

# On the compatibility of GCLs to leachates of extreme chemistry

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**ABSTRACT:** Geosynthetic clay liners (GCLs) are frequently used in lieu of or as an augmentation to compacted clay liners as hydraulic barriers in municipal solid waste containment facilities. GCLs are lately being assessed for use in industrial and mining applications, such as for the temporary storage of process waters and permanent disposal of tailings, but also beneath heap leach pads, where their performance will be subjected to loads, hydraulic heads and leachate chemistries outside the normal conditions found in conventional municipal waste landfills. The paper considers recent and limited research that has assessed the compatibility of GCLs to leachates having extreme chemistry. Extreme chemistry is here defined as strongly alkaline ( $\text{pH} > 12$ ), strongly acidic ( $\text{pH} < 3$ ) and hypersaline ( $I > 1 \text{ M}$ ).

## 1 INTRODUCTION

Geosynthetic clay liners (GCLs) are thin (typically 5 to 10 mm thick) manufactured hydraulic barriers comprised of a thin layer of bentonite bonded to layers of geotextiles and/or a geomembrane. Geotextile based GCLs are bonded by either needle-punching or stitch-bonding, with the bentonite contained by the geotextiles on both sides. For geomembrane-supported GCLs, the bentonite is bonded to the GM using an adhesive and a thin open weave spun-bound geotextile is adhered to the bentonite for protection purposes during installation. The primary differences between GCLs are the mineralogy and form of bentonite (e.g., natural sodium versus sodium activated calcium bentonite, powder versus granular forms, etc.) used in the GCL, the type of geotextile (e.g., woven versus nonwoven geotextiles) and the addition of a geomembrane and the bonding methods. The fluid resistance of GCLs that do not include a geomembrane component is attributed to the bentonite component of the GCL, which swells in the presence of water to form a tight sealing layer.

Over the past two decades GCLs have been used extensively as barriers or components of barriers for a wide variety of hydraulic and gas containment applications, including waste containment liners and covers, ponds or surface impoundments, canals,

storage tanks, and secondary containment of above-grade fuel storage tanks and in transportation facilities (roads and railways) to minimize pollution of subsurface strata from accidental spills and seepage of chemicals (Bouazza 2002). This use stems from the fact that they often have very low hydraulic conductivity to water ( $k_w < 10^{-10} \text{ m/s}$ ), occupy significantly less space to achieve equivalent performance to traditional liners (i.e. CCLs) and are also relatively inexpensive in addition to their good compliance with differential settlements and ease of installation. Furthermore, since they are factory manufactured with good quality control, field construction quality assurance costs are typically less than with traditional liners such as compacted clay liners.

The scarcity of suitable and economical clayey soil resources for traditional liners (i.e. compacted clay liners) throughout mining localities in Australia and worldwide has resulted in recent increased interest in alternative hydraulic barrier materials, such as geosynthetic clay liners (GCLs). Just as for other liner systems, the application of GCLs in a mining environment (ex., uranium mill facility liners, brine evaporation ponds, heap leach pads, waste rock dumps, etc.), generally pushes their performance beyond recommended limits typical for other environmental and engineering applications (Gates et al., 2009). It is not a simple matter of transferring technology from applications common to waste containment facilities to the mining industry, primarily

due to the nature of the extreme ranges in leachate properties generated from the various ore extraction processes. Exposure of the GCL to high overburden and traffic stresses and excessive temperatures as well as high salinity and extreme pH of the leachates and liquors not only affect the geosynthetic components as described in Hornsey et al. (2009b) but also can impact negatively on the performance of the bentonite component. As with all geosynthetics and clay- or bentonite-based lining systems, leachate in-

compatibility is one of the issues that affect the long term performance of GCLs in a mining environment.

Although GCLs have been subject to considerable recent research to determine the effect of a variety of chemical solutions (mostly including inorganic salt or organic chemical solutions) on the hydraulic or gas performance of GCLs (Table 1), very few studies have focussed on mining applications, and in particular how the bentonites may respond hydraulically to leachates having extreme pH.

Table 1: Some hydraulic issues recently noted that may affect the use and performance of GCLs in waste containment applications (modified from Shackelford, 2007)

Factor Studied	Potential Impact	Example Reference(s)
Chemical Compatibility	Chemical incompatibility resulting in an increase in $k$ upon permeation with inorganic or organic chemical solutions with increase in contaminant mass flux	Rowe (1998, 2005, 2006, 2007), Shackelford et al. (2000), Jo et al. (2001, 2004, 2005), Bouazza (2002), Katsumi et al. (2004), Katsumi and Fukagawa (2005), Lee and Shackelford (2005a,b), Touze-Foltz et al. (2006), Katsumi et al. (2008)
Chemical Compatibility with Prehydration	Influence of prehydration (pre-wetting) on the long-term $k$ of GCLs permeated with inorganic or organic chemical solutions	Vasko et al. (2001), Katsumi and Fukigawa (2005), Lee and Shackelford (2005)
Cation Exchange	Desiccation associated with cation exchange ("chemical desiccation") resulting in compromised hydraulic and gas performance of GCLs used in cover systems	James et al. (1997), Lin and Benson (2000), Mazzieri and Pasqualini (2000), Shackelford (2005), Bouazza et al. (2006, 2007), Benson et al. (2007), Meer and Benson (2007), Benson and Meer (2009)
Gas Migration	Gas flux through GCLs used in covers	Aubertin et al. (2000), Didier et al. (2000), Kim and Benson (2004), Vangpaisal and Bouazza (2004), Bouazza and Rahman (2007).
Contaminant Migration	Diffusion and sorption of contaminants through GCLs used as contaminant barriers	Lake and Rowe (2000, 2004, 2005), Ganne et al. (2008), Lange et al. (2009)
Semi-Permeable Membrane Behaviour	The potential for the existence of semi-permeable membrane behaviour in GCLs and the effect of such membrane behaviour on contaminant migration through GCLs used as contaminant barriers	Malusis and Shackelford (2002a, b, 2004), Dominijanni and Manassero (2008), Shackelford and Lee (2003)
Extreme pH (alkaline)	Potential for chemical induced dissolution and/or precipitation reactions of the bentonite component and potential loss of integrity of geotextiles.	Benson et al. (2009); Gates and Bouazza (2009); Hornsey et al. (2009b)
Extreme pH (acidic)	Potential for chemical induced dissolution of the bentonite leading to higher hydraulic conductivity	Kashir and Yanful (2001); Lange et al. (2007); Shackelford et al. (2009); Hornsey et al. (2009b).

The objective of this paper is to highlight some of the issues facing the application of GCLs in mining environments. Attention will be primarily focused on the potential for incompatibility with leachates and how this may affect the hydraulic conductivity of GCLs.

## 2 BENTONITE IN GCLS

Bentonites are predominantly composed of the clay mineral montmorillonite. Montmorillonite is a swelling layered silicate composed of a sheet of octahedrally (8 sided) coordinated cations (positively charged ions, e.g.  $\text{Na}^+$ ) bound on either side by

sheets of tetrahedrally (4 sided) coordinated cations. Each combination of two tetrahedral sheets and one octahedral sheet makes a crystallite layer (Figure 1), and two adjacent crystallites are separated by a largely water-filled interlayer space. Hydrated cations occupy the interlayer space of montmorillonite to neutralize the layer charge due to chemical substitutions in the tetrahedral and octahedral sheets.

Montmorillonites typically have moderately high cation exchange capacities (80 – 150 meq/100g), due to their layer charge. The residual charge on the clay surface attracts hydrated exchange cations such as  $\text{Na}^+$  or  $\text{Ca}^{2+}$ , which each impart different amounts of limited swelling, layer stacking and clay fabric properties due to differences in their hydration en-

ergy, size and charge.  $\text{Na}^+$ -saturated montmorillonites are capable of imbibing several times their mass in water (Odom and Low, 1978; Laird, 2006) whilst undergoing unlimited or osmotic swelling.

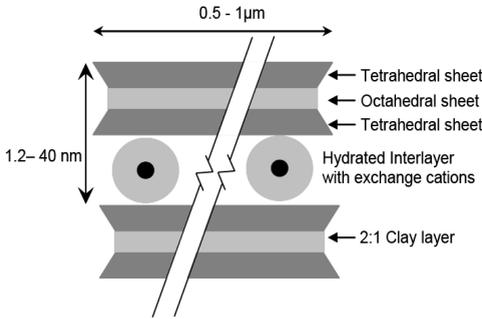


Figure 1. Montmorillonite crystal (fundamental particle). The d-space values of 1.2 – 40 nm are a measure of one dimensional clay swelling. The interlayer space increases with uptake, or decreases with release, of water by the interlayer cations (after Hornsey et al., 2009a).

In  $\text{Na}^+$ -clays (clays containing predominantly  $\text{Na}^+$  as the exchange cation) these crystals randomly arrange to form quasi-crystals where adjacent layers only weakly interact across the interlayer and water sorption results in separation of the interlayer space. The ability to imbibe large amounts of water and swell many times its original volume are key properties of Na-montmorillonite which make it useful as a hydraulic barrier. When under confining stress, the swollen layers restrict the advective flow path of water. In general high swelling and good dispersion of bentonites are correlated with lower void ratios which in turn result in lower hydraulic conductivity (Churchman et al., 2002).

In most bentonites used in GCLs, the dispersed montmorillonite particle size fraction is predominantly  $<0.5 \mu\text{m}$ . This small particle size means that montmorillonites have large specific surface areas approaching  $850 \text{ m}^2/\text{g}$ . High specific surface area due to small particle size, in combination with high swelling, results in a material that presents a tortuous path for water flow, thus very low hydraulic conductivities (Mitchell and Soga, 2005); and also capable of adsorbing a number of heavy metals (Bhattacharyya and Gupta, 2008). Besides montmorillonite, other mineral constituents of bentonite may include a few percentages of quartz, feldspars, carbonites, or mica, as well as additional discrete or mixed-layer clay minerals. Because they are non-swelling, most mineral impurities reduce bentonite quality in terms of its ability to hydrate, swell, disperse and gel. Generally, most commercial bentonites currently used in GCL manufacture have a montmorillonite content exceeding 70%. However,

fundamental particle size of the smectite and the impurities, as well as the relative differences in their sizes are important considerations of the bentonite as well, because a bentonite containing 30% clay-sized quartz might out-perform a bentonite containing 10% sand-sized quartz impurities. Thus, impurities should not be considered out-of-hand as being detrimental to the performance of the GCL; research by Benson et al. (2009) showed that the addition of certain non-swelling “impurities” maintained the performance of a GCL by reaction with high pH solution to form secondary mineral phases that clogged pores within the bentonite. They may also have served to protect the smectite component of the bentonite from dissolution.

The montmorillonite component, with its extremely large specific surface area and capability for both crystalline (interlayer) and bulk (inter-particle) swelling, is responsible for the desirable physical and chemical attributes that make the use of bentonite omnipresent in many industrial and engineering applications, including geosynthetic clay liners. Natural sodium bentonite is the material of choice in GCLs. Natural sodium bentonites occur in extensive deposits in the states of Wyoming, South Dakota and Montana, in the United States, and in a few generally isolated deposits in Greece, Turkey, India and Iran (Harvey and Keeling, 2002), as well as Australia. For this reason, “sodium activation of calcium bentonite (in which the exchangeable calcium cations have been replaced with sodium ions) is a common material in GCLs (Guyonnet et al., 2005). Sodium activation is usually done to increase swelling, dispersion, hydration and gelling properties of the bentonite, which in its normal  $\text{Ca}^{2+}$ -form, would have sub optimal properties (Harvey and Lagaly, 2006). It should be noted that many GCLs are marketed as “sodium bentonites”, rather than sodium activated bentonites.

The typical distribution of cations in sodium bentonite used for GCLs has been given by Egloffstein (2001) to be: 50-90%  $\text{Na}^+$ , 5-25%  $\text{Ca}^{2+}$ , 3-15%  $\text{Mg}^{2+}$ , 0.1-0.5%  $\text{K}^+$ . Much of the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  may be associated with a carbonate phase that precipitates during sodium activation (Guyonnet et al., 2005). Upon hydration, a part of these carbonates dissolve and release  $\text{Ca}^{2+}$  and/or  $\text{Mg}^{2+}$ , which can displace  $\text{Na}^+$ , reforming  $\text{Ca}^{2+}$ -smectite (Gates et al., 2010). Thus swelling, dispersion and gelation of sodium activated bentonites may be sub optimal (Harvey and Lagaly, 2006). In such cases, other additives are often added to improve these properties. The flow behaviour (a measure of the ability of bentonite particles to disperse and form a gel) of sodium activated bentonite suspensions is improved with addi-

tion of 5mmol/g  $\text{Na}_2\text{CO}_3$  (Harvey and Lagaly, 2006). It is now common practice for manufacturers of GCLs to add  $\leq 1\%$  of an anionic polymer to the bentonites. These polymers improve the dispersion and sealing capability of sodium activated bentonites. Calcium bentonite has also been used in GCLs, but since the hydraulic conductivity of calcium bentonite is about one order of magnitude higher than that for sodium bentonite they are not commonly used. Where they are used, GCLs with calcium bentonite typically have a much larger mass per unit area than GCLs with sodium bentonite to help overcome the sub optimal performance.

### 3 HYDRATION MECHANISM OF GCLS

Bentonite's low conductivity to water results primarily from its small particle size, large surface area and correspondingly low void ratio. These result in its ability to adsorb and effectively immobilize pore water through a variety of short-range and long range hydration mechanisms. Understanding these hydration mechanisms provides a basis to better understand the overall hydraulic performance of bentonite for GCL applications. The actual size distribution of processed particles is bentonite-specific, but also depends on the extent to which the clay is milled or pulverized, sieved and size fractionated post mining. A finely processed particle size requires more milling and hence greater energy input, but improves the initial reaction of bentonite with water and contaminant permeants. Decreasing mean particle size, whether at the fundamental and clay domain levels or processed particle size, generally means increasing the reactivity of the bentonite with aqueous surroundings due to the larger surface areas exposed. A larger exposed surface area means that the clay will take up water faster, form an effective seal sooner and limit any preferential flow that might occur due to a more uniform water uptake.

Vangpaisal and Bouazza (2004) have shown that the form of bentonite (i.e., powdered or granular) could affect the hydration mechanisms of the GCLs. This is illustrated in Figures 1 and 2, for GCLs containing dry powdered bentonite, it was shown that the outermost bentonite started to absorb water and hydrate. Consequently, a thin film of hydrated bentonite was formed which had the effect of slowing further water flow through to the dry bentonite deep within the GCL. As dry bentonite absorbed more water, the layers of hydrated bentonite gradually moved inward, until the water potential of the bentonite was equilibrated. Conversely, in the case of GCLs containing dry granular bentonite, it was observed that hydrating water passed through the large

voids between bentonite grains throughout the entire GCL thickness, and all bentonite grains started to absorb water and hydrate simultaneously. The outer surface of each bentonite grain formed a hydrated film covering its dry core. The bentonite then gradually absorbed the water deeper into the aggregate until the water potential was equilibrated.

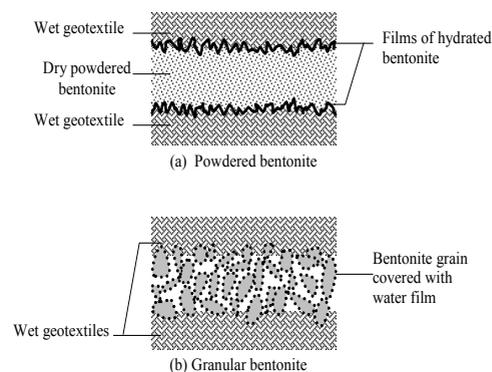


Figure 1. Hydration mechanisms of different forms of bentonite (from Vangpaisal & Bouazza, 2004)

The hydration process described above has some implications on the way GCLs behave when interacting with solutes. Shackelford et al (2000) indicated that aggregate-size distribution (i.e. granular) has little, if any, effect on the hydraulic conductivity of GCLs permeated with water. However, it could affect the rate of swell and the hydraulic conductivity of GCLs permeated with non-standard liquids (liquids other than pure water), as shown by Kolstad et al. (2004) and Benson et al. (2008). As indicated earlier, larger aggregates of bentonite will tend to take longer to fully hydrate because the permeant liquid must migrate to reach particles within the interior of the aggregates. It can be postulated that when in contact with aggressive permeants, the pores between aggregates in granular bentonite are only partially sealed due to a lower level of swelling, leading therefore to a higher hydraulic conductivity. In contrast, the pores in powdered bentonite are much smaller even with limited swelling. Consequently the initial hydraulic conductivity is lower. It is important to note that the studies reported above have been conducted at low confining pressures (less than 50 kPa), therefore representing worse case scenarios. It is expected that at higher compressive pressures such as encountered in heap leach pads or similar, this effect might be minimised since an increase in effective stress will tend to decrease both the hydraulic conductivity and the effect of incompatibility on the hydraulic conductivity (Shackelford et al., 2000, Katsumi and Fukugawa, 2005).

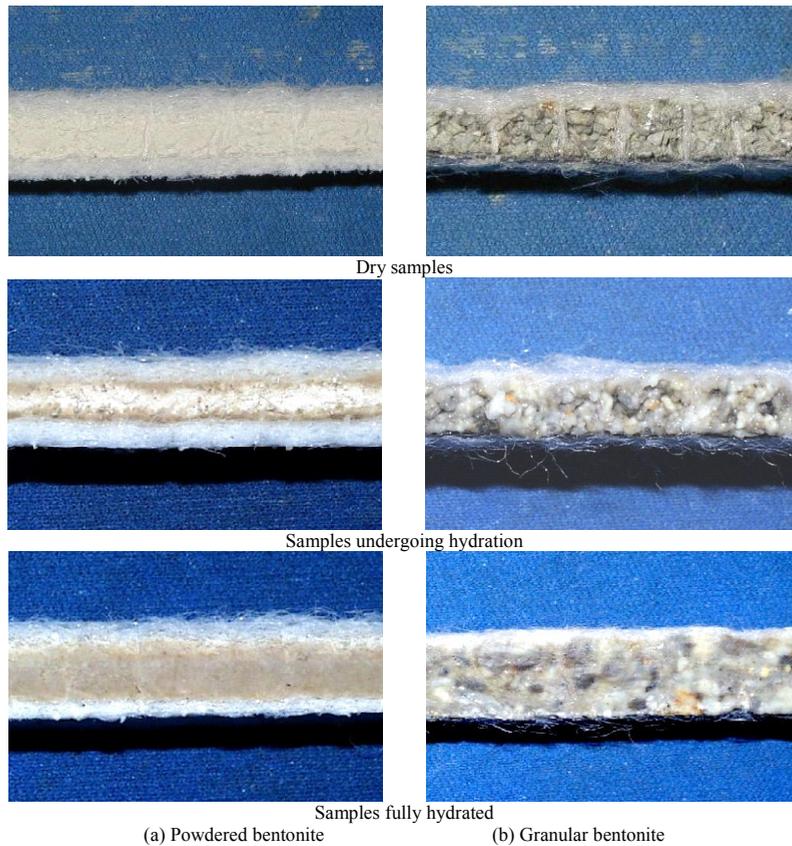


Figure 2. Illustration of hydration mechanisms of powdered and granular bentonite (from Vangpaisal and Bouazza, 2004).

## 4 HYDRAULIC ISSUES

### 4.1 Prehydration

Hydraulic conductivity of GCLs to the actual permeant liquid is usually assessed via a "compatibility test" where the specimen is permeated with the liquid to be contained or a liquid simulating the anticipated liquid. Currently, there is a very large body of work available on this particular topic, i.e. chemical compatibility (see Table 1). One element of GCLs, which influences their hydraulic conductivity with liquids other than water is prehydration (see Bouazza, 2002 for other factors). Shackelford (1994, 2007), Rowe et al. (2004), Bouazza et al. (2002),

Touze-Foltz et al. (2008) and Katsumi, (2010) among many others, indicated that permeation of a GCL specimen (prehydrated with tap water) with a chemical solution having elevated ionic strength (e.g. above about 0.1 molar) can lead to an increase in its hydraulic conductivity relative to that based on initial permeation with water (Figure 3). This is due to compression of the double layer extending from clay surfaces by the permeant liquid, resulting in a bentonite fabric with more open pore structure. However, the resulting hydraulic conductivity is still lower than that based on permeation of a separate, but identical, non-prehydrated specimen. Shackelford (2007) indicated that as a result, the hydraulic conductivity of GCLs permeated directly with chemical solutions typically has been found to be significantly higher than that for the same materi-

als permeated with the same chemical solutions after prehydration with water.

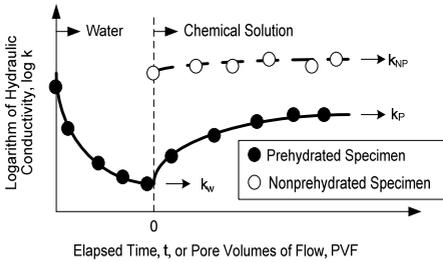


Figure 3. Schematic illustration of the potential difference in hydraulic conductivity resulting from permeating prehydrated and nonprehydrated specimens with chemical solutions (from Lee and Shackelford, 2005)

Prehydration is therefore necessary to prevent, minimize or delay alterations in hydraulic conductivity of GCLs caused by elevated ionic strength. In the field prehydration occurs mostly through absorption of water from sub-base soils - in some cases it can be imposed by spraying water. In the laboratory environment, it is usually imposed by directly contacting the specimens with water. This aspect of prehydration has been documented in Bouazza et al. (2002), however, it is aimed, in this section of the paper, to update the information provided earlier, in the light of recent progress.

Shan and Lai (2002) measured the hydraulic conductivity of GCLs to water, seawater, acidic water, municipal waste leachate and gasoline. Test termination occurred when the EC and pH of the effluent was the same as the influent. Prehydration of a GCL with water before exposure to either seawater or gasoline resulted in lower hydraulic conductivity of the GCL compared to the GCL being 'hydrated' and permeated directly with the non-standard liquid. Prehydration with tap water had minimal effect on the resulting hydraulic conductivity of the acidic and municipal waste leachates, but prehydration resulted in a hydraulic conductivity to seawater that was 3 orders of magnitude lower than when the GCL was hydrated and permeated directly with seawater. With gasoline, no flow was observed if the GCL was prehydrated with tap water or seawater. However, it should be noted that all their hydraulic conductivity tests were completed at low pore volume of flow

Vasko et al. (2001) evaluated how prehydration water content affected the hydraulic conductivity of GCLs permeated with divalent salt solutions. Prehydration water content was found to not have any apparent effects on hydraulic conductivity for solutions having intermediate (~0.025M) and low (<0.01M)

molar concentrations of dissolved salts (Figure 4). For higher (>0.1M) salinity solutions, however, lower hydraulic conductivity was obtained only for those samples having prehydration water content in excess of ~200%. The hydraulic conductivity decreased from  $1 \times 10^{-6}$  m/s to  $3 \times 10^{-9}$  m/s as the prehydration water content increased from 9% to 200% and then remained constant as the prehydration water content increased.

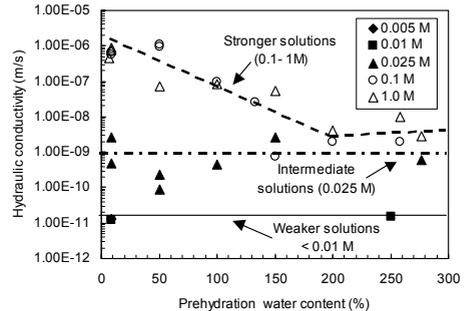


Figure 4. Hydraulic conductivity versus prehydration water content for unconfined GCL samples (modified from Vasko et al. 2001)

Vasko et al. (2001) indicated that the benefits accrued by prehydration with water followed by permeation with a non wetting organic liquid (as obtained by Daniel et al. 1993) are not obtained when the permeant liquid is a wetting aqueous solution. This difference was attributed by the authors to the different hydration mechanisms involved when the GCL is in contact with wetting compared to non-wetting liquids. Organic liquids have varying degrees of miscibility in water, and this will strongly influence how the organic liquid interacts with the bentonite component of the GCL. It follows that if the permeants are miscible in water, the tendency would be for displacement of water from the GCL, regardless of prehydrated conditions. On the other hand for permeants that are poorly miscible in water, prehydration levels are important: while displacement of water by the non standard permeant can occur at unsaturated conditions, at fully prehydrated conditions water will be retained more readily by the bentonite. Another possibility was that the tests conducted by Daniel et al. (1993) were terminated before equilibrium was established.

How uniformly prehydrated the GCL is prior to interaction with contaminants can control its hydraulic performance. In Vasko et al. (2001), a uniform pre-hydration over the entire GCL was achieved by using a filter paper suction method. However, Katsumi et al. (2004)[from Katsumi (2010)] in contrast,

did not attempt to achieve uniform prehydration. They conducted hydraulic conductivity tests on GCLs which were prehydrated by being placed on a compacted soil to simulate field conditions. The needle punched GCLs were placed with the woven geotextile in contact with the base soil. This is not consistent with the pre-hydration tests presented by Vasko et al. (2001), who in contrary put the GCLs with the nonwoven geotextile side in contact with the filter paper to ensure uniform pre-hydration over the entire area of the sample. The pre-hydration condition provided a hydraulic conductivity that was <1 order of magnitude lower than that obtained under the non-prehydration conditions. The increase in the pre-hydration water content did not necessarily cause a decrease in the hydraulic conductivity, as shown by Vasko et al. (2001). Katsumi et al. concluded that field-like prehydration did not effectively contribute to maintaining a low hydraulic conductivity. This was confirmed by Lee and Shackelford (2005) who have shown that the pre-hydration effect is also dependent on the concentration of the prehydrating water, and may be insignificant in terms of hydraulic conductivity when the permeant liquid contains relatively low concentrations of inorganic solutes.

Lee and Shackelford (2005) and Shackelford (2007) indicated that prehydrating GCLs by permeating with water prior to permeation with a non-standard liquid can affect both the duration of the test and the magnitude of the hydraulic conductivity. They pointed out that the effect of prehydration tends to increase with electrolyte concentration of the non-standard liquid. Little difference between the hydraulic conductivity values of prehydrated GCLs versus non prehydrated GCLs were observed based on permeation with relative dilute electrolyte solutions, provided the tests are conducted until chemical equilibrium between the effluent and influent has been established. However, as the ionic strength,  $I$ , increases and the ratio of monovalent cations to multivalent cations (RMD value) of the permeant liquid decreases, hydraulic conductivity for non prehydrated GCLs tends to increase relative to hydraulic conductivity for prehydrated specimens. Thus, the effect of prehydration may be significant when the liquid to be contained is relatively strong.

We must emphasize here that care should be taken when comparing the hydraulic conductivity values of GCLs to different non-standard liquids reported by different researchers to ensure that the prehydration level of the GCL is known. Further we recommend that for future studies, researchers should report whether the GCL is fully hydrated or, if not fully hydrated, then to record the hydration

level for the particular interaction. In addition, the ionic strength, and types of salts present in the hydration water should be reported.

## 5 INTERACTION WITH MINING WASTE LEACHATES/INDUSTRIAL PROCESSING LIQUORS

Our understanding of the behaviour of GCLs when in contact with mining waste leachates or processing liquors and feed waters is growing as more research becomes available. Industrial and mining processes produce huge volumes of liquid and semi-solid wastes that generally have extreme values of pH and ionic strength. High ionic strength and extreme pH do not always result in loss of GCL barrier performance. The complex interaction of high levels of dissolved ions, often near thermodynamic saturation and changes to leachate pH upon contact with bentonite can, in some cases, result in pore filling reactions (Benson et al., 2009; Gates and Bouazza, 2009; Shackelford et al 2009). This section is intended to provide background information regarding chemical reactions of bentonites with high and low pH leachates, highlight the important findings in terms of GCL performance and point where further research is needed.

### 5.1 *Acidic Wastes and Leachates*

Acid dissolution of clays is commonly used to advantage industrially (e.g. Gates et al., 2002), but little is known regarding the long term consequences of permeating strongly acid pH solutions on GCL performance. Because bentonite is in thermodynamic disequilibrium at  $\text{pH} < 3-4$  (Gates et al., 2009), we can assume acid leachates, due to dissolution of montmorillonite, eventually will have detrimental effects on GCL performance (Jozefaciuk and Matyka-Sarzynska, 2006; Shaw et al., 2009). Maintaining the GCL in a hydrated state prior to contact with an acidic leachate will likely slow the ingress of acid and extend its useful lifetime, provided the acidity and ionic strength are not excessive (Shackelford et al., 2000; Gates et al., 2009). In general, we urge a cautious approach in the use of GCLs as barriers to strongly acid leachates.

Shackelford (1994) indicated that chemical solutions with low pH can adversely affect the hydraulic conductivity of fine grained soils in two ways. First, low pH can result in direct dissolution of the clay mineral structure resulting in the creation of larger pores and increasing hydraulic conductivity. Second, a decreasing pH also correlates with a greater extent of dissolution of metal oxides, resulting in increas-

ing ionic strength of the pore liquid and a concomitant increase in hydraulic conductivity. In the case of the study reported by Shackelford et al. (2009) the fact that the pH of the solution of 2.5 was slightly higher than the threshold value of 2.0 below which the onset of clay mineral dissolution is expected (Shackelford 1994) and the lack of any observed murkiness in the permeation outflow from the hydraulic conductivity tests, suggest that clay mineral dissolution was not prevalent. However, Shackelford et al. (2009) stressed the fact that such indicators alone may not be adequate to exclude the possibility of dissolution altogether. Furthermore, in the case reported by Shackelford et al. (2009) the influence of the low pH on exchange properties of the bentonite was expected to be minor relative to the role of ionic strength and RMD.

Acidity, as well as increasing ionic strength of the pore solution, generally decreases swelling and therefore increases hydraulic conductivity. Mildly acidic solutions may initially cause only displacement of exchange cations by protons ( $H^+$ ) and this reaction alone is unlikely to cause serious losses in barrier performance. Ruhl and Daniel (1997) tested the effects of mildly acidic solutions (0.1M HCl, and a simulated municipal waste (MSW) with a pH of 4.4) on the hydraulic conductivity of GCLs and observed no increase in hydraulic conductivity or drop in pH of the permeant after ~8 pore volumes of flow through pre-hydrated GCLs.

Of more concern, however, is that smectites and other minerals containing Al, Fe, Mg and Ca are unstable in an acid solution.  $H^+$ -saturated smectites (the result of permeation of bentonite with low pH water) are unstable and eventually undergo reactions resulting in eventual destruction of the montmorillonite structure (Komadel and Madejová, 2006). The sites of substitution within the smectite structure – which carry the negative surface charge – come under direct attack by acid, which results in significant release of  $Mg^{2+}$ ,  $Fe^{3+}$  and  $Al^{3+}$  (e.g. Gates et al., 2002). Thus, under conditions of continued low proton flux, these metals can potentially displace any  $H^+$  or  $Na^+$  retained on non-dissolved bentonite, and can cause fabric changes (flocculation, reduced swelling, open pore structure) that are conducive to greater hydraulic conductivity.

Dissolution of smectites in acid solutions is incongruent and increases as pH decreases in the acid range. Given sufficient time of contact with acidic solutions, bentonites break down to an “amorphous, porous, protonated and hydrated silica with a three-dimensional cross-linked structure” (Komadel and Madejová 2006). Important parameters for assessing barrier effectiveness are the time required for a ben-

tonite to degrade at a given pH and the effect of intermediate stages in its transformation as solutes are attenuated.

Kashir and Yanful (2001) conducted a series hydraulic conductivity tests on a sodium bentonite with Acid Mine Drainage (AMD) as permeant at confining pressures ranging from 30 to 50 kPa. Acid mine drainage from sulfidic waste rock piles and mine tailings are a significant source of environmental contamination due to potentially high concentration of  $SO_4$ , Fe and contaminant metals in addition to low pH. Sulfide waste tends to oxidize over time resulting in the production of sulfuric acid, a process commonly called acid mine drainage. The AMD was characterized by low pH (2.5) and high sulfate and metal concentrations. The hydraulic conductivity to water was  $2 \times 10^{-11}$  m/s and increased to  $1 \times 10^{-10}$  m/s after 23 pore volumes of flow. The pH of the effluent decreased from 7.6 during water permeation to 3 after only 3 pore volumes of flow, indicating the limited capacity of the bentonite to neutralize acidic solutions. They noted significant mineralogical alteration during this process. They concluded that although the buffering capacity of the bentonite may not have been very high, the final hydraulic conductivity was still within the regulatory limit of  $1 \times 10^{-9}$  m/s typically required for hydraulic barriers.

In addition to low pH, the ionic strength of the leachate can impact on barrier performance. Lange et al. (2007) conducted hydraulic conductivity tests at a confining pressure of 25 kPa on a thermally locked needle punched GCL in which the granular sodium bentonite had a mass per unit area of 5.5 to 6.6 kg/m<sup>2</sup>. The permeant was a synthetic leachate representing a typical AMD (pH=3.3) with an elevated metals content (As, Al, Cd, Cu, Fe, Mn, Ni, Sr and Zn) and a high sulfate loading. The GCL showed a high retention capacity for all metals (caused by the precipitation of the ferrihydrite) whereas the hydraulic conductivity increased by a factor of 8 after 21 pore volumes of flow (from  $2 \times 10^{-11}$  m/s to  $1.3 \times 10^{-10}$  m/s which is still an acceptable value from the regulatory viewpoint). This increase in hydraulic conductivity resulted from the replacement of monovalent ions (Na) by divalent and trivalent metals caused mostly by the high metal loading and low pH. More recently, Lange et al. (2009) showed that significant attenuation of metals typically encountered in AMD was evident from diffusion tests conducted on a needle punched GCL. In particular, they indicated that although solution composition had some effects on the metal diffusion coefficient, sorption to the GCL was the dominant control factor on metal mobility.

In view of chemical changes resulting from acid

reaction of smectites, it is unlikely that bentonites can retain their effectiveness as barriers against strong acids for very long. This is especially true for acid leachates that have low metal ion loadings. Higher metal loadings can induce mineral precipitation reactions within bentonite pores, which may result in leachate attenuation, but it is unclear how long these potentially pore closing reactions will last. Undoubtedly, the rate, path and extent at which smectite disintegration or acid alteration occurs depends strongly on the initial pH, bentonite buffering capacity and reaction conditions. We thus urge continued caution in the use of GCLs for containment of acid leachates. Further, we urge that compatibility estimates of GCLs to AMD be further studied with the view to understanding long-term performance behaviour.

### 5.2 Strongly Alkaline Wastes

In contrast to low pH, high pH enhances bentonite particle dispersion and swelling through increases in both the edge charge and net negative charge. Thus, high pH may actually decrease the initial hydraulic conductivity of a bentonite-based barrier, as has been shown recently by Benson et al. (2009). At pH >10, Si and Al are highly soluble, and the smectite minerals present in bentonite can undergo irreversible chemical change (Gates and Bouazza, 2009). However, the changes to mineral structure and pore volume of bentonite resulting from alkali reaction are less obvious than changes due to acid treatment (Jozefaciuk and Matyka-Sarzynska 2006).

Bentonite dissolution by high pH leachates is initially congruent, but in concentrated KOH (up to 4 M), non-expandable illite layers formed (Bauer and Velde, 1999) that are interstratified with the remaining smectite layers. Bauer and Velde (1999) observed that with time, new mineral phases (eg zeolites) formed, and due to their greater stability other phases (eg feldspars and quartz) increased proportionately. Ramírez et al. (2002) observed alteration of auxiliary minerals in bentonites at pH 13.5 and formation of zeolites, magnesium silicate and calcium silicate hydroxide. Gates and Bouazza (2009) report that bentonite dissolution in 1 M NaOH results in loss of montmorillonite, opaline silica and quartz, but after 6 months at room temperature, hydrous forms of calcium and sodium aluminosilicate and carbonate phases formed. However, all these studies involved batch experiments with high solution to solid ratios, under conditions far from equilibrium and vastly different from those experienced in barriers.

In experiments more relevant to barriers, Taubald et al. (2000) found no observable changes in miner-

alogy of a bentonite column reacted for 18 months with a solution simulating water in equilibrium with dissolved concrete at pH 13.2. However, scanning electron microscopy revealed the formation of CaAlSi hydroxide secondary cement, and this precipitate led to a hydraulic conductivity value an order of magnitude lower than the original one. Generally, only minimal increases in hydraulic conductivity have been observed for bentonite after strong alkali treatment, and hydraulic conductivity decreases often markedly when Ca or Mg, due to dissolution of concrete, forms precipitates that block pores. Even in the absence of Ca and Mg, the formation of new mineral phases compensates for alkali-enhanced chemical degradation (Montes-H et al. 2005; Benson et al., 2009), whereas siliceous cements may also form and block pores. Benson et al (2009) observed that two GCLs, containing different levels of a proprietary additive designed to inhibit the detrimental effects of high pH and ionic strength, had minimal change in hydraulic conductivity compared to permeation in deionised water. As much as 16 pore volume of flow of effluent were collected and analysed for various physico-chemical properties. The ratio of hydraulic conductivity to permeant liquid to hydraulic conductivity to DI water ( $k/k_{DI}$ ) increased between 3 and 5 times for the GCL containing a smaller amount of additive and between 4 and 45 times for the GCL containing a higher level of additive. All final hydraulic conductivity values to 1 M NaOH (+ ~1 mM CsCl) were  $<5 \times 10^{-10}$  m/s. Simpson (2000) conducted a series of GCL hydraulic conductivity tests with a mine tailings solution (TDS =11,500 mg/l, pH=8) as permeant. The test results showed that initial saturation in leachate increased the final hydraulic conductivity by up to 3 orders of magnitude compared to the corresponding samples that were initially saturated with de-ionized water. These results also showed that if it is possible to hydrate the sample with non-reactive permeants prior to introducing the leachate, the long-term hydraulic conductivity would be enhanced.

Currently, it appears that at least some GCLs may be largely compatible with strongly alkaline pH leachates, however further research is required to determine the exact reasons why, and whether performance can be improved. We urge vigilance in the use of GCLs for alkaline leachates until further focused research answers these questions.

### 5.3 Hypersaline Wastes

In general  $\text{Na}^+$ -bentonite GCLs are not expected to perform well to hypersaline ( $>1\text{M}$ ) leachates. Ionic strength can exert simultaneous influence on two effects (Gates and Bouazza, 2009): (1) the pore struc-

ture and fabric of the bentonite; and (2) the activity of water. Together these reactions will result in loss of interlayer or crystalline water and collapse of  $\text{Na}^+$ -bentonite fabric, due to chemical or osmotic desiccation, causing increased pore size and interconnectivity of pores. These reactions will be exacerbated by the presence of divalent and trivalent cations in the leachate. If the leachates are supersaturated with respect to certain ions, the development of a possible pH gradient between the leachate and prehydrated bentonite pore water may result in precipitation of new mineral phases potentially capable of pore clogging reactions which could delay breakthrough of contaminants. These reactions must be considered for realistic modelling of hypersaline-liquid transport through or retention by, bentonite barriers. In general, we urge caution in the use of GCLs as barriers to hypersaline leachates.

The possibility of using organic cations or polymers to increase bentonite barrier performance for both high ionic strength solutions and fluids containing miscible hydrocarbons is promising. In one case, saline solutions actually improve organo-clay swelling (Gates, 2004). It was observed that 0.2 M and 2.0 M NaCl solutions resulted in slight increases in the hydrated X-ray basal spacing of a quaternary ammonium modified (organo-clay) montmorillonite (isolated from an Australian bentonite commonly used in GCLs). While organo-clays typically have unacceptably high hydraulic conductivities to aqueous solutions, the presence of 0.2 M NaCl in water-miscible organic leachates resulted in lower measured hydraulic conductivity values. Increasing the amount of organic content (ethanol) in the permeant to the solubility of 0.2 M NaCl decreased the measured hydraulic conductivity by 2 orders of magnitude (to  $\sim 1 \times 10^{-9}$  m/s). Proprietary polymer-bentonite blends commonly used to protect structures and foundations from damage caused by the accumulation of water and salt (salt damp) may prove useful in GCLs. Katsumi et al. (2007; 2008) reported that certain polar organic solvents form stable complexes with hydrated  $\text{Na}^+$ -montmorillonite and effectively maintain a crystalline swollen state and low hydraulic conductivity ( $< 10^{-10}$  m  $\text{s}^{-1}$ ) to up to 1 M aqueous solution of  $\text{CaCl}_2$ . Other additives designed to improve performance to high pH may also prove useful in hypersalinity applications (e.g. see Benson et al., 2009).

## 6 CONCLUSIONS

GCLs play an increasing role in environmental protection. Improved materials have been developed that prevent migration of many industrial leachates,

but strongly acidic and hypersaline wastes continue to present significant challenges. In the case of GCLs, the bentonite component can undergo dissolution reactions at extreme pH, pore-structure and loss of gel at elevated salinity and shrinkage at elevated temperatures. All these reactions potentially adversely affect the hydraulic performance of the bentonite, but the available data is limited. For some bentonites reactions at strongly alkaline pH appear to have minimal impact on hydraulic performance, but for others the effect can be catastrophic. The available evidence would suggest that reactions of strongly acid pH leachates adversely impact hydraulic performance of bentonite. Leachates of extreme pH from mineral ore processing are nearly universally coupled with very high ionic strength, and at least some of the adverse reactions of these leachates with bentonites are related to this hypersalinity. Recent developments toward improving bentonite resistance to high salinity show promise. It is expected that considerable research will be directed in the future toward improving bentonite performance to extreme pH, hypersalinity and temperature.

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