle containing the Method A or B solution.
  - 10.10 Apply low suction to the filtering flask (<10 kPa).

- 10.11 Wash the soil in the Buchner funnel with four 30 mL portions of Method A or B solution. Add each 30 mL portion slowly and allow the entire 30 mL portion to drain before adding the next 30 mL portion. Do not allow the soil to dry or crack between additions of solution.
- 10.12 Turn the suction off to the filtering flask after the last washing. Leave the washed soil is to be used for determining the cation exchange capacity (CEC).
- 10.13 Rinse the 250 mL volumetric flask with Method A or B solution.
- 10.14 Transfer the filtered aqueous solution into the 250 mL volumetric flask. Preserve the solution to a pH of 2 with ICP-grade nitric acid (Method A) or hydrochloric acid (Method B) and fill the volumetric flask to volume with Method A or B solution.
- 10.15 Analyze the cation concentration (in mg/L) in the aqueous solution using inductively coupled plasma spectrometry or atomic absorption.

### 11 Determination of the Cation Exchange Capacity

- 11.1 Rinse an acid washed 500 mL filtering flask with isopropanol.
- 11.2 Place the Buchner funnel with the Method A or B solution washed sample onto the 500 mL filtering flask (see Fig. 1).
- 11.3 Apply low suction (<10 kPa) to the filtering flask. Do not allow the soil to dry when suction is applied.
- 11.4 Wash the soil with three 40 mL portions of isopropanol. Allow each 40 mL portion to drain before adding the next portion. Washing with isopropanol removes any residual cations from Method A or B solution.
- 11.5 Turn off the suction to the filtering flask when free liquid is no longer visible.
- 11.6 Separate the Buchner funnel from the filtering flask. Discard the isopropanol collected in the 500 mL filtering flask and rinse the flask with Type II DI water three times.
- 11.7 Return the Buchner funnel containing the isopropanol washed soil to the rinsed filtering flask (See Fig. 1).
- 11.8 Apply suction to the filtering flask and wash the soil with four 50 mL portions of 1 M KCl solution. Allow each portion of the 1 M KCl solution to drain before adding the next portion. Do not allow the soil to dry between additions of KCl solution.
- 11.9 Rinse a 250 mL volumetric flask with 1 M KCl.
- 11.10 Transfer the extract into the 250 mL volumetric flask. Rinse the filtering flask with Type II DI Water and transfer the contents into the volumetric flask.
- 11.11 Fill the volumetric flask to volume with water.
- 11.12 Analyze the cation concentration (in mg/L) in the aqueous solution using spectrophotometer (Method A) or inductively coupled plasma spectrometry (Method B).

### 12 Calculations

- 12.1 Calculate the concentration of soluble cations as follows:

$$S = C \times \frac{0.100L}{\text{dry weight of soil (g)}} \times 1000 \frac{\text{g}}{\text{kg}}$$

where :

$S$  = concentration of soluble cations ( $\text{cmol}^+ / \text{kg}$ )

$C$  = concentration of cations in the DI water extract ( $\text{cmol}^+ / \text{L}$ )

- 12.2 Calculate the concentration of bound cations as follows:

$$M^+ = C \times \frac{0.25L}{\text{dry weight of soil (g)}} \times 1000 \frac{g}{kg} - S$$

where:

$M^+$  = concentration of adsorbed cation (cmol<sup>+</sup> / kg)

$C$  = concentration of cation in the Method A or Method B extract (cmol<sup>+</sup> / L)

12.3 Calculate the cation exchange capacity based as follows:

$$CEC = MC^+ \times \frac{0.25 L}{\text{dry weight of soil (g)}} \times 1000 \frac{g}{kg}$$

$CEC$  = concentration of cation exchange capacity (cmol<sup>+</sup>/kg)

$MC^+$  = concentration of adsorbed cation (cmol<sup>+</sup>/L) (Method A: nitrogen & Method B: lithium)

### 13 Report

13.1 Report the following information:

13.1.1 Source and description of the soil.

13.1.2 Source and description of all chemicals used to make mixtures and solutions.

13.1.3 Dilution factor of aqueous samples prior to chemical analysis.

13.1.4 Concentration of bound cations, concentrations of soluble cations, and CEC in units of cmol(+)/kg.

13.1.5 Any modifications to the this standard test method.

### 14 Precision and Bias

14.1 *Precision* – Test data on precision are not presented due to the nature of the soil or rock, or both materials, tested by this standard. It is either not feasible or too costly to produce multiple specimens that have uniform physical properties. Any variation observed in the data is just as likely to be due to specimen variation as to operator or laboratory testing variation.

14.1.1 Subcommittee D18.04 is seeking any pertinent data from users of these test methods that might be used to make a limited statement on precision.

14.2 *Bias* – There is no accepted reference value for these test methods; therefore, bias cannot be determined.

### 15 Keywords

15.1 Bentonite, bound cation; cation exchange capacity; cations; CEC; clay; exchange complex; soluble cations

### 16 References

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- (2) Rhoades, J.D. (1982). Soluble Salts. Pg. 167-180 in Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties, 2<sup>nd</sup> Edition (A. Page, R. Miller, D. Keeney, editors). Soil Science Society of America, Madison, Wisconsin, USA.

### 17 Summary of Changes

- (1) A LiBr matrix solution is now included in the analysis of inorganic fine-grained soils because of the significant presence of ammonium in the exchange complex of clays permeated with real and synthetic municipal solid waste (MSW) leachate.
- (2) HCl or acetic acid is used as a preservative for the LiBr Method B matrix solution as to not mask ammonium in the samples.

## CHAPTER TWO

### EFFECT OF AMMONIUM ON THE HYDRAULIC CONDUCTIVITY OF GEOSYNTHETIC CLAY LINERS

#### 2.1 ABSTRACT

Geosynthetic clay liners (GCLs) consist of a thin layer (<10 mm) of sodium bentonite sandwiched between two geotextiles. GCLs act as a hydraulic barrier in containment scenarios due to sodium bentonite having characteristically high swell and low hydraulic conductivity. Cation exchange of sodium for ammonium ( $\text{NH}_4^+$ ) in nitrogen rich environments, such as municipal solid waste containment facilities, occurs over time and can potentially affect a GCL's hydraulic performance.

To investigate the influence that  $\text{NH}_4^+$  has on the hydraulic conductivity of a conventional Na-bentonite GCL hydraulic conductivity tests were set-up and GCLs were permeated with solutions of varying  $\text{NH}_4^+$  concentrations (0.005, 0.05, 0.1, 0.5 and 1.0 M). Control tests were conducted using deionized (DI) water. To date, hydraulic and chemical (influent  $\text{NH}_4^+$  = effluent  $\text{NH}_4^+$ ) equilibrium criterion have been satisfied for the GCLs permeated with  $\text{NH}_4^+$  solutions of 0.5 M ( $1.9 \times 10^{-6}$  m/s) and 1.0 M ( $5.3 \times 10^{-6}$  m/s), as well as the conventional Na-bentonite GCL ( $1.8 \times 10^{-11}$  m/s) and a mock  $\text{NH}_4$ -bentontie GCL ( $2.9 \times 10^{-11}$  m/s) permeated with deionized (DI) water for the control tests. The hydraulic conductivity of the GCL permeated with the 0.5 M  $\text{NH}_4^+$  solution is greater than four orders of magnitude than that of the GCL permeated with DI water, indicating that solutions > 0.5 M  $\text{NH}_4^+$  can a significant effect on the hydraulic conductivity of GCLs.

Chemical equilibrium has not yet been satisfied for the 0.005, 0.05, and 0.1 M  $\text{NH}_4^+$  hydraulic conductivity tests indicating that cation exchange is still occurring, thus findings reported represent a snapshot in time and may not reflect the long-term equilibrium condition. Initial hydraulic conductivity results show that the hydraulic conductivity relative to the hydraulic conductivity of the Na-bentonite GCL to DI water is 0.9 for the 0.005 M  $\text{NH}_4^+$  test, 1.6 for the

0.05 M  $\text{NH}_4^+$  test, and 3.3 for the 0.1 M  $\text{NH}_4^+$  test. Solutions with low  $\text{NH}_4^+$  concentrations ( $\leq 0.05$  M) currently do not have a significant effect on the hydraulic conductivity of the conventional Na-bentonite GCLs ( $< 1.6$  times) in comparison to a GCL permeated with DI water ( $1.8 \times 10^{-11}$  m/s). The low hydraulic conductivity observed in the mock  $\text{NH}_4$ -bentonite GCL permeated with DI water in comparison to the hydraulic conductivity of a conventional Na-bentonite permeated with DI water indicates that  $\text{NH}_4^+$  in the exchange complex of bentonite has the ability to swell osmotically. Indicating that bound  $\text{NH}_4^+$  can help to keep the hydraulic conductivity of GCLs low as seen in the tests permeated with  $\text{NH}_4^+$  liquids  $< 0.1$  M. However, results are subject to change when chemical equilibrium is reached. At the completion of testing, the exchange complex and swell index for the bentonite will be determined to relate the concentration of  $\text{NH}_4^+$  in the exchange complex to the hydraulic conductivity of the GCL.

## 2.2 INTRODUCTION

Sodium bentonite clay, mainly comprised of the mineral montmorillonite, is the primary component in geosynthetic clay liners (GCLs). GCLs are thin (5-10 mm thick) factory-manufactured hydraulic barriers that use geotextiles or geomembranes to encase a layer of bentonite clay held together by needle punching or glue. GCLs are used in liners and covers in waste containment systems, including municipal solid waste (MSW) landfills to decrease the release of contaminants into the environment.

Ammonium ( $\text{NH}_4^+$ ) concentrations can be high ( $> 0.2$  M) in MSW landfill systems, especially bioreactor landfills (Barlaz et al. 2010, Bradshaw and Setz 2013, Claret et al. 2011, Guyonnet et al. 2009, Kjeldsen et al. 2002, Pivato and Raga 2006). A compilation of reported  $\text{NH}_4^+$  concentrations in landfill leachates is shown in Fig 2.1 (Barlaz et al. 2010, Bradshaw and Setz 2013, Claret et al. 2011, Kjeldsen et al. 2002). An average  $\text{NH}_4^+$  concentration was calculated for reported minimum, maximum, and mean values and are 0.005 M, 0.107 M, and

0.042 M respectively. An outlier  $\text{NH}_4^+$  concentration was reported by Barlaz et al. 2010 as 0.626 M in a bioreactor landfill.

Pivato and Raga (2006) attribute abundant levels of ammonium to the lack of cation degradation under anaerobic conditions within MSW containment facilities. Ammonium is known to continue to accumulate in and percolate through a liner system for over thirty years (Pivato and Gaspari 2005, Pivato and Raga 2006). Recent research has identified that  $\text{NH}_4^+$  found in MSW leachate can induce cation exchange, causing ammonium to comprise a significant portion of the bentonite exchange complex (Guyonnet et al. 2009, Pivato and Raga 2006). Replacement of the sodium cations ( $\text{Na}^+$ ) in the exchange complex of bentonite by other cations in contacting liquids has been shown to affect swelling and hydraulic conductivity of the bentonite. Exchange reactions that cause a decrease in swell and an increase in hydraulic conductivity of the bentonite in GCLs can affect the performance of a waste containment facility adversely.

Currently, the impact on the hydraulic conductivity of varying amounts of  $\text{NH}_4^+$  in the exchange complex of bentonite in GCLs is not well understood. Studying the effects of bound  $\text{NH}_4^+$  on the hydraulic conductivity of GCLs is pertinent due to the elevated presence of  $\text{NH}_4^+$  in MSW landfill leachates, particularly those operating with leachate recirculation or as bioreactors which can have leachates with  $\text{NH}_4^+$  concentrations as high as 0.6 M (Barlaz et al. 2010, Benson et al. 2007).

The influence of  $\text{NH}_4^+$  on the hydraulic conductivity of GCLs for cases where complete or partial replacement of  $\text{Na}^+$  by  $\text{NH}_4^+$  occurs during permeation was explored in this study. Hydraulic conductivity tests were conducted on GCLs containing natural Na-bentonite with permeant solutions having  $\text{NH}_4^+$  concentrations of 0.005, 0.05, 0.1, 0.5, and 1.0 M, with the latter simulating a worst-case scenario (Benson et al. 2007, Barlaz et al. 2010). Control tests were conducted using deionized (DI) water. Most of the tests were not in hydraulic or chemical

equilibrium when this paper was prepared. Thus, the findings represent a snapshot in time, and may not reflect the long-term equilibrium condition.

## **2.3 BACKGROUND**

### **2.3.1 Bentonite and Hydration**

Research has shown the composition of bound cations in the exchange complex of bentonite is dependent on the permeant liquid composition and concentration (Jo et al. 2001, Kolstad 2004, Rauen and Benson 2008, Ruhl and Daniel 1997, Shackelford et al. 2000). Bound cations adsorbed to the mineral surface of clay particles are prone to exchange with cations in the pore water, a process described as cation exchange (Mesri and Olson, 1971). Cation exchange is dependent on clay type and charge density of the ion being replaced (Sposito 1981, Sposito 1989). Polyvalent cations are more preferred on the clay surface over monovalent cations and the preference for exchange (i.e. lyotropic series) described here is from Domenico and Schwartz (1998):  $\text{Li}^+ < \text{Na}^+ < \text{H}^+ < \text{K}^+ < \text{NH}_4^+ < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{Al}^{3+}$ . Because  $\text{Na}^+$  is on the lower end of the series, Na bound to the mineral surface of natural Na-bentonites is frequently exchanged for other cations in permeant solutions. Specifically in MSW containment facilities where  $\text{Na}^+$  is replaced by  $\text{NH}_4^+$  when GCLs come in contact with MSW landfill leachates having moderate  $\text{NH}_4^+$  concentrations (Claret et al. 2011, Guyonnet et al. 2009).

Bentonite clay in a GCL can undergo two phases of hydration; the crystalline phase and the osmotic phase (Norrish and Quirk 1954, Scalia and Benson 2010). The crystalline hydration phase occurs first when water molecules hydrate the mineral surface and associated bound cations, forcing the interlayer space to separate by a distance that is equivalent to several water molecules (McBride, 1994; Scalia and Benson, 2010). Osmotic hydration only occurs with monovalent cations and proceeds crystalline hydration. Water molecules flow into the interlayer and force the interlayer to separate more (i.e. greater swell) than with crystalline hydration alone (McBride 1994, Scalia and Benson 2010). Bentonite in a GCL that undergoes osmotic swelling

exhibits a low hydraulic conductivity  $< 3 \times 10^{-10}$  m/s when compared to bentonite in GCLs that only experience crystalline hydration, which display hydraulic conductivities up to four orders of magnitude higher (Jo et al. 2001, Jo et al. 2004, Lin and Benson 2000, Scalia and Benson 2010).

Gautier et al. (2010) determined that the hydration of an  $\text{NH}_4^+$ -smectite (Wyoming montmorillonite) with water was limited to the formation of a monolayer of water by comparing basal spacing of hydrated clay particles in comparison to a Na-smectite. Gautier et al. (2010) attributed the formation of a single monolayer in  $\text{NH}_4$ -smectite to the size of the ionic radius of  $\text{NH}_4^+$  (0.136 nm (Aranda and Ruiz-Hitzky 1999) to 0.143 nm (Pironon et al. 2003)). The ionic radius of  $\text{NH}_4^+$  is larger than the interlayer clay cavity which Gautier et al. (2010) relates to the prevention of complete closure of the interlayer space and limiting swelling capacity. These results suggest the hydraulic conductivity of a  $\text{NH}_4$ -smectite can be of higher magnitude (5 times) when compared to the hydraulic conductivity of a Na-smectites. In MSW containment facilities the replacement of  $\text{Na}^+$  cations with other cations present in contacting leachates, particularly  $\text{NH}_4^+$ , can occur over time and cause a decrease in the bentonite swell (Gautier et al. 2010).

## **2.4 METHOD AND MATERIALS**

### **2.4.1 Bentonite Material**

The GCL product used in this study is a conventional Na-bentonite ( $\text{Na-B}_t$ ) GCL. The swell index (SI) of the bentonite deionized (DI) water was 26.0 mL/2 g (per ASTM D 5890) and the cation exchange capacity (CEC) was determined to be 81.0  $\text{cmol}^+/\text{kg}$  (per ASTM D 7503). X-ray diffraction indicated that the bentonite contains 84% montmorillonite, 9% quartz, 3% plagioclase, and  $\leq 2\%$  of clinoptilolite, illite, mica, orthoclase, and calcite (via Moore and Reynolds 1989). The mineralogy, cation exchange capacity, and swell index for this bentonite are provided in Table 2.1.

### 2.4.2 Hydraulic Conductivity Testing

Hydraulic conductivity tests were conducted with the Na-B<sub>t</sub> GCL product using a flexible-wall permeameter set up in accordance with ASTM D 5084 Method B-falling headwater-constant tailwater. An average confining stress of 27 kPa was applied to the flexible wall via pressurized cell water. In-cell hydration was conducted by closing the effluent line while the influent line remained open (Scalia 2012). After 48 hours the effluent line was opened to induce flow. The average effective stress was 20 kPa with an average hydraulic gradient of 175. This average hydraulic gradient is higher than a GCL would experience in the field, but is less than a hydraulic gradient (> 500) that would impact hydraulic conductivity for laboratory testing purposes (Shackelford et al. 2000).

The termination criteria outlined in ASTM D 5084 and ASTM D 6766 is used to define hydraulic equilibrium. Hydraulic equilibrium is declared when the ratio of the rate of inflow to the rate of outflow is within 25% for a minimum of three consecutive hydraulic conductivity readings, with no significant upward or downward trend. Termination criteria based on chemical equilibrium (effluent  $\text{NH}_4^+$  = influent  $\text{NH}_4^+$ ) is defined by ASTM D 6766 and conditions set by this study when the ratio of outflow to inflow is within 10% for four consecutive samples for both electrical conductivity (EC) and  $\text{NH}_4^+$  concentration.

The cumulative influent volume and original GCL properties (thickness, diameter, water content, and specific gravity) are used to calculate relative pore volumes of flow (PVF) through the specimen.

### 2.4.3 Swell Index

Swell index (SI) tests were performed on bentonite from the Na-bentonite GCL in accordance with ASTM D 5890. SI results are used as an indicator parameter for bentonite quality and for hydraulic conductivity (Scalia 2012). Swell index tests consist of adding 2.00 g of 105° C oven dried (12 to 16 hr) bentonite ground to pass the No. 200-US-Standard Sieve (ASTM E11) into a 100-mL graduated cylinder of DI water or an  $\text{NH}_4^+$  solution filled to 90 mL.

Bentonite is dusted over the surface of the water column in increments of no more than 0.1 g over a period of 30 seconds. Each increment is allowed to hydrate for at least 10 minutes prior to addition of the next increment. At the conclusion of bentonite addition, the graduated cylinder is filled to 100 mL and the bentonite is allowed to continue hydrating for 16 h, at which time, the volume (swell) of the bentonite at the bottom of the graduated cylinder is recorded in mL of swell per 2.00 g of bentonite solids.

#### **2.4.4 Permeant Solution**

GCLs were permeated with five different solutions of varying  $\text{NH}_4^+$  molar concentrations (0.005, 0.05, 0.1, 0.5, 1.0 M) to mimic the landfill leachate base liner conditions calculated from a literature review of reported  $\text{NH}_4^+$  concentrations in MSW leachates (Fig. 2.1). The 0.005, 0.05 and 0.1 M permeant solutions were selected to represent the average minimum, mean, and maximum  $\text{NH}_4^+$  concentrations reported in real MSW leachates (Barlaz et al. 2010, Bradshaw and Setz 2013, Claret et al. 2011, Kjeldsen et al. 2002). 0.5 M was chosen to represent an outlier  $\text{NH}_4^+$  concentration reported by Barlaz et al. (2010) of 0.626 M. 1.0 M  $\text{NH}_4^+$  solution was to represent a worst case scenario.

The solutions were prepared by mixing 99.9 % pure  $\text{NH}_4\text{OAc}$  salt with Type II DI water (per ASTM D1193) in a 1 L volumetric flask to create solutions of desired ammonium concentrations (Table 2.2). Ammonium acetate ( $\text{NH}_4\text{OAc}$ ) salt was chosen to create the permeant solution for this study. Acetate is a common short-chain fatty acids in MSW landfill leachates (Fang et al. 2012) and commonly used in synthetic MSW leachates to imitate a leachate similar to field scenarios (Ruhl and Daniel 1997). Studies from Petrov and Rowe (1997) and Ruhl and Daniel (1997) also chose to use ammonium acetate in synthetic leachate mixtures due to reported acetate concentrations in MSW landfill leachates.

### 2.4.5 Chemical Analysis

The chemical analysis for concentrations of  $\text{Na}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ , and  $\text{K}^+$  cations typically found in soil pore water (denoted in this paper as Na, Ca, Mg, and K), and of  $\text{Li}^+$  (Li) found in testing solutions was determined using a Varian MPX inductively coupled plasma optimal emission spectroscopy (ICP-OES) following the U.S. Environmental Protection Agency (USEPA) Method 6010B (USEPA, 2007). Calibration curves are created using High Purity Standards of the cation of interest (Na, Ca, Mg, K, and Li) with a starting concentration of 10.0 mg/mL preserved in 1%-4% nitric acid. The matrix solution used to create the ICP calibration curve corresponds with the extraction solution used for bound cation extractions to account for potential interference during the ICP analysis.

Nitrogen, in the form of  $\text{NH}_4^+$ , is measured via the salicylate method (EPA Method 350.1) using high-range (0 – 50 mg/L) N- $\text{NH}_3$  “Test ‘N Tube” vials (Hach Company: Method 10031) by spectrophotometer. This kit measures the total ammonia nitrogen (TAN) where ammonia ( $\text{NH}_3$ ) is present in water systems in two forms; in the unionized form ( $\text{NH}_3$ ) and in the ionized form ( $\text{NH}_4^+$ ). For this study ionized ammonia (i.e. ammonium,  $\text{NH}_4^+$ ) is the form of interest because of the cations ability to satisfy the net negative surface charge of bentonite clay (Emerson et al. 1975). By lowering the pH of the sample to 7 before using the Hach test kit, it is assumed that all ammonia measured in solution is in the ionized form, i.e. as  $\text{NH}_4^+$ . The calibration curve was created using ACS Certified ammonium sulfate dissolved in Type II DI water to ensure calibration of  $\text{NH}_4^+$  concentrations when applied to measurement in testing samples.

Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11 (US EPA, 1986) was used to determine the method detection limit for ammonium on the spectrophotometer. The MDL results are reported in Table 2.3. Dilutions were needed for influent and effluent samples containing  $\text{NH}_4^+$ , and dilution factors were calculated to fall within the range of measureable nitrogen via the Hach testing kit (Hach Company: Method 10031).

#### **2.4.6 Soluble Cation Determination**

Extraction of the soluble cations in the bentonite of the GCL specimen is completed using Type II DI water in accordance with ASTM D 7503 or the “Standard Test Method for Measuring the Exchange Complex and Cation Exchange Capacity of Inorganic Fine-Grained Soils”. Na, Ca, Mg, K, and  $\text{NH}_4$  are washed from the pore space via vacuum filtration. The eluent is analyzed with ICP-OES for Na, Ca, Mg, and K cation concentrations. The spectrophotometer and Hach method are used to measure  $\text{NH}_4^+$  concentrations.

#### **2.4.7 Bound Cation Determination**

Bound cations (BC) were determined using the procedure outlined in ASTM D 7503. However, rather than using the prescribed 1.0 M  $\text{NH}_4\text{OAc}$  extraction solution, BCs are extracted using a 1.0 M LiBr solution. The eluate is analyzed with ICP-OES for Na, Ca, Mg, and K cation concentrations, and  $\text{NH}_4^+$  concentrations were measured with the spectrophotometer and Hach method.

ASTM D 7503 prescribes the use of 1.0 M  $\text{NH}_4\text{OAc}$  for bound cation determination, effectively masking any bound  $\text{NH}_4^+$  occupying the exchange complex of bentonites. An alternative method using a 1.0 M LiBr extraction solution (Setz 2013) was used to determine the bound cations, including ammonium, to measure the cationic make-up of the bentonite exchange complex from GCLs in this study. Changes to the standard are highlighted in Table 2.4 with a comparison of the current ASTM D 7503 method and the alternative LiBr extraction method.

#### **2.4.8 Cation Exchange Capacity**

Table 2.4 describes the current ASTM D7503 and 1.0 M LiBr extraction (Setz 2013) for the determination of the cation exchange capacity (CEC). Residual soil remaining on the filter from the bound cation extraction is used in the cation exchange capacity testing. The soil is then rinsed with isopropanol to rinse any residual LiBr out of the soil pores. Next the isopropanol washed soil is rinsed with 1.0 M KCl, replacing the adsorbed lithium cations with potassium

cations in the interlayer of the soil. The extract is collected and the concentration of lithium in the extract is determined via ICP-OES. The soil CEC is calculated from the measured concentration of Li in the extract solution, assuming that the total negative charge of the soil was satisfied by bound Li and then exchanged for K.

## 2.5 RESULTS

### 2.5.1 Swell Index

Swell index (SI) tests completed on the Na-bentonite from this study in solutions of varying  $\text{NH}_4^+$  concentrations and DI water is shown in Fig. 2.2. Similar to findings in Jo et al. (2000) the bentonite swell index decreased as the concentration of the hydrating solution increased, regardless of the valence of cation in solution. The comparison of varying solution strengths of  $\text{NH}_4^+$  to other cations (Na, Ca, Mg, K) from Jo et al. (2000) is presented also presented in Fig. 2.2.

At hydrating solution concentrations  $\leq 0.1$  M  $\text{NH}_4^+$  the bentonite swell behaves similar to the other monovalent cations, Na and K. At concentrations  $> 0.5$  M the bentonite in the  $\text{NH}_4^+$  hydrating solution results in a SI less than both the mono and divalent cations (Na, K, Ca, Mg) reported by Jo et al. (2000). As the bulk concentration of cations increases in the hydrating solutions the water moves out of the interlay region of the clay and creates a decrease in swell (Sposito 1981). This phenomenon is due to the gradient in free energy induced by the increase in concentration in the bulk pore water (Jo et al. 2000, Sposito 1981, McBride 1994). Norrish and Quirk (1954) state that the ionic strength of the hydrating solution must be below approximately 0.3 M for a clay to experience osmotic (e.g. tremendous) swell, justifying the decrease in swell observed in 0.5 M  $\text{NH}_4^+$  solution. Although  $\text{NH}_4^+$  is a polyatomic ion, from the swell index results presented in Fig. 2.2  $\text{NH}_4^+$  behaves like a monovalent cation allowing for greater swell at solution concentrations  $< 0.1$  M. Due to the increased swell of conventional Na-bentonite in  $\text{NH}_4^+$  concentrations  $< 0.1$  M it is an indicator that  $\text{NH}_4^+$  allows for osmotic swell and

that the hydraulic conductivity of the GCLs permeated with subsequent  $\text{NH}_4^+$  solutions will experience low hydraulic conductivity.

### 2.5.2 Hydraulic Conductivity

Hydraulic conductivity tests were performed for 1 to 6 months to evaluate the effect that varying concentrations of  $\text{NH}_4^+$  (0.005, 0.05, 0.1, 0.5, and 1.0 M  $\text{NH}_4^+$ ) have on the hydraulic conductivity of a conventional Na-B<sub>t</sub> GCL. Chemical equilibrium was considered when influent and effluent ammonium concentration and EC measurements were within 10% for four consecutive readings. Tests were terminated when hydraulic and chemical equilibrium criteria were satisfied. pH was also monitored for chemical equilibrium, but was not considered a test termination criteria. A summary table of the hydraulic conductivity results for each of the permeant solution conditions is summarized in Table 2.5. Because chemical equilibrium criterion (influent  $\text{NH}_4^+$  = effluent  $\text{NH}_4^+$  and influent EC = effluent EC) has not been achieved for the 0.005, 0.05, and 0.1 M  $\text{NH}_4^+$  tests findings reported on these samples in this paper are from a snapshot in time and may not represent long-term conditions.

Hydraulic conductivity of the GCL is shown as a function of  $\text{NH}_4^+$  concentration in Fig. 2.3 for the tests conducted in this study. Equilibrium hydraulic conductivities from long-term hydraulic conductivity tests of conventional Na-bentonite GCLs permeated with conventional and bioreactor MSW leachates containing  $\text{NH}_4^+$  concentrations (<0.005 to 0.05 M) are also shown in Fig. 2.3 (Bradshaw and Setz 2013). For solutions with  $\text{NH}_4^+$  concentrations  $\leq 0.1$  M low hydraulic conductivity is maintained and is comparable to hydraulic conductivity using DI water (shown in Fig. 2.3 with solid lines). The hydraulic conductivities obtained with actual MSW leachates is also similar to the hydraulic conductivities of GCLs permeated with DI water and to the hydraulic conductivities of GCLs permeated with solutions containing  $\leq 0.1$  M  $\text{NH}_4^+$  (Fig. 2.3).

The GCL permeated with the 1.0 M  $\text{NH}_4^+$  solution was continued for 52 pore volumes of flow (PVF) and has an equilibrium hydraulic conductivity of  $5.2 \times 10^{-6}$  m/s. The influent liquid was

then switched to DI water to determine if the hydraulic conductivity would return to the same hydraulic conductivity as obtained for a GCL with Na-bentonite that was permeated with DI water. After 48 PVF with DI water, the equilibrium hydraulic conductivity of this mock  $\text{NH}_4$ -bentonite GCL is comparable ( $2.9 \times 10^{-11}$  m/s) to that of a conventional GCL containing Na-bentonite ( $1.8 \times 10^{-11}$  m/s) permeated with DI water (Fig. 2.3). Thus, replacement of  $\text{Na}^+$  by  $\text{NH}_4^+$  in the bentonite exchange complex allows the clay experience osmotic swell and thus results in a low equilibrium hydraulic conductivity.

Low hydraulic conductivity ( $< 10^{-10}$  m/s) is currently observed for conventional Na-B<sub>1</sub> GCLs permeated with  $\leq 0.1$  M  $\text{NH}_4^+$ , but is subject to change because chemical equilibrium has not been achieved. The hydraulic conductivity increases slightly for the sample permeated with the 0.1 M  $\text{NH}_4^+$  solution (3.3 times the hydraulic conductivity of DI water). The hydraulic conductivities of solutions with  $\text{NH}_4^+$  concentrations ( $\leq 0.05$  M  $\text{NH}_4^+$ ) are within 0.9 to 1.6 times the hydraulic conductivity of a conventional Na-bentonite GCL permeated with DI water. The presence of bound  $\text{NH}_4^+$  in the exchange complex of these bentonites supports the idea that bound  $\text{NH}_4^+$  allows for bentonite clays to experience osmotic swelling similar to that of a Na-bentonite, thus resulting in low hydraulic conductivity. The low hydraulic conductivity achieved by GCLs permeated with solutions  $\leq 0.05$  M  $\text{NH}_4^+$  also supports the results from the swell index testing, where the bentonite in  $\text{NH}_4^+$  solutions  $\leq 0.05$  M exhibited increased swell ( $> 25$  mL/2g), an indication of the formation of osmotic swelling in the bentonite. However, results are subject to change when chemical equilibrium is reached. At the completion of testing, the exchange complex and CEC for the bentonite will be determined to relate the concentration of  $\text{NH}_4^+$  in the exchange complex to the hydraulic conductivity of the GCL.

The hydraulic conductivity increases slightly as the  $\text{NH}_4^+$  concentration approaches 0.1 M (3.3 times the hydraulic conductivity of a GCL permeated with DI water), and increases more than four orders of magnitude as the  $\text{NH}_4^+$  concentration increases from 0.1 to 0.5 M. The GCLs permeated with 0.5 M and 1.0 M  $\text{NH}_4^+$  have high and steady hydraulic conductivity ( $1.9 \times 10^{-6}$  m/s

and  $5.2 \times 10^{-6}$  m/s respectively) in comparison to a conventional GCL permeated with DI water ( $1.8 \times 10^{-11}$  m/s). GCLs in containment systems with exposure to MSW leachates that have high  $\text{NH}_4^+$  concentrations ( $> 0.5$  M) are likely to be very permeable.

### 2.5.3 Chemical Equilibrium

Chemical equilibrium (3 consecutive points of EC and  $\text{NH}_4^+$  within 10%) has been satisfied for the hydraulic conductivity tests permeated with high ( $\geq 0.5$  M)  $\text{NH}_4^+$  concentrations and for the Na-bentonite and mock  $\text{NH}_4$ -bentonite permeated with DI water. Therefore test results for these samples presented in Table 2.5 and Fig. 2.3 are representative of the long-term equilibrium condition. The conventional Na-bentonite GCLs permeated with ammonium solutions  $\leq 0.1$  M have not yet satisfied either hydraulic or chemical equilibrium according to the termination criteria in this study.

The hydraulic conductivity profiles coupled with effluent chemical profiles (EC,  $\text{NH}_4^+$ , and pH) for tests that are not currently in hydraulic or chemical equilibrium are shown in Fig. 2.4-2.6. Hydraulic conductivity and  $Q_{\text{out}}/Q_{\text{in}}$  ratios are steady while the chemical parameters ( $\text{NH}_4^+$  concentration, EC, and pH) are still changing. Note that for the 0.05 M  $\text{NH}_4^+$  hydraulic conductivity tests that as the ratio of effluent to influent  $\text{NH}_4^+$  concentration nears chemical equilibrium there is a slight increase in the hydraulic conductivity, but that the hydraulic conductivity remains low ( $< 10^{-10}$  m/s). Effluent concentrations of  $\text{NH}_4^+$  are lower than influent concentrations for the 0.005 M, 0.05 M, and 0.1 M  $\text{NH}_4^+$  tests indicating that cation exchange reactions are not yet at chemical equilibrium and that  $\text{NH}_4^+$  cations in the permeant solution are still exchanging with other cations in the clay exchange complex. However, effluent measurements of  $\text{NH}_4^+$  concentrations are steadily increasing (Fig. 2.4b, 2.5b, 2.6b) while EC and pH concentrations are slowly nearing chemical equilibrium. Though these samples have not reached chemical equilibrium a significant change of the reported hydraulic conductivities is not expected and therefore results could be representative of the long-term equilibrium condition.

#### 2.5.4 Results Comparison to GCLs Permeated with MSW Leachates

Long-term hydraulic conductivity tests conducted by Rauen (2007) and subsequently reported by Bradshaw and Setz (2013) permeated conventional Na-bentonite GCLs with actual MSW conventional and bioreactor leachates. MSW leachate cation concentration and ionic strength as well as reported equilibrium hydraulic conductivity of subsequent permeated GCLs is summarized in Table 2.6. Major monovalent cations in the bioreactor and conventional leachates included average and maximum concentrations of 0.074 and 0.13 M for Na, 0.028 and 0.052 M for  $\text{NH}_4^+$ , and 0.012 and 0.021 M for K. Major divalent cations in the leachates included average and maximum concentrations of 0.007 and 0.018 M for Mg and 0.001 and 0.01 M for Ca (Bradshaw and Setz 2013). The range of MSW leachate ionic strength was 0.02 to 0.21 M.  $\text{NH}_4^+$  concentrations fall within the calculated range of  $\text{NH}_4^+$  in MSW leachates as previously discussed ( $< 0.05$  M). Hydraulic conductivity tests were run until hydraulic and chemical equilibrium criterion were satisfied (i.e.  $Q_{\text{out}} \div Q_{\text{in}} = 1.0 \pm 0.25$  and effluent  $\text{NH}_4^+ \div$  influent  $\text{NH}_4^+ = 1.0 \pm 0.1$ ).  $\text{NH}_4^+$  in the exchange complex of these bentonites was determined via the lithium bromide (LiBr) extraction method (Chapter One).

Equilibrium hydraulic conductivities for long-term hydraulic conductivity tests with actual MSW bioreactor leachate (Bradshaw and Setz 2013) are shown in Fig. 2.3 as a function of  $\text{NH}_4^+$  concentrations in the leachate along with current hydraulic conductivities of GCLs to  $\text{NH}_4^+$  concentration in this study. Hydraulic conductivity of GCLs permeated with actual  $\text{NH}_4^+$  containing leachates are consistent with that of GCLs permeated with  $\text{NH}_4^+$ -only solutions. Low hydraulic conductivities ( $< 10^{-10}$  m/s) are maintained when  $\text{NH}_4^+$  concentrations are  $< 0.1$  M in comparison to the hydraulic conductivity of the GCL permeated with DI water ( $2.2 \times 10^{-11}$  m/s) for GCLs permeated with actual leachates and with synthetic leachates with  $\text{NH}_4^+$  only. The presence of  $\text{NH}_4^+$  ( $< 0.1$  M) in solutions that come in contact with GCLs, i.e. MSW leachates, can actually help to maintain low hydraulic conductivity.  $\text{NH}_4^+$  in the exchange complex of the bentonites permeated with solutions containing up to 0.1 M  $\text{NH}_4^+$  (Bradshaw and Setz 2013 and

this study) allows for the osmotic swell of the clay, similar to that of a Na-bentonite, and in turn the GCLs are able to achieve low hydraulic conductivities ( $< 10^{-10}$  m/s).

## 2.6 SUMMARY AND FUTURE WORK

The objective of this study was to determine the effect ammonium, a common constituent in MSW leachates, has on the hydraulic conductivity of a conventional Na-bentonite GCL. The effects of the concentration of  $\text{NH}_4^+$  both in the permeant liquid and the exchange complex of the bentonite were examined. Hydraulic conductivity tests with varying concentrations of  $\text{NH}_4^+$  (0.005, 0.05, 0.1, 0.5, and 1.0 M), representative of average minimum, mean, maximum, outlier, and extreme concentrations of  $\text{NH}_4^+$  found in MSW leachates, and DI water (baseline) have been running for 1-6 months and have had 4-74 PVF. The baseline hydraulic conductivity for the conventional Na-B<sub>t</sub> GCL (permeated with DI water) was  $1.8 \times 10^{-11}$  m/s.

Though hydraulic equilibrium has been achieved by all samples, chemical equilibrium has not been attained for the GCLs permeated with  $\text{NH}_4^+$  concentrations  $\leq 0.1$  M. Because cation exchange reactions are still occurring, the hydraulic conductivity results only represent a snapshot in time but hydraulic conductivities are not expected to change considerably. At this time, GCLs permeated with low concentrations of  $\text{NH}_4^+$  ( $\leq 0.05$  M) resulted in slight changes in hydraulic conductivity (0.9-1.5 times) when compared to permeation with DI water. The hydraulic conductivity for the 0.1 M  $\text{NH}_4^+$  solution, representing an average maximum  $\text{NH}_4^+$  concentration in a landfill leachate, increases about 3.3 times the hydraulic conductivity of a GCL permeated with DI water. Permeation with DI water of a mock  $\text{NH}_4$ -bentonite has resulted in a hydraulic conductivity approximately 1.6 times higher ( $1.1 \times 10^{-10}$  m/s) than that of a conventional Na-bentonite indicating that  $\text{NH}_4^+$  allows for osmotic swell in bentonite clay and when in the exchange complex of bentonite can help to maintain low hydraulic conductivity. Results at this point in time for the GCLs permeated with  $<0.1$  M  $\text{NH}_4^+$  and equilibrium hydraulic

conductivities for GCLs permeated with real MSW leachates containing up to 0.05 M  $\text{NH}_4^+$  seem to support this hypothesis. The hydraulic conductivity of the GCLs permeated with 0.5 and 1.0 M  $\text{NH}_4^+$  solutions are greater than four orders of magnitude than that of the GCL permeated with DI water, indicating that solutions  $> 0.5$  M  $\text{NH}_4^+$  can a significant effect on the hydraulic conductivity of GCLs.

Changes in the cation composition of the GCLs permeated with 0.005, 0.05, and 0.1 M  $\text{NH}_4^+$  solutions will continue to be monitored until hydraulic and chemical equilibrium criteria are reached. The equilibrium hydraulic conductivity, bentonite exchange complex and swell index will then be measured for all tests to verify the long term effects of ammonium on GCL performance in MSW containment facilities and other  $\text{NH}_4^+$  rich containment environments.

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## 2.8 TABLES

Table 2.1 Properties of the Na-Bentonite.

Properties	Na-B <sub>t</sub> GCL	Determination Method
Montmorillonite (%)	84	XRD, Moore and Reynolds (1989)
Quartz(%)	9	
Plagioclase(%)	3	
Clinoptilolite (%)	2	
Illite, Mica, Orthoclase (%)	1	
Average calcite by mass (%)	1.03	ASTM D4373
CEC (cmol <sup>+</sup> /kg)	81.0	ASTM D7503
Swell Index (mL/2 g)	29.5	ASTM D 5890

Table 2.2 Summary of product used for the permeant solution.

Desired concentration of $\text{NH}_4^+$ (M)	Compound Used	Compound source and purity	Mass (g) salt for creation of desired solution dissolved in 1 L Type II DI water*
1.0	$\text{NH}_4\text{OAc}$	MP Biomedicals 99.9 % pure MP	77.1
0.5			38.6
0.1			7.7
0.05			3.9
0.005			0.4

\*Refer to Specification D1193

Table 2.3 Method detection limit for nitrogen in Hach High Range (0 – 50 mg/L) Nitrogen Test 'N Tube kit on the spectrophotometer.

Concentration of $\text{NH}_4^+$ (M)	Method Detection Limit (M)	95% Lower Confidence Limit (M)	95% Upper Confidence Limit (M)
$3.6 \times 10^{-5}$	$2.6 \times 10^{-5}$	$1.7 \times 10^{-5}$	$5.8 \times 10^{-5}$

Table 2.4 Comparison of ASTM D 7503 and proposed LiBr (Setz 2013) bound cation and CEC extraction method.

Step #	Process	ASTM D 7503	Alternative LiBr Extraction
1	24-hour soil hydration in extraction solution	Extraction solution: 1 M NH <sub>4</sub> OAc	Extraction solution: 1 M LiBr
		Bound index cation 1: NH <sub>4</sub>	Bound index cation 1: Li
2	Bound and soluble cation determination: index cation 1 replaces originally bound cations from mineral surface and washes soluble cations from soil pores	Extraction solution: 1 M NH <sub>4</sub> OAc Bound index cation 1: NH <sub>4</sub>	Extraction solution: 1 M LiBr Bound index cation 1: Li
		Collect extract: Na, Ca, Mg, K measure using ICP-OES or atomic absorption Acid preservation: 10% HNO <sub>3</sub>	Collect extract: Na, Ca, Mg, K measure using ICP-OES or atomic absorption and NH <sub>4</sub> measure using spectrophotometer Acid preservation: 10% HCl
3	Removal of soluble index cation (from step 2) from soil pore water	Rinsing solution: Reagent grade isopropanol	Rinsing solution: Reagent grade isopropanol
4	Cation exchange capacity determination: exchange of index cation 1 for index cation 2	Extraction solution: 1 M KCl Bound index cation 2: K	Extraction solution: 1 M KCl Bound index cation 2: K
		Collect extract of cation 1: NH <sub>4</sub> Measure using spectrophotometry	Collect extract of cation 1: Li Li Measure using ICP-OES or atomic absorption

Table 2.5 Summary of results of hydraulic conductivity tests conducted at varying  $\text{NH}_4^+$  concentrations.

Permeant Liquid	Effluent Parameters			Overall Test Results				Termination Criterion Met (y/n)?				
								Hydraulic Equilibrium		Chemical Equilibrium		
	EC ( $\mu\text{S}/\text{cm}$ )	pH	$\text{NH}_4^+$ (M)	Time (d)	PVF	k (m/s)	k / $k_{\text{DI}}$	Steady k	Flow Ratio	$\text{NH}_4^+$ ratio	EC ratio	pH ratio
0.005 M $\text{NH}_4\text{OAc}$	794	8.8	0.0002	270	16	$1.6 \times 10^{-11}$	0.9	y	y	n	n	y
0.05 M $\text{NH}_4\text{OAc}$	4,230	8.4	0.016	242	19	$2.8 \times 10^{-11}$	1.6	n	y	n	n	y
0.1 M $\text{NH}_4\text{OAc}$	6,200	7.7	0.06	71	13	$5.9 \times 10^{-11}$	3.3	n	y	n	n	y
0.5 M $\text{NH}_4\text{OAc}$	28,900	6.5	0.47	22	74	$1.9 \times 10^{-6}$	106,000	y	y	y	y	y
1.0 M $\text{NH}_4\text{OAc}$	55,300	6.6	0.65	37	52	$5.2 \times 10^{-6}$	290,000	y	y	y	y	y
DI Water $\text{NH}_4\text{-B}_t$	160	7.6	0.004	145	48	$2.9 \times 10^{-10}$	1.6	y	y	n	y	y
DI Water $\text{Na-B}_t$	--	8.9	--	39	4	$1.8 \times 10^{-11}$	1	y	y	--	--	n

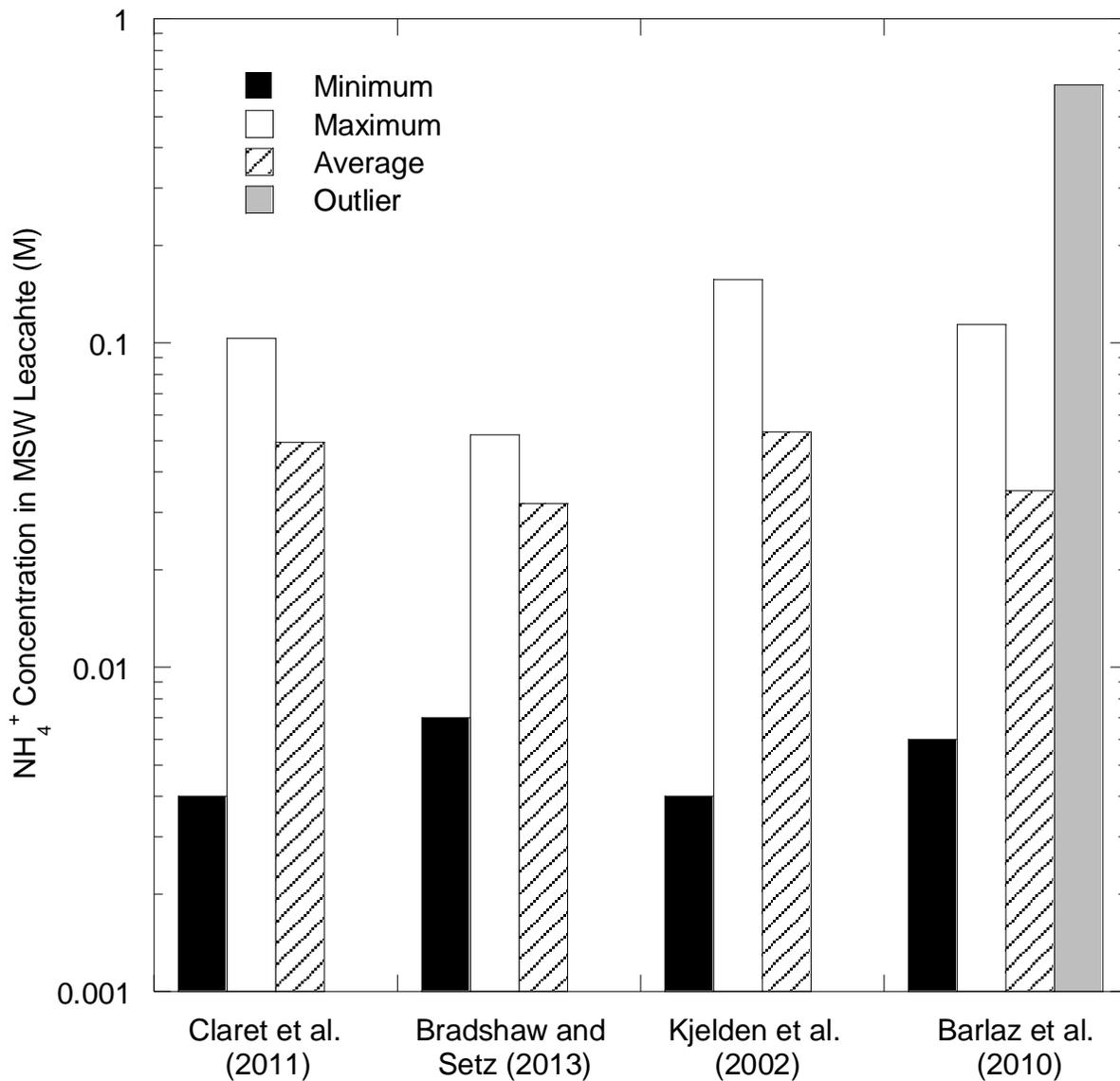
Notes: EC and pH of effluent, PVF, k, and  $k/k_{\text{DI}}$  correspond to conditions at the time of most recent measurement ('Time' column in Table 5); k = hydraulic conductivity;  $k_{\text{DI}}$  = hydraulic conductivity of standard Na-bentonite to DI water; ratio = effluent  $\div$  influent.

Table 2.6 Summary of cations and ionic strength for real MSW leachates used in long-term hydraulic conductivity tests of GCLs by Rauen (2007) and Bradshaw and Setz (2013).

Permeant Liquid	Cation Concentration (M)					Ionic Strength (M)	Equilibrium Hydraulic Conductivity (m/s)
	Na	K	Mg	Ca	NH <sub>4</sub> <sup>+</sup>		
C1	0.13	0.021	0.018	0.0001	0.052	0.21	2.0x10 <sup>-11</sup>
BR1	0.043	0.009	0.003	0.006	0.048	0.06	2.0x10 <sup>-11</sup>
BR2	0.104	0.015	0.006	0.0009	0.041	0.13	1.1x10 <sup>-11</sup>
BR3	0.082	0.011	0.007	0.0006	0.028	0.11	2.3x10 <sup>-11</sup>
BR4	0.047	0.008	0.003	0.001	0.023	0.05	1.2x10 <sup>-11</sup>
BR5	0.078	0.011	0.005	0.0007	0.023	0.05	1.8x10 <sup>-11</sup>
BR6	0.058	0.009	0.008	0.002	0.007	0.1	1.8x10 <sup>-11</sup>
BR7	0.052	0.008	0.007	0.0005	<10 <sup>-5</sup>	0.07	4.2x10 <sup>-11</sup>
<b>Range</b>	<b>0.043-0.130</b>	<b>0.008-0.021</b>	<b>0.003-0.018</b>	<b>0.0001-0.006</b>	<b>&lt;10<sup>-5</sup>-0.052</b>	<b>0.05-0.21</b>	<b>4.2x10<sup>-11</sup>-1.1x10<sup>-11</sup></b>

\*Trace levels of Fe<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Al<sup>3+</sup>, Mn<sup>4+</sup> were measured and are reported by Rauen (2007) but are not shown.

## 2.9 FIGURES



\*Outlier  $\text{NH}_4^+$  concentration was noted in the Barlaz et al. (2010)

Fig. 2.1 Minimum, maximum, average, and reported outlier of  $\text{NH}_4^+$  concentrations reported in MSW leachates.

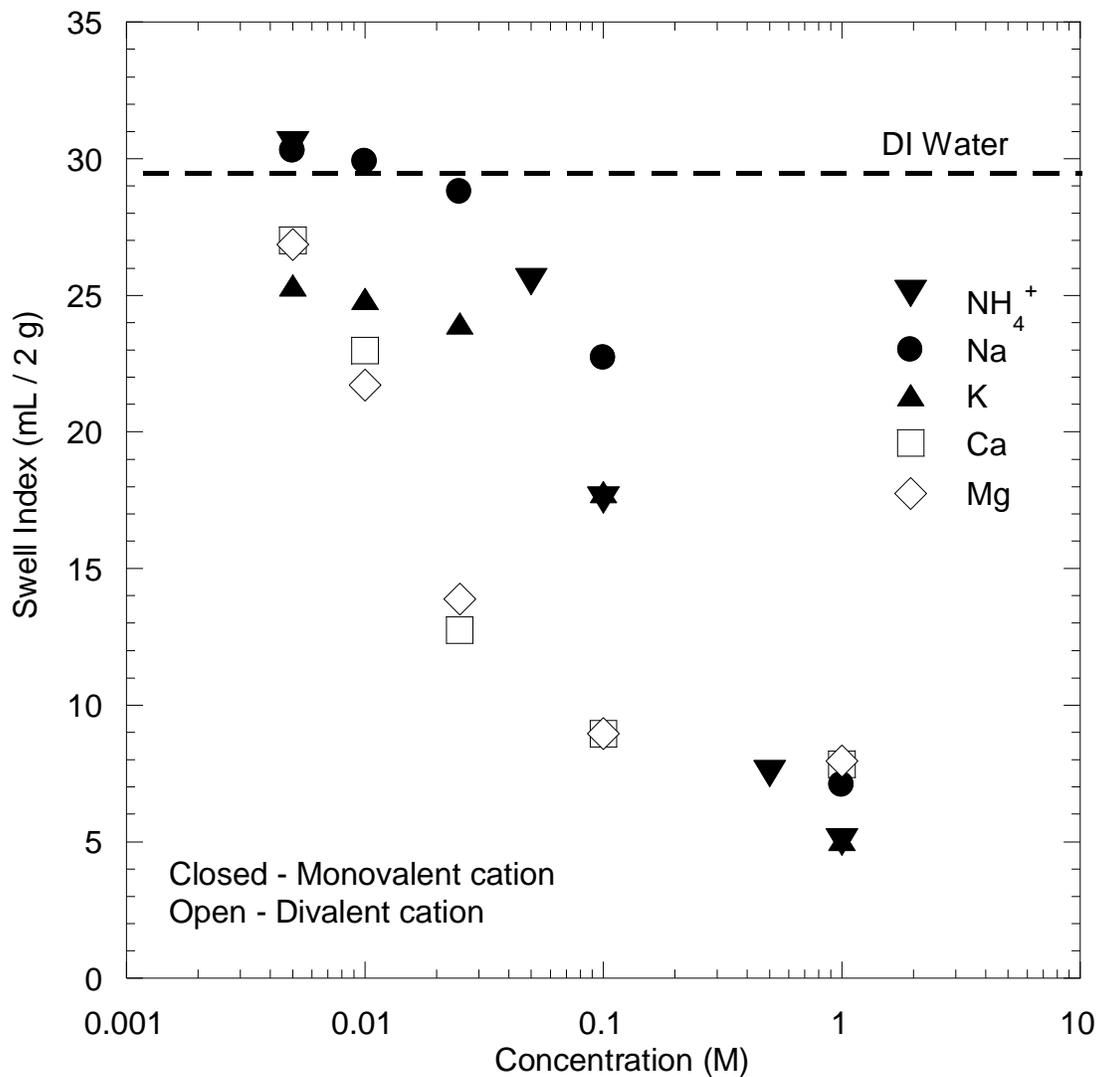


Fig. 2.2

Effect of concentration on the swell index of standard Na-bentonite from a GCL in solutions of differing index cations. Results from the  $\text{NH}_4^+$  solution are from this study and results for Na, K, Ca, and Mg are from Jo et al. (2000).

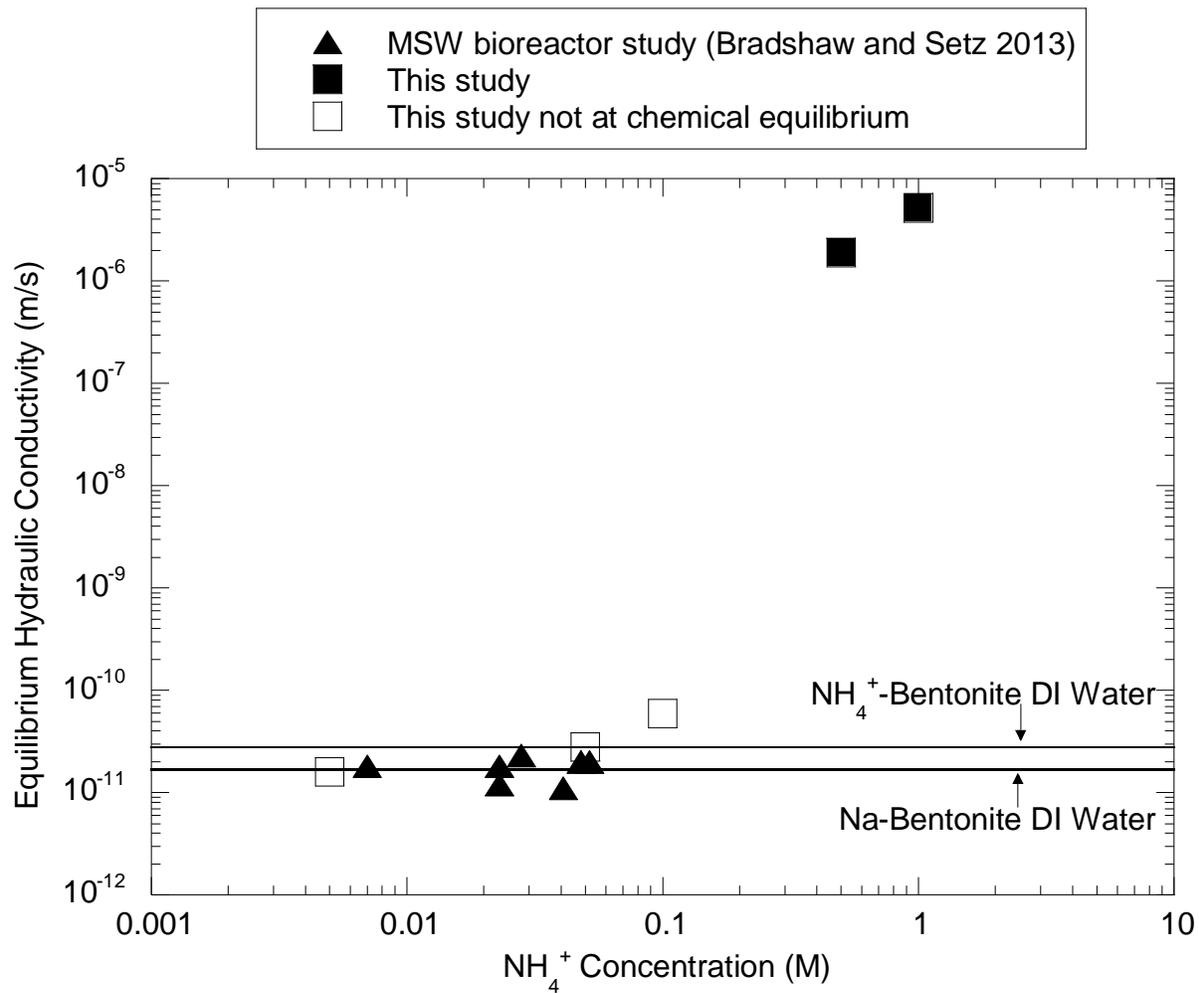


Fig. 2.3 Effect of  $\text{NH}_4^+$  concentration in permeant solution on the hydraulic conductivity of GCLs.

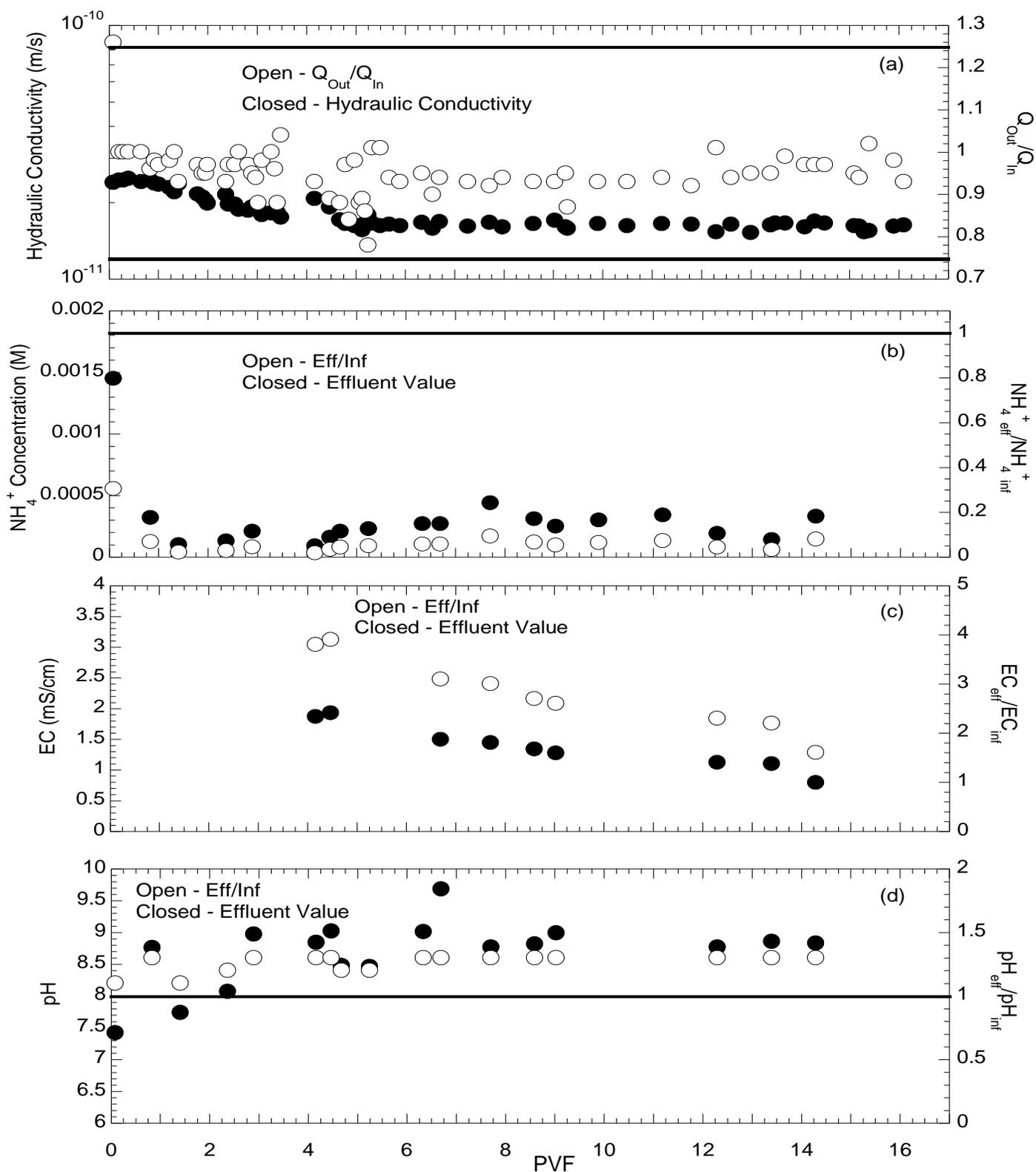


Fig. 2.4 Hydraulic conductivity (a),  $NH_4^+$  concentration (b), electrical conductivity (EC) (c), and pH (d) as a function of pore volumes of flow (PVF) for the GCL permeated with 0.005 M  $NH_4^+$  solution.

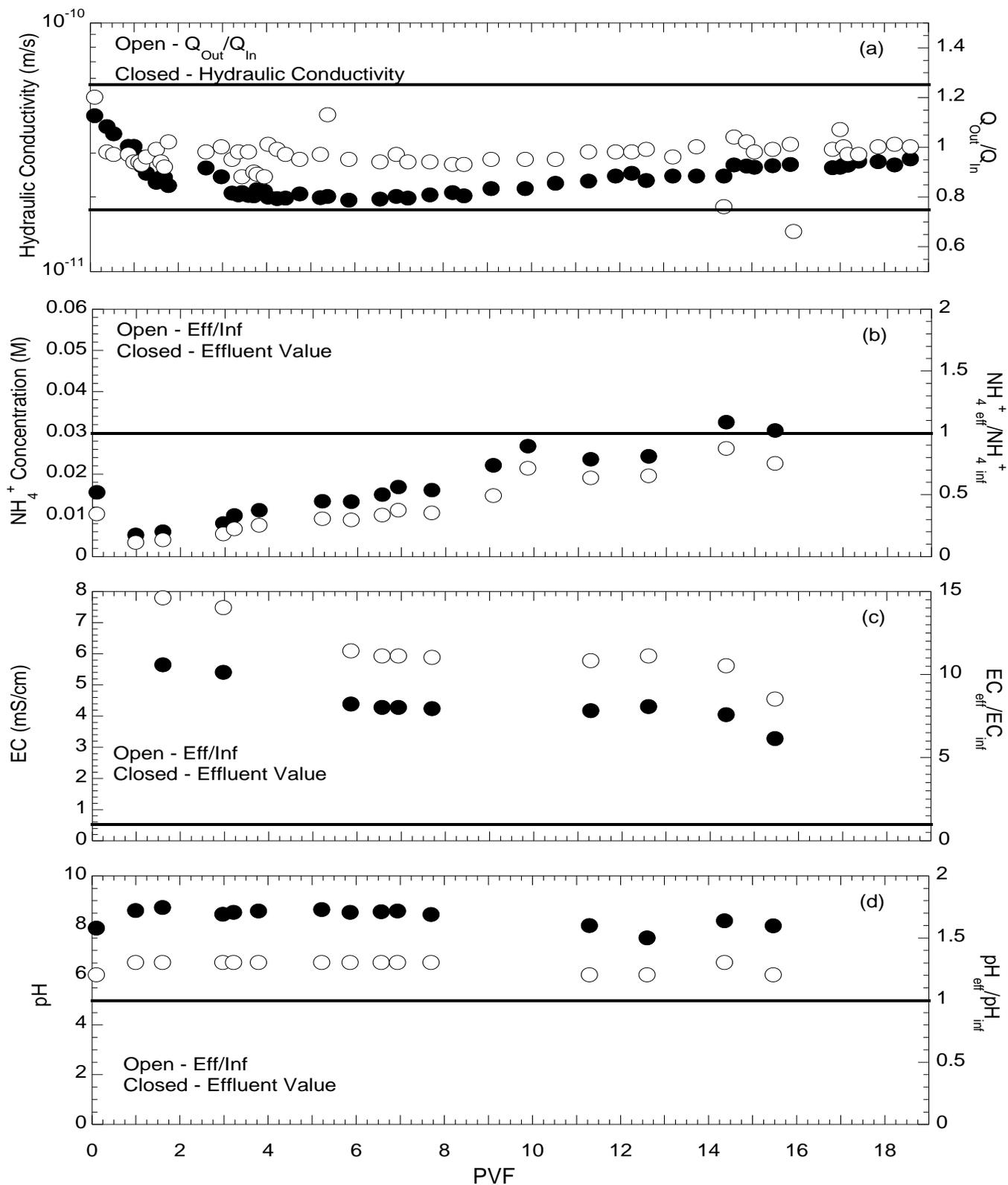


Fig. 2.5 Hydraulic conductivity (a),  $\text{NH}_4^+$  concentration (b), electrical conductivity (EC) (c), and pH (d) as a function of pore volumes of flow (PVF) for the GCL permeated with 0.05 M  $\text{NH}_4^+$  solution.

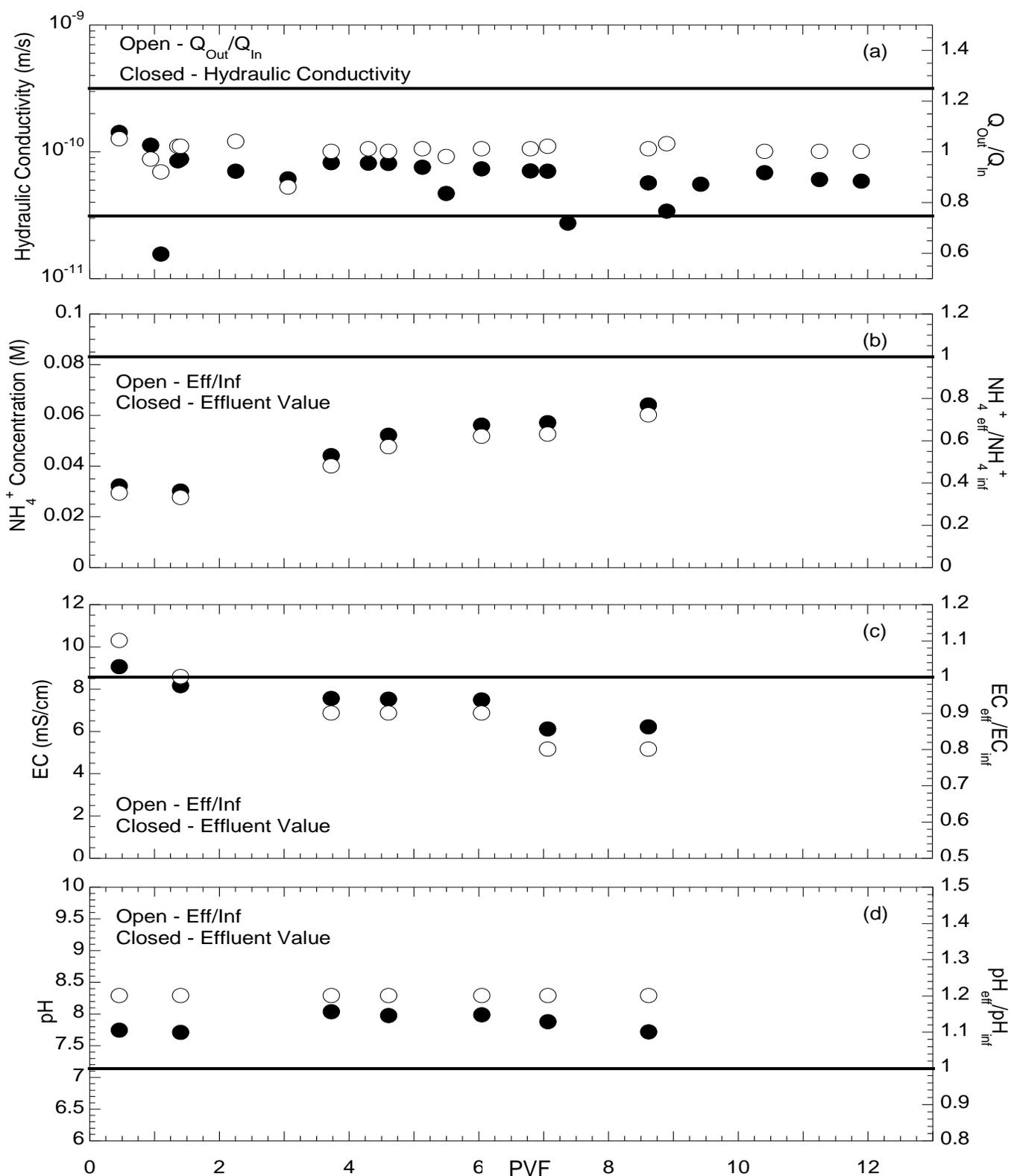


Fig. 2.6 Hydraulic conductivity (a),  $\text{NH}_4^+$  concentration (b), electrical conductivity (EC) (c), and pH (d) as a function of pore volumes of flow (PVF) for the GCL permeated with 0.1 M  $\text{NH}_4^+$  solution.

## **CHAPTER THREE**

### **HYDRAULIC CONDUCTIVITY TESTING ON POLYMER MODIFIED BENTONITES**

#### **3.1 ABSTRACT**

GCLs containing bentonite with polymer additives and conventional Na-bentonite were studied by permeating GCLs with inorganic salt solutions of varying ionic strengths (I) and ratio of monovalent to divalent (RMD) cations to determine effects on ion exchange, swelling, and hydraulic conductivity. Various I and RMD concentrations in the permeant solution will impact the cationic make-up of the bentonite exchange complex thus affecting bentonite swell and hydraulic conductivity of GCLs. Three GCLs products were tested and include a bentonite polymer nanocomposite (BPN) GCL, a dry polymer bentonite mixed GCL, and a standard untreated Na-bentonite GCL. The purpose of this study is to determine the thresholds of I and RMD at which the hydraulic conductivity of polymer modified bentonite and convention Na-bentonite GCLs increases appreciably. By measuring the hydraulic conductivity of these tests, iso-hydraulic conductivity lines in the I-RMD space will be created to determine the effectiveness of the GCL and suggested bentonite (i.e. polymer modified or conventional Na) in various environmental conditions. Three GCLs products were tested and include a bentonite polymer nanocomposite (BPN) GCL, a dry polymer mix bentonite GCL, and a conventional untreated Na-bentonite GCL.

#### **3.2 INTRODUCTION**

Conventional sodium bentonite (Na-bentonite) in geosynthetic clay liners (GCLs) has been modified at the nanoscale to improve the chemical compatibility of GCLs in hydraulic barrier applications (Scalia, 2012). Polymer modifications were completed so that low hydraulic conductivity would be maintained under adverse conditions (i.e. in contact with solutions of high ionic strength, extreme pH, etc.). Many studies have been completed on engineered bentonite alterations to decrease the material sensitivity to solutions that are typically incompatible with

convention Na-bentonite GCLs (Ashmawy et al. 2002, Di Emidio et al. 2011, Katsumi et al. 2001, Katsumi et al. 2008, Kondo 1996, Mazzieri 2011, Onikata and Kondo 1996, Onikata et al. 1999, Scalia 2012, Trauger and Darlington 2000).

This study presents the hydraulic conductivity results for samples permeated with solutions of various I and RMD concentrations on conventional Na-bentonite GCLs, dry-blended polymer Na-bentonite GCLs, and bentonite-polyacrylate nanocomposite GCLs. The material properties and testing methods for this study are described. Hydraulic conductivities and supplemental chemical data are presented for tests that have achieved both hydraulic and chemical equilibrium and for on-going tests. Ion exchange, bentonite swelling, and hydraulic conductivity parameters were all measured for this objective to report the influence that ionic strength (I) and the ratio of monovalent to divalent cations (RMD) has on GCL performance. The testing solution matrix and overall goals of this project are similar to those in Kolstad (2004).

The purpose of this study is to determine the thresholds of I and RMD at which the hydraulic conductivity of polymer modified bentonite and conventional Na-bentonite GCLs increases appreciably. By measuring the hydraulic conductivity of these tests, iso-hydraulic conductivity lines in the I-RMD space will be created to determine the effectiveness of the GCL and suggested bentonite (i.e. polymer modified or conventional Na) in various environmental conditions. Three GCLs products were tested and include a bentonite polymer nanocomposite (BPN) GCL, a dry polymer mix bentonite GCL, and a conventional untreated Na-bentonite GCL.

### **3.3 MATERIALS**

#### **3.3.1 GCLs**

Three geosynthetic clay liners with different bentonite modifications were used in this study. All GCLs comprised of Na-bentonite that was encased by two geotextiles (silt-woven geotextile and non-woven staple filter geotextile) and bounded by needle punching. All of the GCLs were manufactured by the same company. The initial thickness for all GCLs ranged from between 5 to 7 mm. The material properties for each GCL are described below and bentonite

mineralogy and physical characteristics for all bentonites are presented in Table 3.1 and Table 3.2 respectively.

### **3.3.1.1 Na-Bentonite GCL**

The GCL with a conventional Na-bentonite with no modifications had a mass per unit area of  $5.7 \text{ kg/m}^2$  and an initial water content of the bentonite from the GCL was 4.7%. The conventional Na-bentonite GCL is referred to herein as S-GCL. X-ray diffraction showed that the bentonite contained 84% montmorillonite, 9% quartz, 3% plagioclase, 2% clinoptilolite, 1% illite and mica, 1% orthoclase, and trace amounts of kaolinite which can be referred to in Table 3.1. The average CEC of the bentonite from S-GCL was  $81.0 \text{ cmol}^+/\text{kg}$  with 38% of the CEC being satisfied by Na, 36% Ca, 10% Mg, 3% K.

### **3.3.1.2 Dry-Blended Polymer Na-Bentonite GCL**

The Na-bentonite GCL that was dry-blended with polymer is referred to herein as R-GCL. R-GCL had a mass per unit area of  $6.5 \text{ kg/m}^2$  and an initial water content of 5.3%. The conventional Na-bentonite GCL is referred to herein as S-GCL. X-ray diffraction showed that the bentonite contained 86% montmorillonite, 8% quartz, 3% plagioclase, 1% clinoptilolite, 1% illite and mica, 1% orthoclase, and trace amounts of kaolinite which can be referred to in Table 3.1. The average CEC of the bentonite from S-GCL was  $78.2 \text{ cmol}^+/\text{kg}$  with 49% of the CEC being satisfied by Na, 35% Ca, 9% Mg, 2% K.

### **3.3.1.3 Bentonite-Polyacrylate Nanocomposite GCL**

Na-bentonite was modified at the nanoscale by polymerizing acrylic acid within a bentonite slurry to form an interconnected super-swelling structure, and the resulting material is referred to as bentonite-polymer nanocomposite (BPN) (Scalia 2012). The GCL with the BPN material is referred to herein as BPN-GCL. BPN-GCL has a mass per unit area of  $6.1 \text{ kg/m}^2$  and an initial water content of 7.2%. X-ray diffraction showed that the bentonite contained 78%

montmorillonite, 8% quartz, 5% plagioclase, 1% clinoptilolite, 7% illite and mica and trace amounts of orthoclase and kaolinite which is summarized in Table 3.1. The average CEC of the BPN-bentonite was 116.4 cmol<sup>+</sup>/kg. The sum of the bound cations was calculated to be higher than the reported CEC. The measured exchange complex of the BPN-GCL can be referred to in Table 3.2.

### 3.3.2 Permeant Solutions

The permeant solutions used in this study were comprised on anhydrous inorganic salts (> 99% purity) dissociated within deionized (DI) water to form aqueous solutions. A NaCl salt was chosen to investigate the effects of monovalent cations (+1) and CaCl<sub>2</sub> was chosen to investigate the effects of divalent (+2) cations. The anionic background (Cl<sup>-</sup>) was held constant for all of the permeant solutions similar to Kolstad et al. (2004). DI water was used as the reference solution.

This study, similar to Kolstad et al. (2004), focused on the effect of multi-species solutions. Solutions were prepared by dissolving varying concentrations of NaCl and CaCl<sub>2</sub> salts in DI water. Concentrations of these salts were selected to achieve a desired ratio of monovalent to divalent (RMD) cations at particular total ionic strengths (I) (Kolstad et al. 2004). The total ionic strengths of the permeant solutions were 0.01, 0.05, 0.2, 0.5, 1.0, and 1.5 M. Total ionic strength is defined as:

$$I = \sum_{i=1}^n (c_i z_i^2) \quad (3.1)$$

Where  $c_i$  is the molar concentration (M, mol/L) of ion  $i$  and  $z_i$  is the charge number of ion  $i$ . Na, Ca, and Cl ions (i.e. total ionic strength) were taken into account when calculating the concentrations of salts to use in the creation of the permeant solutions. The RMD ratios used in the permeant solutions was 0.005, 0.05, 0.5, and 5 M<sup>1/2</sup>. The ratio of monovalent to divalent cations, or RMD, is defined by Kolstad et al. (2004) as:

$$RMD = \frac{M_M}{\sqrt{M_D}} \quad (3.2)$$

Where  $M_M$  is the total molarity of monovalent cations (M, mol/L) and  $M_D$  is the total molarity (M, mol/L) of divalent cations in solution. A summary of the target permeant solution I and RMD matrix can be found in Fig. 3.1. Cation concentrations in the permeant solutions were verified using inductively coupled plasma optical emission spectrometry (ICP-OES) using a Varian MPX ICP-OES (Melbourne, Victoria, Australia) following USEPA Method 6010 B. Conservation of mass was assumed for the Cl anion and the inclusion of Cl in total ionic strength (i.e. including cations and anions) was calculated based on measured Na and Ca concentrations in the permeant solution from ICP analysis (i.e. conservation of mass).

NaCl and CaCl<sub>2</sub> salts were chosen for this study based on results from Rauen (2007) where Na was the most abundant cation in the leachates and Cl was the most abundant anion. Rauen (2007) also found that Ca concentrations in bioreactor leachates was elevated. Ca was chosen to investigate the effects of divalent cations and also because of its potential to exchange with bound Na in GCLs in the environment (Bradshaw 2008).

### **3.4 METHODS**

#### **3.4.1 Swell index**

Swell index tests were conducted on the bentonite from all GCLs according to the methods described in ASTM D 5890. Swell index results of fresh bentonite from each GCL is reported in Table 3.2. Prior to testing, the bentonite was ground using a mortar and pestle until 100% passed the No. 200 US Standard Sieve (ASTM E11) and then dried for 12 to 16 hours at 105° C. Bentonite was placed into a 100-mL graduated cylinder containing 90 mL of Type II DI water in increments of 0.1 g over a period of 30 sec until 2 g of bentonite had been added. An additional 10 mL of test solution was used to rinse particles adhering to the graduated cylinder once the entire 2 g of bentonite was added. Swell volume was recorded in mL after 24 hr of hydration. Swell index will also be completed on bentonites from GCLs that have reached hydraulic and chemical equilibrium.

### 3.4.2 Hydraulic Conductivity Tests

GCL test specimens were prepared using the methods described in ASTM D 6766 and Jo et al. (2001). A square sample with uniform thickness was cut from the GCL roll. The GCL specimen was cut from the square sample using a sharp razor knife and a 152-mm-diameter circular acrylic trimming ring. Prior to removal of the GCL from the cutting ring, the edges of the GCL were hydrated using a small amount of DI water to prevent loss of bentonite. After removing the GCL specimen from the cutting ring, the edges of the geotextiles were trimmed using a scissors. Initial and final weights of each GCL were measured to 0.1 g using a laboratory balance. Initial and final GCL thicknesses were measured at six locations using a caliper. The average of each set of measurements is reported and was used in calculations.

Hydraulic conductivity tests were conducted using a flexible-wall permeameter set up in accordance with procedures described in ASTM D 5084 Method B-falling headwater-constant tailwater and ASTM D 6766. Direct permeation was employed to the GCL sample to simulate the worst case scenario (i.e. no hydration time). An average confining stress of 27 kPa was applied to the flexible wall via pressurized cell water. The average effective stress applied was 20 kPa. Hydraulic conductivity tests with permeant solutions with ionic strengths  $> 0.5$  M had an average hydraulic gradient between 75 and 50 while tests with permeant solutions with ionic strengths  $\leq 0.5$  M had an average hydraulic gradient of 175. This average hydraulic gradient is higher than a GCL would experience in the field, but is less than a hydraulic gradient ( $> 500$ ) that would impact hydraulic conductivity for laboratory testing purposes (Shackelford et al. 2000).

The termination criteria outlined in ASTM D 5084 and ASTM D 6766 is used to define hydraulic equilibrium. Hydraulic equilibrium is declared when the ratio of the rate of inflow to the rate of outflow is within 25% for a minimum of three consecutive hydraulic conductivity readings, with no significant upward or downward trend. Termination criteria based on chemical equilibrium is defined by ASTM D 6766 and conditions set by this study when the ratio of

outflow to inflow is within 10% for four consecutive samples for both electrical conductivity (EC) and Na and Ca concentrations. pH is also monitored, but is not a requirement for the chemical equilibrium termination criterion.

The influent solution was contained in 50-mL glass burettes. Influent samples were stored in collapsible carboys with no headspace to minimize interactions with atmospheric carbon dioxide (CO<sub>2</sub>). Effluent samples were collected in 60 mL high-density polyethylene bottles and were collected approximately every 30 to 50 mL. Samples were analyzed within 6 months of the sample date using ICP-OES following US EPA Method 6010B.

The cumulative influent volume and end-of-test GCL properties (thickness, diameter, water content, and mass) are used to calculate relative pore volumes of flow (PVF) through the specimen.

### **3.4.3 Loss on Ignition**

Polymer content via loss on ignition (LOI) was conducted as described by Scalia (2012) for the BPN-GCL prior to and post hydraulic conductivity testing. The BPN material was ground pass a No. 10 woven wire sieve (ASTM E11) and was oven dried at 105°C for 12 to 16 hr. The oven dried material was then placed in a 550°C furnace for 4 h to ignite volatile substances. After testing, the crucible was allowed to cool in a water free atmosphere (i.e. in a container with desiccant). The mass loss on ignition of each material was then determined. Polymer content was calculated by assuming the mass loss percentages of base bentonite (1.6 %) and sodium-polyacrylate (74.7 %) based on values from LOI testing performed by Scalia (2012). Bentonite from the BPN-GCL was determined to initially contained 12-13.0 % polymer by mass.

### **3.4.4 Chemical Analysis**

The chemical analysis for concentrations of Na<sup>+</sup>, Ca<sup>+2</sup>, Mg<sup>+2</sup>, and K<sup>+</sup> cations typically found in soil pore water (denoted in this paper as Na, Ca, Mg, and K) found in testing solutions was determined using ICP-OES. To test chemical equilibrium status Na and Ca cation

concentrations from influent and effluent samples were also tested via ICP-OES. Calibration curves are created using High Purity Standards of the cation of interest (Na, Ca, Mg, K) with a starting concentration of 10.0 mg/mL preserved in 1%-4% nitric acid. The matrix solution used to create the ICP calibration curve corresponds with the matrix solution used for permeant solution (influent and effluent) and soluble cation extraction solution (i.e. DI water) or bound cation extractions (i.e. 1 M  $\text{NH}_4\text{OAc}$ ) to account for potential interference during the ICP analysis.

### **3.4.5 Soluble Cation Determination**

Extraction of the soluble cations from the GCL bentonite was completed using Type II DI water in accordance with ASTM D 7503 or the “Standard Test Method for Measuring the Exchange Complex and Cation Exchange Capacity of Inorganic Fine-Grained Soils”. Type II DI water was used to create a 1:50 solid-water ratio that was tumbled at 30 rpm for 1 h. Afterwards, the extract was filtered by vacuum through Whatman No. 42 filter paper and preserved with 1% (by volume) trace-metal-grade nitric acid. Na, Ca, Mg, and K are washed from the pore space via vacuum filtration and the eluent is analyzed with ICP-OES for Na, Ca, Mg, and K cation concentrations. Calculation methods for soluble cation concentrations are presented in ASTM D 7503.

### **3.4.6 Bound Cation Determination**

Bound cations (BC) were determined using the procedure outlined in ASTM D 7503. A mixture of 10 g of air-dried bentonite crushed to pass the No. 10 US standard sieve and 40 mL of 1 M  $\text{NH}_4\text{OAc}$  was tumbled at 30 rpm for 5 min and then let to stand for 24 h then tumbled again at 30 rpm for 15 min. The free liquid was then removed by vacuum filtration using Whatman No. 42 filter paper. The bentonite was then rinsed with four 30-mL portions of 1 M  $\text{NH}_4\text{OAc}$  with vacuum applied. The  $\text{NH}_4\text{OAc}$  rinse eluate was transferred to a 250-mL volumetric flask, filled to volume with 1 M  $\text{NH}_4\text{OAc}$ , and preserved with 1% (by volume) trace metal grade nitric acid. Cation concentrations (Na, Ca, Mg, K) in the extract were measured

using ICP-OES. The calculation methods used to compute concentrations of bound cations within the bentonite are in ASTM D 7503, where the measured bound cation concentrations were calculated as the difference between the soluble cation concentration and the cation concentration from the ammonium acetate eluate.

### **3.4.7 Cation Exchange Capacity**

Residual soil remaining on the filter from the bound cation extraction is used in the cation exchange capacity (CEC) testing. The soil is then rinsed with three 40-mL portions of isopropanol to rinse any residual  $\text{NH}_4\text{OAc}$  ( $\text{NH}_4^+$ ) out of the soil pores. Next the isopropanol washed soil is rinsed with four 50-mL 1.0 M KCl portions, replacing the adsorbed ammonium ( $\text{NH}_4^+$ ) cations with potassium cations in the interlayer of the soil. The extract is poured into a 250-mL volumetric flask and filled to volume with Type II DI water. The concentration of ammonium in the extract is measured via the salicylate method (EPA Method 350.1) using high range (0 – 50 mg/L)  $\text{N-NH}_3$  “Test ‘N Tube” vials (Hach Company: Method 10031) with a Spectronic 20 Gensys spectrophotometer (ThermoFisher Scientific, Waltham, Massachusetts). The CEC was calculated using the measured  $\text{NH}_4^+$  in the extract and calculations can be found in ASTM D 7503.

## **3.5 RESULTS**

A summary of hydraulic conductivity tests that have been set-up for testing can be found in Table 3.3. The hydraulic conductivity tests reported were conducted within a time period of 5 months. Hydraulic conductivity tests that did not satisfy both hydraulic and chemical equilibrium will continue to be permeated until termination criterion has been reached. Thus, some of the reported hydraulic conductivities found in Table 3.5 represent a snapshot in time and may not represent long-term equilibrium conditions. Hydraulic conductivity testing will continue for the three GCL products until the testing matrix is completed and results will be analyzed by a subsequent researcher.

### 3.6 REFERENCES

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### 3.7 TABLES

Table 3.1 Mineralogy of bentonite from GCLs used in this study.

Properties	GCLs			Determination Method
	S	R	BPN	
Montmorillonite (%)	84	86	78	XRD, Moore and Reynolds (1989)
Quartz(%)	9	8	8	
Plagioclase(%)	3	3	5	
Clinoptilolite (%)	2	1	1	
Illite, Mica (%)	1	1	7	
Kaolinite (%)	trc	trc	trc	
Orthoclase (%)	1	1	trc	
Average calcite by mass (%)	1.03	trc	1.02	ASTM D4373

\*trc is < 1%

Table 3.2 Mass per unit area, water content, swell index, loss on ignition, bound cations in the exchange complex, and cation exchange capacity of fresh bentonite from GCLs used in this study.

Bentonite Material	Mass per unit area (kg/m <sup>2</sup> )	Water Content (%)	Swell Index (mL/2g)	Loss on Ignition (%)	Bound Cations (cmol <sup>+</sup> /kg)				CEC (cmol <sup>+</sup> /kg)
					Na	Ca	Mg	K	
S-GCL	5.7	4.7	26.0	2.06	30.5	28.8	8.4	2.2	81.0
R-GCL	6.5	5.3	27.0	2.18	38.4	27.7	7.4	1.7	78.2
BPN-GCL	6.1	7.2	85.5	13.7	118.3	10.0	5.2	2.2	116.4

Table 3.3 Summary of results of hydraulic conductivity tests conducted at varying I and RMD for S-GCL, R-GCL, and BPN-GCL

GCL Material	Test Set Up							Test Results									
	Ionic Strength (M)		RMD ( $M^{1/2}$ )		pH	EC (mS/cm)	Ave. i	EQ Status	PVF	k (m/s)	k/k <sub>DI</sub>	Swell Index (mL/2g)	Loss on Ignition (%)	Bound Cations (cmol <sup>+</sup> /kg)			
	Target	*Actual	Target	Actual*										Na	Ca	Mg	K
BPN-GCL	DI		DI		--	--	175	N	4.9	* $1.6 \times 10^{-12}$	1						
	1.5	1.39	0.5	0.47	8.3	77.1	50	Y	23.1	$4.7 \times 10^{-7}$	294,000						
		1.54	5	5.77	7.06	57.1	75	Y	26.5	$1.9 \times 10^{-7}$	119,000						
	1.0	0.87	0.05	0.054	7.92	41.3	75	Y	62.8	$4.9 \times 10^{-7}$	306,000						
		0.92	0.5	0.49	6.25	57.1	50	N	7.7	* $2.2 \times 10^{-7}$	138,000						
		0.94	5	5.06	6.27	73.5	75	Y	52.2	$1.1 \times 10^{-7}$	69,000						
	0.5	0.61	0.05	0.073	8.21	26.9	175	Y	64.7	$8.9 \times 10^{-7}$	556,000						
		0.54	0.5	0.61	9.84	32.3	175	N	66.7	* $6.4 \times 10^{-7}$	400,000						
		.64	5	5.37	6.52	42.8	175	N	9.4	* $2.1 \times 10^{-12}$	1.3						
	0.2	0.15	0.005	0.003	7.21	11.34	175	N	7.5	* $1.7 \times 10^{-11}$	10.6						
		0.22	0.05	0.036	6.68	12.29	175	N	0.1	* $8.9 \times 10^{-12}$	5.6						
		0.24	5	5.59	6.14	18.36	175	N	1.5	* $2.2 \times 10^{-12}$	1.4						
	0.05		0.05								*h						
			5								*h						
	0.01		0.05								*h						

Notes: \*Actual = calculated from ICP influent solution cation concentrations and assumes conservation of mass for the anions, RMD = ratio of monovalent to divalent cations, EC and pH of influent, PVF, k, and k/k<sub>DI</sub> correspond to conditions at the time of most recent measurement; k = hydraulic conductivity; \*k = reported hydraulic conductivity is not at either hydraulic nor chemical equilibrium; k<sub>DI</sub> = hydraulic conductivity of respective GCL to DI water; \*h = hydrating at time of most recent measurement (i.e. no effluent solution collected)

## 3.8 FIGURES

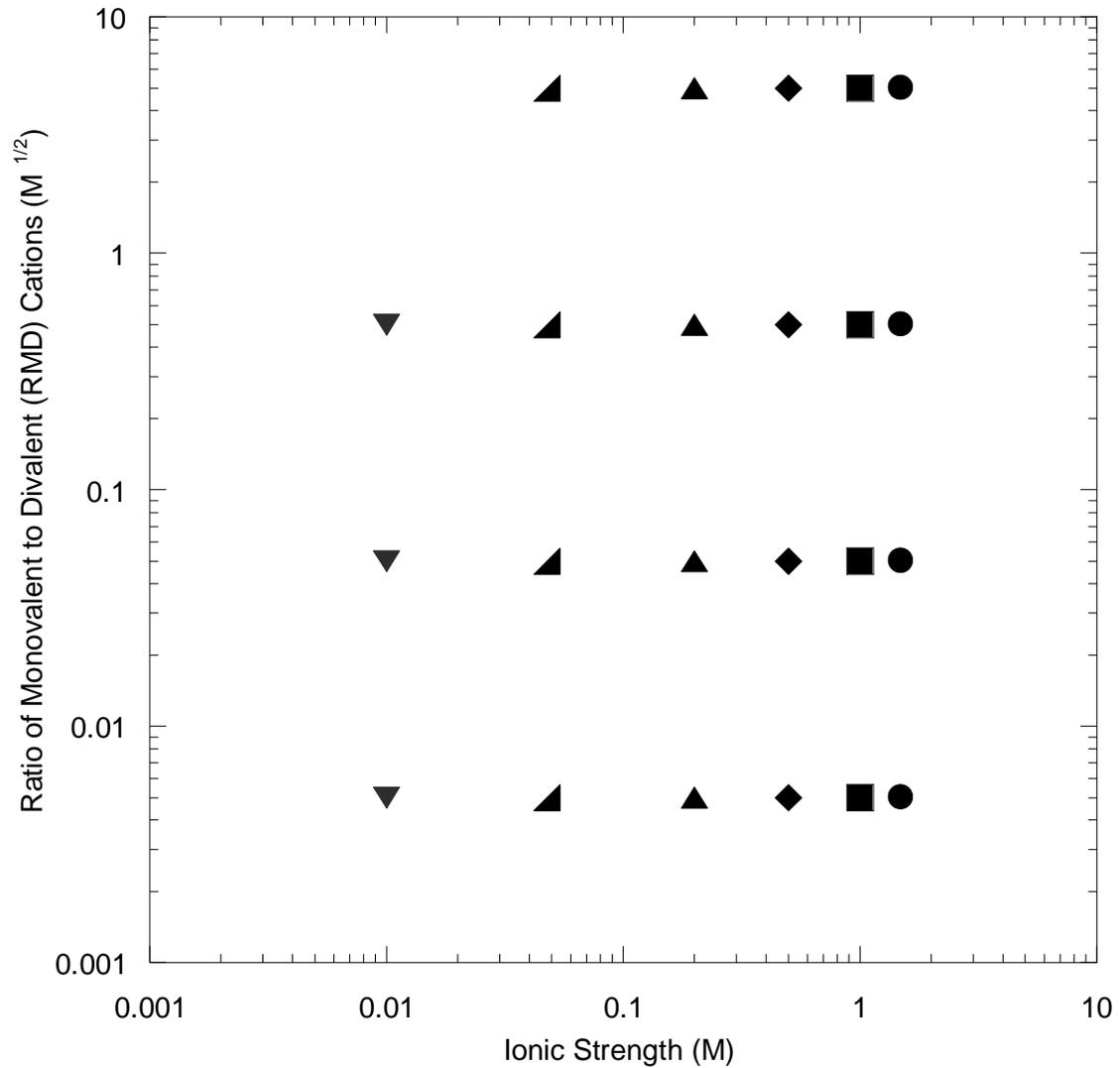


Fig. 3.1 Permeant solution matrix for hydraulic conductivity testing of polymer modified bentonite GCLs and conventional Na-bentonite GCLs.