

# Hydraulic conductivity of bentonite-polymer composite geosynthetic clay liners permeated with bauxite liquor from China

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## ABSTRACT

The high ionic strength of the porewater in red mud (i.e., bauxite liquor) can suppress swelling of montmorillonite, resulting in geosynthetic clay liners (GCLs) that are too permeable to be effective as liners in red mud disposal facilities. Bentonite-polymer composite GCLs (BPC-GCLs) have been developed as more resilient lining materials, and some BPC-GCLs have been shown to have very low hydraulic conductivity to bauxite liquors that have extreme ionic strength and pH. In this study, a nationwide investigation was conducted in China to evaluate the characteristics of bauxite liquor in Chinese impoundments, and to evaluate the suitability of GCLs containing granular sodium bentonite or BPCs for containment. Hydraulic conductivity tests were conducted on three BPC-GCLs with two characteristic Chinese bauxite liquors that are hyperalkaline ( $\text{pH} > 12$ ) and have ionic strengths of 76.9 mM and 620.3 mM. The BPC GCLs had hydraulic conductivities ranging from  $10^{-9}$ - $10^{-12}$  m/s, which is higher than the hydraulic conductivity of BPC GCLs to deionized water ( $10^{-11}$ - $10^{-12}$  m/s), but lower than the hydraulic conductivity of conventional GCLs with granular sodium bentonite GCLs to the same liquors ( $10^{-8}$ - $10^{-7}$  m/s). The hydraulic conductivity of the BPC-GCLs depends on the chemical properties of the leachate, the polymer loading, and the type of polymer. Microstructural analysis by scanning electron microscopy (SEM) suggests that the hydraulic conductivity of BPC GCLs is controlled by the polymer hydrogel filling pores, which can be affected by the bauxite liquor.

## 1. INTRODUCTION

Approximately 275 Tg (million tons) of bauxite ore is mined globally each year for alumina production, with Australia (33%), China (20%), and Brazil (16%) the leading bauxite producers (Xue et al. 2016, Kishida et al., 2017). Red mud (RM), a highly alkaline residue from refining bauxite ore to produce aluminum, is generated each year as a byproduct of aluminum refining (60 Tg globally; 6 Tg in China). Most red mud (85%) is stored in impoundments on-site or adjacent to alumina refining plants.

RM consists primarily of fines (particles  $< 0.075$  mm) and has high alkalinity (Sun et al. 2019). The major chemical components of RM include  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{K}_2\text{O}$ , most of which are soluble in water depending on the pH (Burke et al. 2012, Liu et al., 2014). The porewater in red mud is "bauxite liquor," having high pH ( $> 14$  in some cases) and high ionic strength ( $> 1$  M in some cases). Bauxite liquor contains elevated concentrations of potassium (K), sodium (Na), calcium (Ca), magnesium (Mg), and aluminum (Al), as well as the anions fluoride ( $\text{F}^-$ ), chloride ( $\text{Cl}^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ) (Sun et al. 2019). Heavy metals in the bauxite liquor, including arsenic (As), lead (Pb), zinc (Zn), copper (Cu), nickel (Ni), chromium (Cr), and vanadium (V), often are at concentrations in excess of groundwater quality standards in China and the United States (Sun et al. 2019). For example, Sun et al. (2019) found the concentration of As and Cr in bauxite liquor is 2 to 200 times higher than the maximum contaminant level (MCL) published by the US Environmental Protection Agency. Consequently, bauxite liquor has the potential to contaminate groundwater if not stored in a properly engineered and managed disposal facility.

Compacted clay liners (CCLs) and geosynthetic clay liners (GCLs) are used as liners in RM disposal facilities (Athanasopoulos et al. 2015, Tian and Benson 2019), generally in conjunction with a geomembrane in a composite liner (geomembrane directly over a CCL or GCL). The hydraulic conductivity ( $k$ ) of CCLs and GCLs controls their effectiveness as hydraulic barriers. The sodium bentonite (NaB) in traditional GCLs is composed primarily of the clay mineral montmorillonite, which swells when hydrated in water to form a gel with very low hydraulic conductivity (Jo et al. 2001, Kolstad et al. 2004a, Benson et al. 2010). However, the high ionic strength of bauxite liquor can suppress swelling of the montmorillonite, resulting in high hydraulic conductivity for some GCLs (Benson et al. 2010, Tian and Benson 2019).

Bentonite-polymer composite GCLs (BPC-GCLs) have been developed as alternatives to traditional sodium bentonite GCLs for use with aggressive leachates (Scalia et al. 2011, Tian et al. 2016, Ozhan 2018, Chen et al. 2019, Hosney and Rowe 2019). Some BPC-GCLs have been shown to have very low hydraulic conductivity to liquids that have extreme pH and/or ionic strength, like bauxite liquors. (Athanasopoulos et al. 2015, Tian and Benson 2019). Athanasopoulos et al. (2015) evaluated the hydraulic conductivity of NaB and BPC GCLs to two leachates with high pH: trona ash leachate ( $\text{pH} = 11$ ,  $I = 1.05$  M) and bauxite liquor ( $\text{pH} = 13$ ,  $I = 2.35$  M). Hydraulic conductivity of the BPC GCL was up to 4 orders of magnitude lower than the hydraulic conductivity of the NaB GCL to the same liquids. Tian and Benson (2019) measured

the hydraulic conductivity of a NaB GCL and a BPC GCL (polymer content = 6.8%) to a bauxite liquor (pH = 13,  $I = 700$  mM) and found that the BPC GCL had much lower hydraulic conductivity ( $4.3 \times 10^{-12}$  m/s) than the NaB GCL ( $\sim 10^{-7}$  m/s). The low hydraulic conductivity of the BPC GCL was attributed to polymer blocking intergranular pores rather than swelling of bentonite. Chen et al. (2019) report similar findings for BPC and NaB GCLs permeated with coal combustion product leachates. The BPC GCLs were much less permeable to the CCP leachates than the NaB GCLs, provided the BPC GCLs had sufficient polymer loading.

In this study, a nationwide investigation was conducted in China to evaluate the geochemical characteristics and environmental impacts of red mud impoundments. As part of this investigation, hydraulic conductivity tests were conducted on one NaB GCL and three BPC-GCLs using two characteristic Chinese bauxite liquors. Hydration behavior of the NaB and BPC with bauxite liquor was investigated using swell index tests, and micro-scale image analysis was used to understand mechanisms controlling the hydraulic conductivity of BPC GCLs permeated with bauxite liquor.

## 2. MATERIALS AND METHODS

### 2.1 Geosynthetic Clay Liners

One conventional NaB GCL and three BPC GCLs were evaluated in this study, all of which are commercially available in China (GETCO Technologies Suzhou Co. Ltd., Suzhou, China). The BPC GCLs are manufactured by dry mixing granular proprietary polymers (one or more polymers) with granular sodium bentonite. These BPC GCLs are labeled as CP6.3, CP7.5, and CP10.8, with the numerical suffix representing the polymer loading in % dry mass. For each GCL, the BPC mixture was encased between woven ( $170 \text{ g/m}^2$ ) and nonwoven ( $206 \text{ g/m}^2$ ) geotextiles bonded by needle-punching. The NaB GCL contained the same bentonite and employed the same geotextiles as the BPC GCLs.

Physical properties, bentonite mineralogy, and polymer loading are summarized in Table 1 for each of the GCLs. Polymer loading was determined based on loss on ignition (LOI) using the procedure described in Scalia et al. (2014). Bound cations (i.e.,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ) and cation exchange capacity (CEC) were determined by ammonium acetate extraction following the methods in ASTM D7503 (ASTM 2010).

Each BPC GCL contained sand-sized bentonite granules with a median particle size between 0.7 and 0.9 mm. Quantitative X-ray diffraction (XRD) was conducted on the bentonite using the methods in Moore and Reynolds (1989) for clay minerals and bulk minerals. The bentonite has 67% to 85% montmorillonite with measurable quartz, feldspar, illite, calcite, kaolinite, potassium feldspar. Sodium is the main bound cation in the exchange complex of each GCL, with the mole fraction ranging from 0.40 to 0.59 (Table 1).

Table 1. Properties of bentonite-polymer composite (BPC) GCLs used in this study.

Properties	Geosynthetic Clay Liner				
	NaB	CP6.3	CP7.5	CP10.8	
Bentonite Mass per Unit Area ( $\text{kg/m}^2$ )	3.6	3.6	3.7	3.6	
Initial Thickness (mm)	6.1-7.5	5.6 - 6.7	5.9 - 6.7	6.5 – 7.3	
Initial Water Content (%)	6.0	4.0	4.8	5.6	
Median Granule Size (mm)	0.8	0.8	0.7	0.9	
Montmorillonite Content <sup>a</sup> (%)	85	67	67	85	
Bound Cations <sup>b</sup> (Mole Fraction)	Na	0.46	0.40	0.40	0.46
	K	0.02	0.02	0.02	0.02
	Ca	0.35	0.37	0.37	0.35
	Mg	0.15	0.09	0.09	0.15
Loss on Ignition <sup>c</sup> (%)	$4.0 \pm 0.2$	$7.8 \pm 0.3$	$9.0 \pm 0.3$	$12.2 \pm 0.4$	
Polymer Loading <sup>c</sup> (%)	0	$6.3 \pm 0.3$	$7.5 \pm 0.3$	$10.8 \pm 0.4$	

Note: <sup>a</sup>Montmorillonite content is from X-ray diffraction, <sup>b</sup>bound cations using ASTM D7503, <sup>c</sup>loss on ignition (LOI) and polymer loading after correcting for the LOI of the bentonite fraction with the method of Scalia et al. (2014).

### 2.2 Water Chemistry Analysis

Accumet XL50 bench-top meters (Fisher Scientific, Hanover Park, IL) were used to measure pH, EC, and oxidation-reduction potential (ORP) of the bauxite liquor sampled from the field sites and the influent and effluent from the hydraulic conductivity tests. Samples for additional analysis were filtered using 0.45- $\mu\text{m}$  filter paper (HAWG04700 MF-Millipore, Massachusetts, USA) and acidified with trace-grade nitric acid ( $\text{HNO}_3$ ) to  $\text{pH} < 2$ . Concentrations of major elements (Na, K, Ca, Mg, Al, and Si) and heavy metals (Cr and Pb) in the bauxite liquor, the influent, and the effluent were measured by inductively coupled plasma mass spectrometry (ICP-MS, Agilent Technologies 700 Series, Santa

Clara, CA, USA) in accordance with USEPA Method 6010C (USEPA 2007). Anions in the bauxite liquor, including chloride (Cl<sup>-</sup>), fluoride (F<sup>-</sup>), and sulfate (SO<sub>4</sub><sup>2-</sup>), were measured by ion chromatography (IC, Shimadzu HIC-SP, Kyoto, Japan) in accordance with USEPA Method 6010B (USEPA 1996).

### 2.3 Bauxite Liquor

Samples of bauxite liquor were obtained from six red mud management facilities in four provinces of China (i.e., Shanxi, Henan, Guangxi, and Shandong): GX-A1 (Pingguo County, Guangxi), GX-A2 (Pingguo County, Guangxi), GX-B (Jingxi County, Guangxi), SD-A (Zibo, Shandong), HN-A (Xingyang, Henan), SX-A (Yuncheng, Shanxi), and SX-B (Zhaofeng, Shanxi). Bauxite liquors GX-A2L and GX-A2 were collected from two adjacent impoundments (A1 and A2) at the same plant. All bauxite liquors were collected from the drainage pipe of the red mud impoundment and transported at 4 °C in sealed high-density polyethylene (HDPE) sample bottles with no headspace. Bulk chemical parameters, including pH, EC, ORP, ionic strength, and relative abundance of monovalent and polyvalent cations (RMD) of the bauxite liquors are summarized in Table 2. The bauxite liquor is hyperalkaline, with pH ranging from 11.3 to 13.2. The ionic strength ranges from 77.3 to 620.3 mM, which is lower than the very high ionic strength (2350 mM) of bauxite liquor reported by Athanassopoulos et al. (2015). EC of the bauxite liquor ranges from 0.44 to 5.11 S/m at 25 °C. The ORP ranges from -110.0 to -63.0 mV, indicating a reducing condition. Elemental analysis indicates the major elements in the bauxite liquor are Al (152.9-1095.5 mg/L) and Na (1200.5-41290.0 mg/L) and the major anions are Cl<sup>-</sup> (150.0-6588.1 mg/L) and SO<sub>4</sub><sup>2-</sup> (162.0-7453.3 mg/L). Other elements and anions had concentrations in the following ranges: 1.5-194.6 mg/L for Ca, 0.4-29.1 mg/L for Mg, 81.8-4900.0 mg/L for K, 13.0-89.9 mg/L for Si, and 49.8-299.6 mg/L for F<sup>-</sup>. The concentration of the heavy metals Cr and Pb ranged from 0.1-5.9 mg/L and 0.2-1.1 mg/L, respectively.

Kolstad et al. (2004a) indicate that ionic strength and relative abundance of monovalent and polyvalent cations in a permeant liquid are master chemical variables controlling the hydraulic conductivity of GCLs containing NaB. Osmotic swelling of bentonite is suppressed by solutions with higher ionic strength or lower RMD, which generally results in higher hydraulic conductivity of NaB GCLs (Jo et al. 2001, Kolstad et al. 2004a, Scalia et al. 2014). RMD is defined as:

$$RMD = \frac{M_M}{M_D} \quad [1]$$

where  $M_M$  is the total molarity of the monovalent cations, and  $M_D$  is the total molarity of polyvalent cations in the permeant solution. Based on the concentrations in Table 2, RMD of the bauxite liquors ranges from 0.03 to 5.4 M<sup>1/2</sup>, or predominantly polyvalent (low RMD) to predominantly monovalent (high RMD).

Table 2. Bulk chemical parameters and concentrations of major elements, anions, and heavy metals of bauxite liquors.

Leachate Samples	GX-A1	GX-A2	GX-B	SD-A	HN-A	SX-A	SX-B
<b>Bulk Chemical Parameters</b>							
pH	12.1	12.6	12.4	12.6	12.6	13.2	13.1
EC@25 °C (S/m)	0.97	0.44	2.63	5.11	3.76	3.15	2.78
ORP (mV)	-46.0	-29.0	-63.0	-110.0	-72.0	-	-
Ionic Strength (mM) *	224.5	77.3	238.8	620.3	550.0	293.7	259.5
RMD(M <sup>1/2</sup> )	0.03	0.06	1.9	2.6	1.6	5.4	1.2
<b>Major Elements and Anions</b>							
Al (mg/L)	1095.5	118.3	152.9	745.5	1327.4	670.0	864.0
Ca (mg/L)	88.9	120.6	194.6	57.1	22.6	-	1.5
Na (mg/L)	3506.0	1200.5	4707.0	10650.0	7634.5	41290.0	4860.0
Mg (mg/L)	15.0	19.5	29.1	10.5	8.1	-	0.4
K (mg/L)	239.3	114.4	197.6	81.8	1016.0	4900.0	323.0
Si (mg/L)	41.7	13.0	26.5	89.9	31.8	-	-
Cl <sup>-</sup> (mg/L)	877.1	511.4	6459.8	6490.5	6588.1	280.0	150.0
F <sup>-</sup> (mg/L)	49.8	88.0	178.6	121.8	299.6	-	-
SO <sub>4</sub> <sup>2-</sup> (mg/L)	741.7	502.5	6593.0	7453.3	2386.4	640.0	162.0

\*Calculated using Visual MINTEQ, charge differences <5%.

Ionic strength vs. RMD of the bauxite liquor is shown in Fig. 1. In this study, two characteristic liquors were selected for hydraulic conductivity testing: (1) SD-A ( $I = 620.3$  mM, RMD= 2.6 M<sup>1/2</sup>) with the highest ionic strength was selected to represent the worst-case scenario that might be encountered in a red mud impoundment in China, and (2) GX-A1 ( $I = 224.5$  mM, RMD= 0.03 M<sup>1/2</sup>) with an ionic strength similar to that of geometric mean, but lower RMD was selected to

represent the general chemistry of bauxite liquor, but with more divalent cations and therefore having a great impact on hydraulic conductivity relative to typical conditions.

Synthetic SD-A liquor was created with the same concentrations of major elements and anions as actual SD-A liquor but without the heavy metals. Reagent grade salts (>99% purity) were dissolved in ASTM Type II DI water to match the major element and anion concentrations shown in Table 2. The solution was titrated with NaOH to match the pH of the actual SD-A liquor. This synthetic liquor had the same ionic strength and RMD as the actual SD-A bauxite liquor and was used to evaluate the efficacy of hydraulic conductivity testing using synthetic solutions.

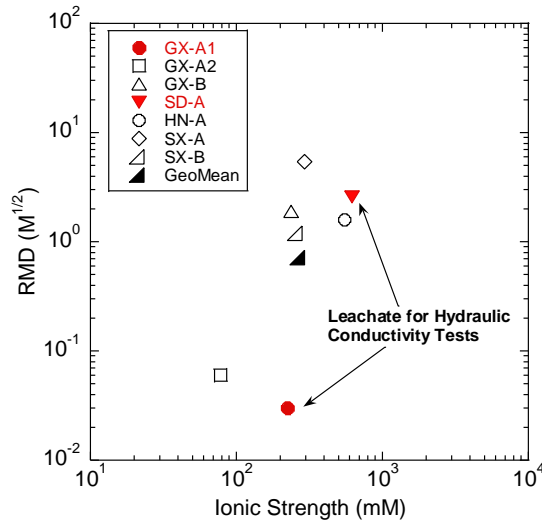


Fig. 1. The relationship between RMD and ionic strength for the bauxite liquors.

#### 2.4 Hydraulic Conductivity of GCLs

Hydraulic conductivity of the GCLs was measured in flexible-wall permeameters using the falling headwater - constant tailwater method in ASTM D5084 (ASTM 2016) and ASTM D6766 (ASTM 2012a). GCL specimens with a diameter of 150 mm were prepared and assembled in flexible-wall permeameters following the procedure in Jo et al. (2001). Bauxite liquors GX-A1 and SD-A were used as permeant solutions to represent the worst-case chemistry (GX-A1) and a moderate chemistry (SD-A) with a predominance of divalent cations. Control tests were conducted using ASTM Type II deionized (DI) water.

The GCLs were hydrated in the permeant solution for 48 h prior to permeation under an effective stress of 20 kPa and no hydraulic gradient. Permeation continued until the hydraulic conductivity was stable, the ratio of incremental outflow to inflow ( $Q_{out}/Q_{in}$ ) was within  $1 \pm 0.25$ , and the pH, electrical conductivity (EC), and concentration of major cations (i.e.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) of the effluent were within 10% of the influent. These termination criteria generally are indicative of hydraulic and chemical equilibrium between a NaB GCL and a permeant solution (Jo et al. 2005). However, they may not correspond to equilibrium conditions for BPC GCLs. Additional studies regarding chemical interactions between permeant solutions and the polymers in BPCs are needed to fully define termination criteria for BPC GCLs.

The influent of specimens with high hydraulic conductivity ( $k > 10^{-8}$  m/s) was spiked with rhodamine WT dye at the end of the test to mark flow paths and to identify if sidewall leakage occurred. If sidewall leakage was identified, the test result was rejected, and a new test was conducted.

#### 2.5 Swell Index

The swell index of bentonite from each GCL was measured in accordance with ASTM D5890 (ASTM 2011) with GX-A1, SD-A, or ASTM Type II DI water as the hydrating liquid. The bentonite was ground with a mortar and pestle to pass the No. 200 US standard sieve (0.075 mm) and oven-dried for 24 hours at 105 °C. A 100-mL graduated cylinder was filled with 90 mL of the test liquid, and 2 g of ground bentonite was added to the cylinder in 0.1 g increments. The graduated cylinder was then filled to 100 mL and let sit for 24 h prior to recording the swell index.

## 2.6 Pore-Scale Analysis

The pore-scale structure of the bentonite in the BPC and NaB GCLs was analyzed by scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDS). Specimens were pretreated by freeze-drying with liquid nitrogen (-90 °C) under 20 kPa vacuum (Vacuum Freeze Drier, LGJ-10, Beijing, China) following the procedure in Tian et al. (2016). This freeze-dry method retains the original microstructure that exists in the hydrated condition. Specimens 2-mm-thick were cut from the freeze-dried samples using a surgical knife and then coated with gold by sputtering (Denton Vacuum Desk II, Moorestown, NJ, USA). SEM images were obtained using an FEI Nova Nano SEM (SEM450, Hillsboro, OR, USA) using a 3 keV electron beam and a conventional secondary electron detector.

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of Ionic Strength on Hydraulic Conductivity

Hydraulic conductivity of the NaB and BPC GCLs as a function of the ionic strength of the bauxite liquors is shown in Fig. 2. Hydraulic conductivity of NaB GCL is strongly related to the ionic strength of bauxite liquor (shaded area in Fig. 2), with higher hydraulic conductivity at higher ionic strength. The NaB GCL has a low hydraulic conductivity ( $2.4 \times 10^{-11}$  m/s) to DI water, but much higher hydraulic conductivity to bauxite liquors ( $>3.6 \times 10^{-9}$  m/s). The hydraulic conductivity of the BPC GCLs is lower than the hydraulic conductivity of the NaB GCLs to the same permeant solutions (zone enclosed by the dashed line in Fig. 2).

The effect of ionic strength on the hydraulic conductivity of BPC GCLs is evident. When permeated with DI water and the more dilute GX-A1 bauxite liquor, the hydraulic conductivity is less than  $7.1 \times 10^{-11}$  m/s. However, the BPC GCLs (especially, CP6.3) have higher hydraulic conductivity ( $6.6 \times 10^{-12}$  to  $4.0 \times 10^{-10}$  m/s) to the SD-A bauxite liquor, which has higher ionic strength. Hydraulic conductivity of tests with synthetic leachate is generally higher than that of tests with actual leachate. For these tests, the BPC GCLs have up to 5.5 times higher hydraulic conductivity (GCL CP10.8) to synthetic SD-A liquor than actual SD-A liquor. The lower hydraulic conductivity of BPC GCL to actual bauxite liquor is likely due to aspects of the liquor geochemistry that were not accounted for in the synthetic leachate and may have led to precipitation of minerals in the pore space (e.g., carbonates) that block flow paths.

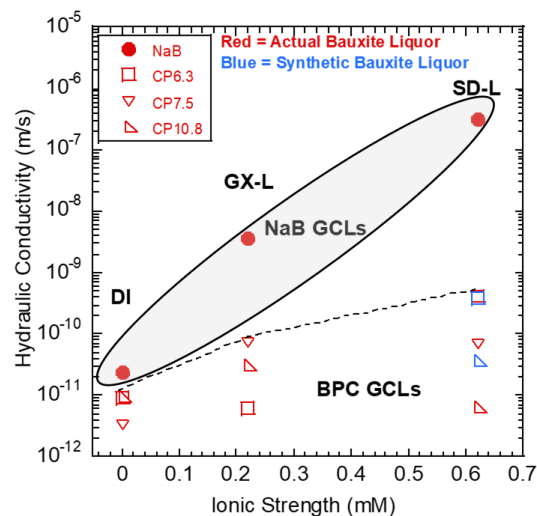


Fig. 2. Hydraulic conductivity versus ionic strength of bauxite liquor. Shaded zone indicates the hydraulic conductivity of NaB GCLs to bauxite liquor, while the dashed line delineates the upper bound hydraulic conductivity of BPC GCLs to bauxite liquor.

### 3.2 Effect of Polymer Loading on Hydraulic Conductivity

Sufficient polymer loading is necessary to block the pore space between the bentonite granules so that a BPC GCL will maintain low hydraulic conductivity ( $< 10^{-10}$  m/s) when permeated with an aggressive solution that suppresses osmotic swelling of the bentonite (Tian et al. 2019). The hydraulic conductivity of BPC GCLs to the bauxite liquors is shown in Fig. 3 as a function of polymer loading. Hydraulic conductivities from Tian and Benson (2019) are also shown in Fig. 3 for comparison. Tian and Benson (2019) permeated a BPC GCL having a polymer loading of 6.8% with a bauxite liquor having pH 13.0 and  $I = 700$  mM. As the polymer loading increases, the maximum hydraulic conductivity of the BPC GCLs

decreases, and the hydraulic conductivities become increasingly consistent. For example, when the polymer loading is less than 7.5%, the hydraulic conductivity of the BPC GCLs ranges from  $10^{-12}$  to  $10^{-9}$  m/s and yet is lower than the hydraulic conductivity of the NaB GCLs (0% polymer loading,  $k = 10^{-11}$  to  $10^{-7}$  m/s). In contrast, when the polymer loading exceeds 7.5%, the BPC GCLs generally have hydraulic conductivity less than  $1 \times 10^{-10}$  m/s.

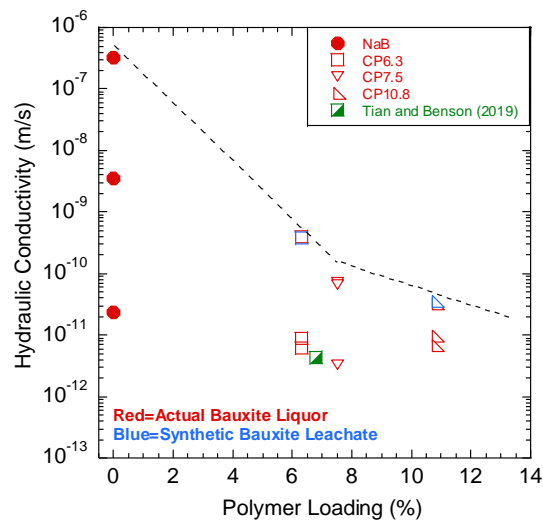


Fig. 3. Hydraulic conductivity of BPC GCLs to bauxite liquor as a function of polymer loading.

### 3.3 Mechanisms Controlling Hydraulic Conductivity of BPC GCLs to Bauxite Liquor

Hydraulic conductivity of the NaB GCLs and BPC GCLs vs. swell index is shown in Fig. 4 for DI water and the bauxite liquors. Hydraulic conductivity of the NaB GCL is strongly related to swell index of the bentonite (Fig. 4 solid symbols), which indicates that the swelling mechanism of bentonite controls the hydraulic conductivity of these NaB GCLs. Others have shown similar findings for NaB GCLs (Jo et al. 2001, Kolstad et al. 2004a, Chen et al. 2018). In contrast, the hydraulic conductivity of the BPC GCLs is not consistently related to swell index. For example, the hydraulic conductivity of BPC GCLs CP10.8 is essentially independent of swell index, whereas the hydraulic conductivity of BPC GCL CP6.3 is modestly related to swell index. Thus, the BPC GCLs function by mechanisms other than swelling of the bentonite and/or swelling of the polymer.

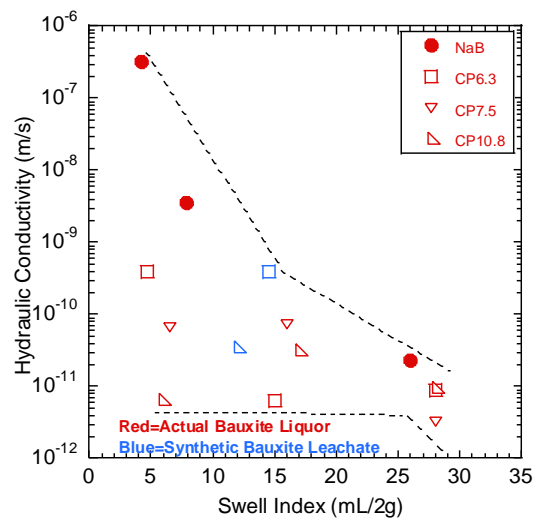


Fig. 4. Hydraulic conductivity vs. swell index for different bauxite liquor.

Tian et al. (2019) and Chen et al. (2019) indicate that BPC GCLs function by polymer hydrogel filling intergranular pores that control hydraulic conductivity. Depending on the polymer used in the BPC, hydrogels form a linear or crosslinked



polymer structure (Chen et al. 2019, Tian et al. 2019). Both structures are comprised of hydrophilic functional groups that bind water molecules (Tian et al. 2016, 2019). A SEM image of the microstructure of BPC GCLs with crosslinked-network structures (CP7.5) is shown in Fig. 5a for hydration with DI water. The crosslinked-network consists of a glutinous hydrogel that fills voids between bentonite granules and coats the surface of the bentonite. A SEM image of the same BPC GCL permeated with bauxite liquor is shown in Fig. 5b, illustrating how bauxite liquor affects the polymer hydrogel. The 3-D network is absent in Fig. 5b, indicating that the bauxite liquor collapsed the polymer hydrogel. Collapse of the hydrogel structure renders the polymer vulnerable to elution, leaving intergranular pore spaces open and resulting in higher hydraulic conductivity ( $> 10^{-10}$  m/s) (Tian et al. 2016, 2019; Chen et al. 2019). However, if the polymer loading is sufficient, the polymer hydrogel remaining in the pore space can block flow paths even if some of the hydrogel is eluted.

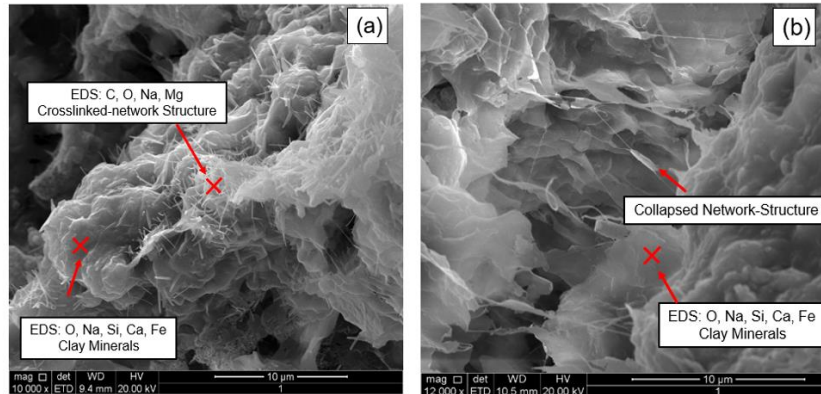


Fig. 5. SEM images of BPC GCL CP7.5 permeated with (a) DI water and (b) SD-A bauxite liquor.

#### 4. SUMMARY AND CONCLUSIONS

A nationwide investigation was conducted in China to evaluate the characteristics of red mud stored in impoundments employed by the aluminum industry, and to evaluate the efficacy geosynthetic clay liners (GCLs) to contain bauxite liquor contained in the red mud. Hydraulic conductivity tests were conducted on three BPC-GCLs and one NaB GCL using two characteristic bauxite liquors representative of bauxite liquors in China. Based on the findings of this study, the following conclusions and recommendations are drawn:

- The bauxite liquors in Chinese red muds are hyperalkaline (pH > 12) with ionic strength ranging from 77 to 620 mM. The major elements and anions are Al, Na, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. Chinese bauxite liquor also contains 0.1-5.9 mg/L of Cr and 0.2-1.1 mg/L of Pb.
- The BPC GCLs had hydraulic conductivities to the liquors ranging from  $10^{-9}$ - $10^{-12}$  m/s, which is higher than the hydraulic conductivity of BPC GCLs permeated with DI water ( $10^{-12}$ - $10^{-11}$  m/s), but lower than the hydraulic conductivity of conventional NaB GCLs to the same liquors ( $10^{-8}$ - $10^{-7}$  m/s).
- The hydraulic conductivity of BPC-GCLs depends on the chemical properties of the liquor, the polymer loading, and the type of polymer. Higher hydraulic conductivity was obtained with bauxite liquors having higher ionic strength. Sufficient polymer loading is needed to ensure BPC GCLs have adequately low hydraulic conductivity to contain bauxite liquor. The necessary polymer loading likely depends on the chemistry of the liquor and the type of polymer.
- Bauxite liquor affects the morphology of polymer hydrogels formed in BPC GCLs. The gelatinous structure associated with a hydrated crosslinked polymer diminishes when the polymer in a BPC is contacted by bauxite liquor with high ionic strength. Changes to the hydrogel structure due to contact with the bauxite liquor can promote polymer elution and more open pore spaces, resulting in higher hydraulic conductivity.

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